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CONTEMPORARY MURAL PAINTINGS

Study of emulsion paints' stability and evaluation of innovative conservation treatments

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“Art for anybody; anyone who walks past, owns it”

David McShane

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SOMMARIO

Scopo di questo lavoro è stato lo studio di vari aspetti connessi alla conservazione di dipinti murali contemporanei.

In questo contesto, il compito del *conservation scientist* è innanzitutto quello di collaborare con varie professionalità (tra cui restauratori-conservatori, storici dell'arte, artisti…) per definire lo stato dei dipinti ed individuare le strategie più adeguate per la loro conservazione.
Questo non può prescindere dall'identificazione dei materiali con i quali le opere sono state create e dalla conoscenza delle proprietà di tali materiali, in relazione alle condizioni ambientali cui l'opera si trova esposta.
L'intervento può essere poi realizzato secondo delle tecniche ben consolidate nella prassi del restauro, spesso poco adeguate alle particolari caratteristiche di queste opere, o avvalendosi di materiali e metodi messi a punto ex-novo dal *conservation scientist*.
L'attività di ricerca presentata in queste pagine è stata impostata cercando di coprire entrambi questi aspetti: lo studio dei materiali e dei loro processi di degrado da un lato, la messa a punto di nuove tecniche di restauro dall'altro.

La prima parte della sperimentazione è stata quindi sviluppata con l'obiettivo di studiare alcuni materiali comunemente impiegati dagli artisti contemporanei per creare dipinti murali. Sono state selezionate alcune pitture in emulsione (ovvero prodotti la cui fase legante è una dispersione acquosa di un polimero di sintesi ad alto peso molecolare) formulate per applicazioni di tipo artistico e caratterizzate da tre diversi tipi di legante: un polimero acrilico per la linea Heavy Body-Liquitex®, uno vinilico per la linea Flashe®-LeFranc&Bourgeois ed uno acrilico-stirenico per la linea Brera-Maimeri®. Per ciascuna delle tre linee sono state incluse cinque pitture, caratterizzate dagli stessi pigmenti, di cui tre inorganici (Bianco di Titanio -PW6-, Blu Oltremare Artificiale -PB29-, Giallo di Marte -PY42-) e due organici (Rosso Quinacridone -PV19- e Verde Ftalocianina -PG7-).
La composizione delle pitture selezionate è stata preliminarmente definita tramite: analisi di spettroscopia FTIR; analisi elementari condotte con sonda EDX (abbinate ad indagini in Microscopia Elettronica a Scansione); analisi termogravimetriche (tese a valutare il rapporto percentuale in peso tra il legante e le componenti inorganiche presenti all'interno delle pellicole pittoriche).

Poiché le caratteristiche del supporto influenzano in maniera sostanziale le proprietà ed il degrado di opere murali, le pitture sono state applicate su dei supporti in malta a legante misto calce-cemento. Dopo aver studiato la morfologia dei film così ottenuti (mediante osservazioni in microscopia ottica ed elettronica a scansione) ed averne definito il colore (mediante misurazioni condotte con uno spettrocolorimetro), i provini sono stati invecchiati simulando alcune delle condizioni cui sono soggette le opere reali.
Una serie di campioni è stata esposta a radiazioni UVA con spettro di emissione paragonabile a quello solare in esterno (λ_{max} di emissione 340 nm), un'altra serie è stata invece sottoposta a cicli di assorbimento capillare di acqua distillata attraverso i supporti in malta.

Nel primo caso, indagini di spettroscopia FTIR, misure di colore ed osservazioni condotte con microscopio ottico e microscopio elettronico a scansione, hanno evidenziato una buona stabilità delle pitture studiate. In seguito ad 800 ore di irraggiamento UVA infatti, le varie pitture sono risultate soggette a moderati processi di tipo foto-ossidativo a carico dei leganti. Queste forme di degrado sono più evidenti per le pitture contenenti pigmenti inorganici, soprattutto il Blu Oltremare Artificiale (PB29).
Il degrado dei leganti determina una variazione delle caratteristiche morfologiche delle pellicole pittoriche (che diventano più sottili determinando, nel caso di formulazioni ad alta P.V.C., un incremento della rugosità superficiale) e variazioni di colore (sbiadimenti).

Uno dei principali obiettivi nel simulare i cicli di risalita capillare è stato invece quello di studiare i processi di smiscelamento e migrazione delle componenti pittoriche solubili in acqua. Tramite indagini di spettroscopia FTIR condotte in riflettanza sulle superfici dei campioni è stato possibile verificare che l'acqua proveniente dal supporto può determinare l'affioramento di tensioattivi non ionici del tipo alchilfenolo etossilato (di fatto riscontrati sulle superfici dei campioni Heavy Body-Liquitex®). Il processo è più o meno favorito in relazione ad una serie di fattori tra cui: la concentrazione dei tensioattivi, l'affinità chimica tra tensioattivi e il legante polimerico, il grado di coalescenza della pellicola pittorica, la diversa affinità delle pellicole pittoriche nei confronti dell'acqua.
Parallelamente all'affioramento dei tensioattivi sono stati riscontrati, nel caso di film permeabili all'acqua (campioni Heavy Body-Liquitex® ed alcuni campioni Flashe®-LeFranc&Bourgeois), processi di carbonatazione e/o cristallizzazione superficiale di sali provenienti dal supporto (principalmente gesso). La cristallizzazione di sali solubili all'interfaccia film-supporto è risultata essere inoltre la principale causa di distacchi delle pellicole pittoriche.

Relativamente a quest'ultimo aspetto, la termografia IR, impiegata in modalità attiva con sensore nel *range* 3-5 μm, si è rivelata una tecnica particolarmente adatta all'individuazione di sollevamenti di pellicole pittoriche organiche (spessori dell' ordine di alcune centinaia di micron) dai supporti inorganici. È stato inoltre verificato che questa tecnica può essere efficacemente impiegata per valutare la qualità dell'avvenuta (o meno) riadesione delle pellicole pittoriche ai supporti, in seguito ad interventi di consolidamento.

Tecniche come la termografia IR e la spettroscopia IR in riflettenza sono per altro particolarmente adatte al monitoraggio dello stato di conservazione di opere murali, che andrebbero studiate preferenzialmente *in situ* secondo un approccio di tipo non invasivo.

I dati emersi dallo studio dei campioni allestiti in laboratorio sono stati incrociati con quelli ottenuti dalla caratterizzazione di opere reali appartenenti al M.A.C.A.M. (Museo di Arte Contemporanea all' Aperto di Maglione). La totale coerenza dei risultati ha permesso di delineare alcuni dei processi di degrado cui sono comunemente soggetti i murali contemporanei e di definire una serie di 'Linee Guida' cui gli artisti potrebbero scegliere di attenersi per conferire alle loro opere future una maggiore stabilità.

La seconda parte della sperimentazione è stata sviluppata con l'obiettivo di mettere a punto dei sistemi innovativi per la reintegrazione pittorica di opere murali acriliche/viniliche.

Oltre a garantire un elevato grado di mimetismo tra aree originali e trattate, un’adeguata pittura da ritocco dovrebbe rispondere a criteri di compatibilità (rispetto alle pellicole pittoriche originali), stabilità, reversibilità e riconoscibilità dell’intervento.
Considerati questi requisiti, due resine di sintesi sono state selezionate come leganti per la formulazione di pitture da ritocco: Aquazol 200® (polimero della 2-etil-2-ossazolina, solubile in acqua) e Laropal A81® (resina urea aldeide, solubile in solventi idrocarburici a basso contenuto di componenti aromatiche).
Come evidenziato da misure di colore ed osservazioni condotte in microscopia ottica, additivando entrambe le resine con opportune quantità di pigmenti in polvere è possibile ottenere degli interventi altamente mimetici.
La stabilità delle formulazioni è stata quindi valutata in seguito a 400 ore di esposizione a radiazioni UVA (λ_{max} di emissione 340 nm).
I dati ottenuti con varie tecniche analitiche (spettroscopia FTIR, OM, SEM, misure di colore) hanno evidenziato come le pitture formulate con Laropal A81® siano soggette a reazioni foto-ossidative che ne alterano la solubilità già dopo 200 ore di esposizione. Le pitture formulate con Aquazol 200® degradano invece secondo processi foto-ossidativi e di depolimerizzazione che, non comportando una sostanziale variazione della solubilità, garantiscono la reversibilità degli interventi in acqua.

La reversibilità è stata studiata non solo in relazione alla solubilità dei leganti, ma anche in funzione di un *interlayer* tra supporto e strati pittorici. In questo senso, i migliori risultati sono stati ottenuti impiegando una resina idrocarburica a basso peso molecolare (Regalrez 1094®, solubile in solventi idrocarburici) che, pur non formando un vero e proprio film, limita l’assorbimento delle pitture nelle porosità dei supporti in malta.

La riconoscibilità delle reintegrazioni è stata invece perseguita additivando le formulazioni pittoriche con un complesso organico dello ione Europio(III), $Eu(DBM)_3Phen$, che stimolato con radiazioni ultraviolette (λ 365 nm) dà una caratteristica luminescenza rossa.
La presenza di questo complesso all’ interno delle pellicole pittoriche non ne altera le proprietà morfologico-cromatiche, né la stabilità.
Sulla base di valutazioni preliminari, il principale limite all’impiego di questo complesso sembrerebbe essere la sua moderata stabilità, con conseguente riduzione delle caratteristiche di luminescenza.

Dato l’apporto innovativo di questa parte della sperimentazione, si intende proseguire la messa a punto di pitture da ritocco che consentano la realizzazione di interventi ‘mimetici- riconoscibili’ in funzione delle condizioni di illuminazione, migliorando la stabilità del complesso già impiegato e testando le caratteristiche di ulteriori complessi.

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THESIS GENERAL PURPOSE and OUT-LINE

This thesis was developed in the attempt of exploring different issues related to the conservation of contemporary mural paintings.

It has been extensively pointed out that, the treatment of these works of art poses a number of ethical and practical concerns, which should be dealt with by proper committees, encompassing a wide range of disciplines and points of view.

In this context, conservation science plays a very important role.

First of all, the conservation scientists support the conservators and the other experts in defining the condition of the mural painting, evaluating if it is in the urgent need of a treatment, and giving some pieces of advice as far as the best and safest strategies to follow for preserving it. A proper understanding of the condition of a mural, actually comes from the identification of the materials used for its creation and a deep knowledge of materials' properties and responses to environmental conditions.

The first part of this thesis was thus developed with the purpose of increasing the technical knowledge related to the stability of different paints used in contemporary murals. For this reason, a total of 15 emulsion paints, encompassing three binders and five pigments, were studied.
The chemical composition of these commercial products was preliminary assessed, as well as the morphological and physical properties of the films which form when brushing the paints on mural substrates.

The paint responses to different weathering conditions were subsequently evaluated.
For this reason, a number of samples were artificially aged simulating both, outdoor UV-light exposure and water absorption into the mural supports through capillary rise mechanism. Particular attention was devoted to the study of the phase-separation and leaching processes involving paints' water-soluble components (mainly surfactants).

When possible, the degradation processes were evaluated using portable analytical techniques, such as Mid-Near reflection spectroscopy and Mid-IR active thermography. This non-invasive approach perfectly suits the need of studying the murals *in situ*.

On one hand, the pieces of information coming from this part of the experimentation aid the definition of the condition of real case studies (presented at the end of the work). On the other hand, they allow an evaluation of the suitability of the selected paints to create murals (thus becoming the pieces of advice that contemporary artists could decide to follow in order to create long-lasting paintings).

Another important role of conservation science is that of developing *state-of-the-art* treatments to use for preserving the works of art.

The second part of this thesis was thus developed with the purpose of evaluating the suitability of different materials for inpainting contemporary murals.

A number of retouching paints were especially formulated, by adding two synthetic resin binders (Aquazol 200® and Laropal A81®) with proper amounts of powder pigments.
The chemical, morphological and physical properties of the films coming from these formulations were evaluated and compared to those previously gathered for the emulsion paints.
The stability of the retouching paints was later assessed, evaluating the variation of the same properties after accelerated ageing simulating outdoor UV-light exposure.

Particular attention was directed to those issues dealing with the *reversibility* and *discernibility* of the treatments.
In the attempt of achieving the first purpose, the influence of a polymer resin interlayer between the mortar support and the retouching paints was evaluated.
In order to enhance the differences perceived when comparing original and treated areas under an UV lamp (λ_{em} 365nm), a molecular lanthanide compound (an Eu (III) β-diketonate complex) was added to the retouching formulations.
The suitability of this complex in the conservation field was evaluated focusing on both, the durability of the complex itself and its potential influence on the visual and stability properties of the materials it was added to.

Notwithstanding the considerable amount of information, the two main themes, that dealing with the study of commercial emulsion paints and that concerning the evaluation of retouching materials, were tentatively presented in a coherent way.

At the same time, the thesis was structured in order to develop the two themes in a independent but comprehensive way. For this reason, the *Introduction*, as well as the following chapters presenting the materials, the casting procedure, the results and the conclusions were divided into sections dealing with one topic or the other.
The reading is therefore supposed to work either, from the beginning to the end, or just focusing on the sections related to a specific item.
The first part of the introduction (*1.1 Theory and practice in the conservation of contemporary mural paintings*) as well as the description of the analytical instrumentations (*2.4. Investigation techniques*) and the ageing conditions used for testing the stability to UV-light exposure (*2.3.2 UV-light stability testing*) are the only sections shared by the two topics.

A selection of three case studies is finally presented.

Chapter 1

INTRODUCTION

1.1 Theory and practice in the conservation of contemporary mural paintings

Within the context of mural paintings, the term *contemporary* is commonly used only to include them into a specific time period, without assessing any other kind of evaluation.[1] If compared to other *contemporary* works of art (based on unconventional modes of expression, composite or totally experimental materials, etc…),[2] mural paintings look therefore quite traditional.

Since these murals are traditional in form, matter and materials, their conservation can be actually approached in a traditional way, focusing on the need of preserving the original material substance through *state-of-the-art* treatments.
This typically Western conservation approach, developed from the acknowledgment of the historical and artistic values of the work of art.
But treatments carried out according to this approach might sometimes lead to questionable results. This is for instance the case of those paintings that have been removed from their original site and transferred to movable supports to be exposed (or sometimes just stored) in different contexts.[3]

As usual, the first step to preserve a work of art is understanding its meaning and function.[4]

Murals are environmental object, primarily though for integrating into a specific space and talking to an audience. Recalling Francis V. O' Connor words, *"a mural, unlike portable works of art, is an environmental artifact that was conceived in relation to its*

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[1] It is difficult to give a fulfilling definition of the adjective *contemporary*, referring to works of art. When conservators or art historians trained in different countries discuss about this point misunderstandings are quite frequent. This is due to the different meaning that words such as *modern* and *contemporary* have in different countries, for instance, in Italy and the countries belonging to the Anglo-Saxon area. (Schwartzbaum, 2010). Since this thesis deals with murals based on waterborne paints, the adjective *contemporary* will be used referring to works of art painted from the 1960s to the present days.

[2] Let us think about the *performativity* and *intangibility* factors related to the conservation of many modern and contemporary works of art (Muñoz-Viñas, 2010).

[3] This was, for instance, the case of the indoor mural painted by Peter Nyborg at the Royal Academy of Fine Arts of Copenhagen, or the case of Asger Jorn's mural originally executed in the summerhouse of Børge Birch and later donated to the ARKEN museum of Copenhagen (Brajer, 2010).

[4] This could even imply the acceptance of the disappearance of the murals, as in the case of the ephemeral charcoal works by Jorge Rodriguez Gerada.

natural and/or architectural setting; the original site is an intimate part of its formal attributes".[5]

The meanings and functions of contemporary murals are further related to a number of intangible values. First of all, they are means of aesthetic expression and carry out a decorative purpose. Secondly, being eye-catching and monumental in size, they also have a message-bearing function. In addition, they often acquire a social, political and public dimension, thus reflecting individual and communities concerns and becoming part of an ongoing social and economical process.[6]

For all these reasons, the need of preserving the *appearance of the fresh image* or the *original social creative process* of a mural can prevail on the need of preserving its original material substance.
The conservator has therefore to balance between the traditional approach, and alternative treatments options encompassing the collaboration with artists, the involvement of the communities, and repainting.[7]

The acceptance of these *unconventional treatments* is also due to other aspects, such as a different concept of authenticity (murals are often executed by a number of assistants following the artist's project) and economic constraints.
Most of these works of art are still in their awkward years. It is to say that they do not belong to the common heritage yet and they lack a traditional market value (which usually arise because of longevity, artist's recognition [8] or artist's death…).

For all these reasons: "*With the impermanence of many materials being used today and the sheer number of murals on exterior walls, it is not possible to preserve all of them* "[9]

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[5] Rainer, 2003: 4

[6] All these aspects have been deeply discussed during two symposiums. The first one, *Mural Painting and Conservation in the Americas*, was organized by the Getty Research Institute and the Getty Conservation Institute, held May 16-17, 2003. In addition to the symposium presentations (partially accessible on-line), the reader is referred to: Kelly, 2003.
The second symposium, *Modern and contemporary mural paintings. Technique, value and conservation*, was organized by the Instituto de Restauración del Patrimonio-Universidad Politécnica de Valencia, held May 4-5, 2012. The proceedings of this latter event are still not available.

[7] This is for instance the case of the *Hubbard Street Mural Project* in Chicago, where older murals have being repainted, renewed, or covered by new works through the years (Brajer, 2010).
A similar approach (the idea of artists repainting their original works) was allowed for the murals of the *East Side Gallery* of Berlin (cfr. to Ignasi Blanch-Gisbert' s presentation during the *Modern and contemporary mural paintings* symposium, Valencia May 4, 2012).
Actually, there are many concerns about the option of an artist renewing his/her own mural (potential design changes, issues related to the significance of each paint layer, conservation problems due to the creation of a complex multi-layer system…).
An example of a restoration developed thanks to the collaboration between conservators and an artist (Janet Braun-Reinilz) is that carried out for Eva Cockcroft's *The Grand Jatte in Harlem: Homage to Seraut* (originally painted in 1986, New York). More pieces of information about this project can be read on-line: http://www.heritagepreservation.org/RPM/archive6.html

[8] Nowadays, maybe no-one would discuss the idea of preserving Bansky' s street-artworks. A few years ago, the same works were often painted over by the municipalities, because considered acts of vandalism.

It is difficult to decide on the murals which are worthy of preservation and, to assess the most appropriate conservation strategies, many factors have to be considered (neighborhood/community desires, historic values, artistic/aesthetic values, artist's canon and rights, owner's rights, etc…).

It is almost impossible to give a comprehensive approach to follow.

The significance and conservation priorities of a mural should be assessed *case by case*, by a committee encompassing a number of different disciplines and points of view (ranging from conservators to art historians, social historians, artists, community members, etc…).[10]

In addition to documentation, the best way to prolong the life of a mural, thus allowing an evolution of its value through the years, is turning to *preventive conservation strategies*.

In this context, the conservation scientist plays a very important role.

First of all, possibly collaborating with paint manufacturers, the conservation scientists assess the properties of the materials (both, paints and supports), studying their interactions and their stability to exposure conditions. The information coming from these experimentations become the *best practice for mural creation* (so, those pieces of advice that contemporary artists could decide to follow in order to create long-lasting works of art).

Previous research projects[11] have for instance pointed out that, when painting an outdoor mural, pigments characterized by lightfastness rated 1 (ASTM D5098) should be

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[9] Rainer, 2003: 7

[10] An example of a murals' preservation project developed according to these principles is the *Rescue Public Murals Project*, began in 2006. Based on the U.S. non-profit organization *Heritage Preservation*, it was developed in the attempt of bringing attention to U.S. murals, documenting their artistic and historic contributions and securing the expertise and support to save them. The project committee of advisers includes a variety of professions ranging from muralists to conservators, art historians, and public art professionals. To date, it has brought to the condition evaluation of 16 murals, two of which have been already restored (these are: Eva Cockcroft's *The Grand Jatte in Harlem: Homage to Seraut*, 1986, New York; Meg Saligman's *Common Threads*, 1998, Philadelphia). All the information is accessible: http://www.heritagepreservation.org/RPM/index.html

[11] One of the aim of the *Rescue Public Murals Project* was to collect and disclose the information on material and techniques to consider for painting long-lasting outdoor murals.
At the moment, the entries of th *Mural Best Practice* encompass some pieces of advice concerning the best strategies to prepare, to paint and to maintain the walls.
(http://www.heritagepreservation.org/RPM/MuralBestPractices.html).
The information came both from paints manufacturers and conservation scientists.
Golden Artists Color and Novacolor paint manufacturers actually listed their available products, discriminating between stable pigments to use for exterior works and lightfast pigments prone to minimal color shifts. (Golden, 2002; http://www.novacolorpaint.com/PDF/Mural_Painting_Tips_10-2011.pdf). One of the limitations of these lists is the fact that paints are referred to using their commercial name, without direct references to the Color Index code system.
In 2005, the Winterthur/University of Delaware graduate programs in art conservation launched a multi-year project dealing with the conservation of mural materials. One of the aim of this project was to test

preferred. However, some of these excellent lightfast pigments turned out to be less durable than others[12] and, when cutting a colored paint with a white paint (based on Titanium White, PW6), faster discoloring rates were detected. In addition, Cadmium based pigments (oranges, reds and particularly yellows) and the Ultramarine Blue pigment (PB29) have been proved not to suit exterior murals use because they degrade in moisture and alkaline conditions, respectively.

Notwithstanding the important task of testing materials, the conservation scientists are also involved in the development of *state-of-the-art* treatments to use for preserving the murals. From the perspective of *preventive conservation*, some projects focused on the evaluation of adequate protective coatings and anti-graffiti coatings have been recently carried out.[13]

To the best of our knowledge, there is still a lack of research instead, as far as the development of materials and treatment techniques to tackle other challenging conservation problems. In addition to fading and acts of vandalism, many contemporary murals are affected by cracking, flaking, abrasions, chalking, salt crystallization underneath the paint layer, mold and mildew growth, surface deposits, paint losses…

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the properties of some paints usually chosen by Philadelphia muralists. These paints encompassed: Keim potassium silicate paints, Golden, Novacolor and Sher-Cryl acrylic paints.

The results of this research are accessible: Keister, Hill-Stoner and Weber, 2007; http://www.heritagepreservation.org/rpm/NorbutusBlog.html

Meg Saligman's *Fertile Ground* mural (Omaha, 2009) was painted according to the suggestions coming from this research, using Sher-Cryl paints.

http://www.heritagepreservation.org/RPM/FertileGround.html

[12] The Golden paints based on lightfast pigments which may undergo minimal color shifts are: Ceruleum Blue (PB36); Quinacridone Red (PV19); Turquois Phthalo (PB15:4/PG7); Diarilide Yellow (PY83); Hansa Yellow Opaque (PY74). Novacolor paints possibly affected by color shifts when used outdoor are: Quinacridone Red, Quinacridone Magenta, Arylide Yellow, Silver Super Pearl White, Super Pearl Gold and Sun Gold.

[13] One of the first studies evaluating the properties of different organosiloxane protective coatings added with a Hindered Amine Light Stabilizer (HALS) or an Ultraviolet Light Stabilizer (UVLS) was carried out at the I.C.R. facilities in Rome: Gurgone *et al.* 2005

Within the previously referred project carried out by the Winterthur/University of Delaware, the properties of different coatings were evaluated as well. The tested coating were: Paraloid B-72 and Novacolor varnish (both added or not with the Ciba 777 HALS); Golden MSA varnish added with an UVLS; Triangle catalyzed polyurethane antigraffiti coating; a totally innovative coating (coming from an aqueous based polymer added with a proper UV absorber, which would result in stable films, removable by using an aqueous-based system relying on a targeted pH level).

Some of the results coming from this research are already accessible: Kerr-Allison, 2007; http://www.heritagepreservation.org/RPM/entries.html (with related links). Further results will be presented when Amanda Norbutus will discuss her PhD dissertation concerning *Coatings for Outdoor Painted Surfaces and the Preservation of Public Murals*.

A research dealing with the evaluation of several commercially-available anti-graffiti coatings (ranging from waxes to polysaccharides, acrylics and polyurethanes) is still being developed as part of the *Outdoor Painted Surface* project at the Getty Conservation Institute (Los Angeles). Some of these results were presented by Emily MacDonald-Korth during the *Modern and contemporary mural paintings* symposium, Valencia May 4, 2012 (*Research into Anti-graffiti Coatings for Acrylic Murals: Preliminary analysis and Evaluation*).

Further research should be therefore carried out as far as the development of adequate consolidation, cleaning [14] and inpainting techniques.

Finally, the conservation scientists should support the conservators and the other experts in defining the actual condition of a mural, evaluating if it is in the urgent need of a treatment on the base of the measurement of some parameters. For this purpose, a number of non-invasive analytical techniques can be used for characterizing the murals and monitoring their condition *in situ*. The same techniques can be sometimes used to assist the conservators while carrying out the treatments, and to evaluate the quality of the final result.

As previously explained, the present work was developed in the attempt of covering all these purposes.

The first part of the thesis was carried out to assess the suitability of different paints to create murals.

After considering the materials usually chosen by Italian muralists, three waterborne products were included in the experimentation. These encompassed three binder typologies (a vinyl *co*-polymer, an acrylic *co*-polymer and a styrene-acrylic *ter*-polymer) and five different pigments. The artificial ageing conditions were thought in the attempt of simulating both, outdoor UV-light exposure and rising damp mechanism. Particular attention was devoted to the study of the phase-separation and leaching processes of the surfactants and other water-miscible materials.

The suitability of two portable non-invasive techniques to assess the condition of the murals was also evaluated: Mid-Near FTIR reflection spectroscopy was used for monitoring the surfactant phase-separation process, while Mid-IR active thermography was used for detecting paint layers delaminations.

In order to allow a proper understanding of the results, the salient features concerning the chemical composition, film properties and main degradation processes of emulsion paints, are reviewed in the following section.

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[14] As far as the cleaning issues the information can be indirectly inferred from the exhaustive research carried out for acrylic canvas paintings. Among the most important projects concerning this topic, those recently completed by the researchers at the Tate Modern are: *The cleaning of Acrylic Paints*, 2003-06; and *Tate AXA Art Modern paints project-Evaluating the Effects of Cleaning Acrylic Paintings,* 2006-09.
Many studies dealing with cleaning of acrylic and PVac paint layers have been also presented during the *Modern Paints Uncovered* symposium (London, May 16-19, 2006; Learner, *et al.* (eds) 2007) and the *Cleaning 2010* conference (Valencia, May 26-28, 2010; Fuster-López, *et al.* (eds) 2010).
Silva's PhD dissertation (2011) was also partially devoted to the study of the cleaning effects on acrylic and PVAc dispersion paints.
These issues are also still investigated by Getty Conservation Institute researchers (*Modern Paints. An evaluation of cleaning Methods for Modern Paintings*).

1.2 Emulsion paints

In the past years, development of *modern paints* has been widely reviewed in specialized literature.[15]

Within the conservation field, the adjective *modern* generally refers to those paints based on synthetic resins binders, ranging from acrylic to alkyd, polyvinyl acetate, cellulose nitrate, polyurethane, epoxy, silicon resins, etc…

In this context the so called *emulsion paints*,[16] have been often reported as products which changed the paint and coating sectors in deep.

Originally intended for the household and industrial market, these paints were enthusiastically received by artists between the 1950s and the 1960s,[17] and they are still one of the most diffuse paint typology used both, for industrial and artistic purposes.

Due to the ever increasing need of preserving works of art based on these paints, a number of studies have been recently carried out with the aim of exploring their composition, properties and response to different environmental conditions and conservation treatments.

The information coming from these studies is reviewed in this section, in particular:

- section 1.2.1 deals with the chemistry of the emulsion paints, which are very complex systems encompassing the binder (usually an acrylic or vinyl polymer), the pigments and a multitude of additives included in different stages of paints' production.
- since the drying mechanism of the emulsion paints is of fundamental importance for understanding the properties and durability of the final paint layers, the film formation process is described in section 1.2.2

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[15] As far as the historical development of *modern paints*: Bensi, 2000; Cappitelli, 2002; Chiantore and Rava, 2005; Learner, 2000; Learner, 2004; Learner, 2007; Standeven, 2011. A specific study concerning alkyd paints was recently developed by Rebecca Ploeger in her PhD dissertation (a.a. 2007/08). Further references about alkyd paints in: Ploeger, Scalarone and Chiantore, 2008; Ploeger, Musso and Chiantore, 2009; Ploeger, Scalarone, and Chiantore, 2009. The impact of modern paints on art has been treated as well: Crook and Learner, 2000.

[16] As far as the information concerning the historical development of emulsion paints the reader is referred to the text of previous note and to: Jablowsy *et al.*, 2003.

[17] They were enthusiastically received by the artists because of a number of reasons: the great advantage of being thinned with water; the possibility of being applied over a number of different surfaces, thus allowing the experimentation of new methods and techniques; good optical and physical properties (e.g. colorlessness and transparency of the pure binder, flexibility, good gloss and gloss retention, good adhesion); rapid drying; high resistance (to chemicals, hydrolysis, thermal stresses and UV light exposure); ease of use and convenience.

As more artists began to use these paints, the first formulations specifically intended for artistic use were developed. *Liquitex*, the first artists' grade acrylic emulsion paint line, was developed by Henry Levison (Permanent Pigments Inc.) in 1954. This product was available in tubes from 1963. Starting from 1964, many other artists' paints manufacturers introduced their own acrylic emulsion paints' brands.

- in section 1.2.3 the ageing properties of the paint layers are reviewed, focusing on two degradation processes which possibly affect mural works of art (additives phase-separation and photooxidative prcesses induced by UV-light exposure).

1.2.1 The chemistry of emulsion paints [18]

As reported in a quite old book exploring paint technology:

"paint can be defined as a mixture of pigment and binding medium, which can be spread to a dry, thin film to decorate or protect a surface. A third component which acts to allow the combination of pigment and binding material to be spread to a thin film, is at times included…this is generally a solvent…the mixture or solution of binding medium and solvent are known to the paint industry as the vehicle."[19]

When considering *emulsion paints*,[20] the vehicle is an aqueous phase colloidal dispersion of synthetic resin particles. These particles are prepared, by emulsion polymerization of ethylenically unsatured monomers, through a complex process involving numerous components. Since these polymer emulsions are usually intended for coating and/or for adhesive purposes, a number of additives are commonly post added to the system, in order to improve the film performance characteristics and the film formation process.

Polymer emulsions are almost never developed for use in paint, even less for use in artists' grade paints. Paint manufactures usually rely on raw products intended for more commercial use. Among these, the most widespread are vinyl and acrylic products (either on their own or in blends with other polymers).

Even though the properties of poly(vinyl-acetate) polymers (PVAc) are slightly inferior to those of acrylics (as far as toughness, binding power and resistance to weathering), they are less expensive and perfectly suite standard uses. For these reasons, PVAc polymers have remained the principal type of binder used in interior emulsion house paints in many European countries.[21]

Within acrylic products, the most commonly used emulsions are those from Röhm and Haas' Primal™ series (Rhoplex® in the U.S.). Among these, the AC-33 formulation [22] was

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[18] Croll, 2007; Jablowsky *et al.*, 2003; Learner, 2004; Learner, 2007

[19] Radcliffe,1964: 50

[20] According to the language used in paint industry, hereinafter the term *emulsion* will be used referring to the vehicle of waterborne paints. The word emulsion actually defines a system consisting of two immiscible liquids, while the vehicle is here a dispersion of a polymer in water (which could be better defined as a *latex*).

[21] PVac resins firstly become available in the emulsion form in the late 1940s. Learner, 2007:9

[22] The Primal AC-33 formulation, based on a p(EA-MMA) co-polymer, was firstly available in 1953. Another formulation which is often reported is the AC-34 one. This was introduced in 1961 and, despite being very similar to the AC-33, it contained some additional ureido functionalities (Croll, 2007:25).

largely used until the end of the 1980s. Subsequently, many formulations have switched to polymers with higher hydrophobic character and toughness[23] (both of which are beneficial properties for the primary application of these resins, that is exterior house paint).

In the 1953 styrene-acrylic emulsions were introduced (with styrene replacing the harder acrylic resins monomers to save manufacturing costs). Thanks to their good hydrophobicity, these binders were widely considered for house paints during the 1970s and 1980s and are still used in Europe (even though they have been disregarded in the U.S. because of questionable stability to heat and UV-light exposure).[24]

As stated above, in order to turn these polymer emulsions into paints, some pigments have to be included. Formulating the emulsion paints, the polymer latex is usually added with pigmented pastes (not powder pigments). These slurries are water dispersion of pigments, containing a number of further additives.[25]

It is thus clear that waterborne paints are complex systems, consisting of numerous components. Among these, there are many additives included both, for manufacturing reasons and for achieving especial paint performances (as shelf life, application, longevity, etc…). Since the majority of these additives remain in the dry film, they have to be considered when studying the properties, durability and treatments' effects on emulsion paint layers. A simplified model of an acrylic emulsion paint formulation is shown in the table 1.2-1.

Ingredients	Volume (gallons)	Function
Water	41	Carrier fluid
Acrylic latex (60% solid)	32	Polymer binder
Titanium dioxide	6.5	White pigment
Silicate mineral	7.3	Extender/filler; reduces cost
Calcinated clay	2.2	Extender pigment
Coalescent	1.16	Film formation aid
Thickeners	0.56	Thickener (viscosifier)
Glycols	6.72	Antifreeze, coalescent, evaporation control
Polyacrylate dispersant	0.69	Pigment suspension stabilization aid
Non-ionic surfactant	0.11	Wetting agent
Biocides	1	Fungicide, mildewcide
Defoamer	0.26	Inhibits air entrapment
Ammonium hydroxide solution	0.29	Maintains alkaline pH
Total	100	

Tab.1.2-1: The simplified model of the formulation of a typical emulsion acrylic exterior house paint (white). The amounts are expressed for 100 gallons (Ormsby and Learner, 2009:29)

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[23] These are mainly based on p(*n*BA-MMA) co-polymers. Two formulations which are often reported are: AC-235 or AC-2235. Jablowsky *et al.*, 2003; Learner 2007: 6

[24] Croll, 2007:25

[25] A small portion of a binding medium is usually included as well.

The basic concepts of waterborne paints' chemical composition are reviewed in the following sections, focusing on:

- the polymer emulsion (latex) binder (section 1.2.1.1)
- the additives of the emulsion binder (section 1.2.1.2)
- the pigments (section 1.2.1.3)
- the additives included when formulating the paints (section 1.2.1.4)

1.2.1.1 Polymer emulsion (latex) binders [26]

The vehicle of an *emulsion paint* is an aqueous dispersion of insoluble tiny beads of a thermoplastic[27] high molecular weight polymer.[28]

These particles are prepared by addition polymerization from molecules containing a C=C double bond that can be reacted with, during the process.

Even though the monomer units in the molecular chain may be exclusively of one species (thus leading to a *homopolymer*),[29] in the majority of the cases the polymers are based on combinations of different monomers (thus being co-polymers or terpolymers).

Many monomers may be involved in the polymerization (vinyl acetate, vinyl chloride, styrene…). Among these monomers two series, derived from the acrylic acid and the methacrylic acid, are of particular importance. These are esters coming from the reaction of the two acids with an alcohol, whose nature completes the nomenclature of the monomer. Polymers derived from the polymerization of acrylates and methacrylates are known as acrylic resins.

Sometimes, monomers presenting a functional group with a cross-linking capacity (hydroxyl, carboxyl, amide, epoxy) may be included.[30]

The chemical structure of the most common monomers used in industrial co-polymer emulsions is shown in figure 1.2-1.

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[26] Oldring and Hayward, 1987: 121-291; Learner, 2004: 7-17; Šňupárek, 1996

[27] Thermoplastic polymers harden by solvent evaporation, allowing film formation without the occurrence of any external chemical action.

[28] Polymers with an average molecular weight of over 1,000,000 Da would not be unusual when produced in emulsion (particles' diameters ranging between 100-500 nm). Due to these high molecular weights, the dried films coming from emulsions are stronger and tougher than those coming from solution products (molecular weights in the 50,000-100,000 Da range). Learner, 2004: 12-13

[29] The only acrylic homopolymer suitable as paint binder is poly butyl methacrylate, p(*n*BMA). Learner, 2004: 10

[30] Reactive polymers are obtained including hydroxyethyl acrylate or acrylamide monomers.
When manufacturing acrylic resins, small amounts (less than 1% by weight), of acrylic or methacrylic acids are sometimes added in order to assist the adhesion to certain surfaces by providing the hydroxyl side group (which is more polar). These carboxylated acrylic copolymers are also known for having higher water permeability than the unmodified acrylic ones (Oldring and Hayward, 1987).

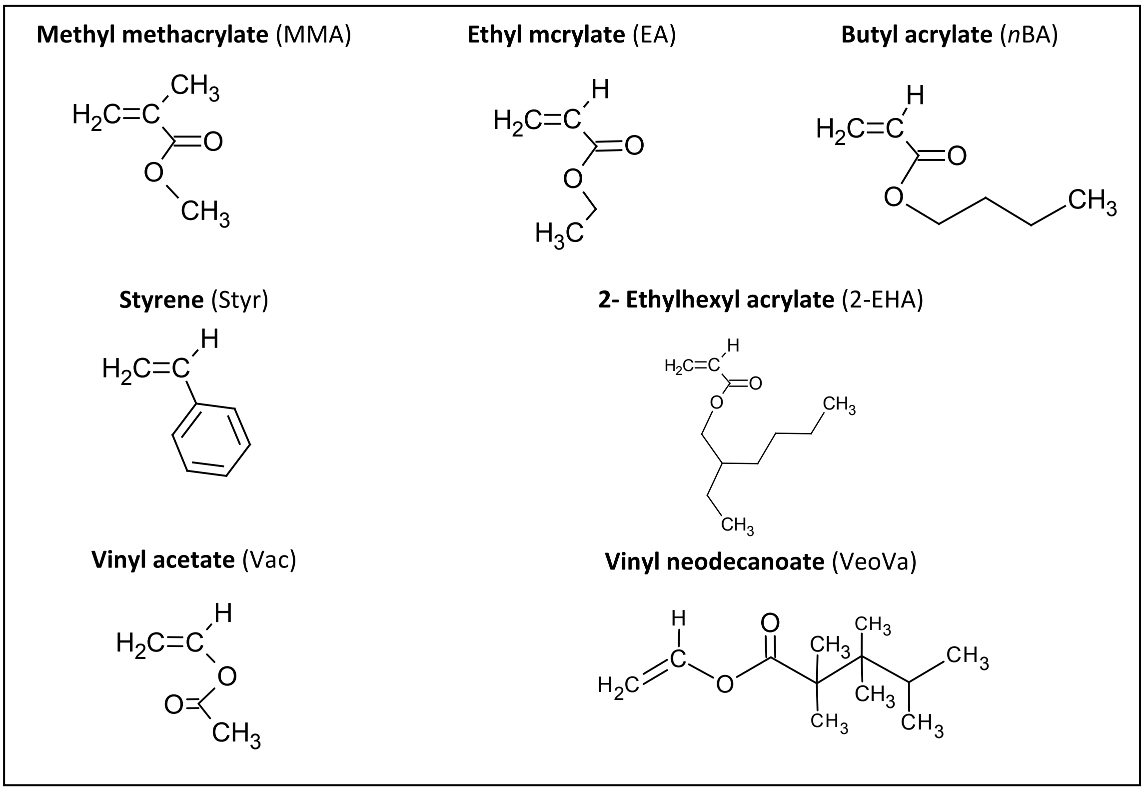

Fig.1.2-1: The chemical structure of the most common monomers used in industrial co-polymer emulsions.

The selection of the monomers mainly depends upon the need of preparing a resin which would result in good coating performances (considering properties such as adhesion, flexibility, abrasion resistance, water resistance, ease of coalescence, etc…), minimizing the cost of the final product.

Selecting the monomers, one of the most important properties that has to be considered is their Glass Transition temperature (Tg). At the Tg, significant rotations in the backbone or side chains occur, due to thermal excitement. Polymer properties change, as it passes through this temperature: below the Tg the polymer is rigid, glassy, hard and brittle; at higher temperatures it becomes softer, rubbery and flexible.

The polymers to be used in paints require a Tg sufficiently low for the film to remain flexible and unlikely to crack in normal use, but high enough to prevent the dried film from becoming tacky and absorbing dirt. Usually, the Tg of these resins are just below the ambient temperature to which the finish will be subjected.

Even though the absolute Tg value of a polymer may be affected by many factors (as tacticity, degree of crystallinity, degree of cross-linking, etc…), the structure of the monomers has a primary influence on it. Within acrylic monomers, the longer and more branched is the aliphatic ester chain, the lower is the Tg.

The Tg of the resins coming from the homo-polymerization of some monomers which are typically used in the coating industry are shown in table 1.2-2, together with their solubility in water.

Monomer name and abbreviation	Glass transition temperature, Tg (°C)	Solubility (%)
Styrene (Styr)	100	0.01
Ethyl acrylate (EA)	-22	1.5
n-Butyl acrylate (*n*-BA)	-56	0.13
Methyl methacrylate (MMA)	105	1.5
2-Ethylhexyl acrylate (2-EHA)	-50	0.01
Vinyl acetate (VAc)	29	2.8
Vinyl neodecanoate (VeoVa)	-3	0.01

Tab.1.2-2: Typical monomers found in industrial co-polymer emulsions (Karsa, 2003:2)

Co-polymers are actually thought to balance monomers' individual properties.
The Tg of a hard polymer, as vinyl acetate, styrene or methyl methacrylate can be reduced either by adding an external plasticizer [31] or by co-polymerization with a softer monomer. Ethylene, vinyl versatates (VeoVa)[32] and 2-ethylhexyl acrylate co-monomers are often used to soften vinyl acetate resins. The use of α-olefins is common too (even though these olefins are very difficult to polymerize by a free radical mechanism).
Within acrylic resins instead, the harder methyl methacrylate (MMA) is usually copolymerized with softer monomers such as ethyl acrylate (EA) or *n*-butyl acrylate (*n*-BA).

In addition to the Tg, other important films'properties which come from the selsction of the monomers are: gloss, chemical resistance, permeability to gases and vapors.
As far as this latter aspect, among the commercial polymers, poly(vinyl acetate) has the highest permeability, meanwhile acrylates and styrene-acrylates show intermediate values.[33]
The method of preparation of a polymer has a major influence on its properties. Coatings and paints resins are normally prepared by *emulsion polymerization*. The main components involved in this complex process are reviewed in the following section.[34]

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[31] External plasticizers, such as phthalates, were commonly add to early poly(vinyl acetate) formulations (sometimes up to 20% by weight). Though being better on a cost effective basis, the addition of an external plasticizer may result in a less durable product. The plasticizers could actually be lost through slow evaporation and/or they could diffuse into the substrate. For these reasons, since the 1960s co-polymerization is preferred to the use of external plasticizers.

[32] VeoVa monomers are highly branched C9 and C10 vinyl esters which are normally purchased as commercial mixtures. If compared to ethylene or 2-ethylhexyl acrylate, the VeoVa monomer is easier to incorporate, resulting in films with surprisingly good water, alkali and UV resistance. Nevertheless it does not provide efficient softening on a weight basis and is inefficient on a cost basis.

[33] Generally, the higher is the polymer hydrophilic character, the faster is the transport of water vapor in the coating film. The presence of styrene is however known for increasing the diffusion of gases. Considering the properties of paint layers, the water vapor permeability depends also on the pigmentation. Oldring, and Hayward,1987; Perera, 2004

[34] Further information as far as the emulsion polymerization process in: Chern, 2006; Gilbert, 1995; Oldring and Hayward, 1987. The emulsion polymerization process has been moreover reviewed by Learner, 2004: 10-11. The last book references a number of further texts as far as this topic).

1.2.1.2 Emulsion additives [35]

The emulsion polymerization process involves numerous components among which, the main ones are: initiators, chain transfer agents and surfactants.[36] Other components included during the polymerization are buffers and protective colloids. Preservatives, sequestering agents, coalescing solvents and wetting agents are commonly post added to the emulsions in order to improve the film formation and the other performances of the products, which are usually thought for the coating industry.

Initiators

They are used as source of free radicals to initiate the polymerization process. Typical initiators are molecules which thermally decompose to form free radicals (e.g. sodium, potassium and ammonium persulfates). In order to allow room temperature reactions, redox activators may be introduced in the system. These are usually salts of polyvalent metals (such as ferrous sulfates and thiosulphates…). Other initiators are: diacyl peroxides (e.g. di-benzoyl peroxide), AZO initiators (e.g. azo-bis- isobutyronitile), peresters (e.g. t-butyl peroxybenzoate), alkyl hydroperoxides (e.g. t-butyl hydroperoxide), dialkyl peroxides (e.g. di-t-butyl peroxide), peridicarbonates, perketales and ketone peroxides.

Chain Transfer Agents

Modifiers or chain transfer agents are incorporated in order to better control the final molecular weight of the polymer. They are molecules containing an atom (usually a hydrogen or halogen atom) which is abstracted by the growing polymer chain, thus stopping the propagation of the polymer chain itself. The overall effect of these species is thus to transfer the free radical from one polymer chain to another. Typical chain transfer agents are: carbon tetra bromide, t-butyl mercaptan and ethanethiol.

Buffers

They are commonly add in order to stabilize the pH of the emulsion. Most of the emulsion components (e.g. surfactants, initiators…) are actually more stable in a specific pH range. The final pH of an emulsion depends upon the chemical nature of the polymer. For instance, vinyl acetate is prone to hydrolysis at pH below 4 and above 9. Other monomers, such as acrylic and methacrylic acids, do not copolymerize easily above pH 5. For this reason, buffers (as borax, sodium hydrogen phosphate and sodium bicarbonate) may be used for keeping the pH acidic during polymerization. Since the

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[35] All the pieces of information come from: Croll, 2007; Jablowsky *et al.*, 2003; Learner, 2004; Martens, 1964; Oldring and Hayward 1987; Silva, 2011; Tadros, 2005: 1-17; Tethford, 2003

[36] Another component is water, which plays an important role in dispersing the heat produced from the reaction. Some authors (Jablowsky *et al.*, 2003) also include the residual monomers resulting from incomplete polymerization, among the components of a base emulsion polymer. When considering acrylic resins these residual monomers are reported to be present at 50 to 1,000 parts per million or so.

emulsions are used at pH above 7.5, ammonia is subsequently add to ensure a slightly alkaline final product.

Surfactants [37]

Surfactants play an important role in creating those conditions which allow a proper development of the emulsion polymerization process,[38] and in subsequently stabilizing the latex. Usually a combination of anionic and non-ionic surfactants is employed.

The most common anionic surfactants are alkyl sulfate and alkyl-aryl sulfonate (e.g: sodium lauryl sulfate, dodecyl benzene sulfonate,…). They are typically added at 1-4%/wt and work through electrostatic stabilization.[39] They are very effective in promoting monomers solubilization and limiting particle size (the higher the concentration of anionic surfactants, the lower the size of emulsion particles). They are also very resistant to acids, hard water and high temperatures (thus being very important during the initial stage of the polymerization process). If compared to the non-ionic surfactants, they have a greater tendency to foam and to impart water sensitivity to the final film.

Usually, non-ionic surfactants are molecules presenting a polar group resulting from a number of Ethylene Oxide units (EO, generally between 15 and 30). The most common ones are alkyl phenol ethoxylates, fatty alcohol ethoxylates and fatty acid monoethanolamide ethoxylates. They are typically added at 2-6%/wt and work through steric hindrance stabilization.[40] They are particularly effective in stabilizing the latex, opposing against freeze-thaw cycling coagulation and lowering latex sensitivity to electrolytes and pH changes.

Conventional surfactants are not permanently adsorbed at the surface of latex particles but are subjected to a continuous adsorption-desorption process. Since the adsorption driving force is stronger for non-ionic surfactants than for the anionic ones, unless the electrolyte concentration is very high, the ratio of non-ionic to anionic surfactants at the

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[37] The term surfactant is used referring to a surface-active agent, it is to say a compound which modifies the properties of an interface with which it is in contact. This surface activity arises from their amphiphatic structure (so to the presence in their molecules of two groups of opposite solubility or polarity). This structure leads to particular solution behaviors as micelle formation, adsorption and orientation at interfaces. In aqueous systems the polar group is called hydrophilic, while the non-polar group is known as hydrophobic or lipophilic. Depending on the charge of the polar group, surfactants are classified in anionic, cationic and non-ionic. As will be seen, dealing with emulsion polymers or paints, anionic and non-ionic surfactants are largely used to different purposes .

[38] Allowing the solubilization of the water-insoluble monomers by the formation of micelles, aiding to the particle nucleation mechanism, stabilizing the emulsion during polymer particles growth and controlling the particles size.

[39] Electrostatic stabilization develops when ionic repulsive forces keep particles apart.

[40] Steric stabilization develops when polymer particles are kept apart by a the presence of a surfactant's layer adsorbed on their surfaces.

polymer surface is usually much higher than the ratio in bulk solution. Nevertheless, under stress conditions, surfactants may desorb from the latex, losing their stabilizing effect. In addition, the occurrence of surfactants' phase-separation during the film formation process is one of the decay typology affecting emulsion coatings and paints.

For these reasons non-migratory polymerizable surfactants are sometimes used (e.g. maleates; block copolymers of ethylene oxide and propylene or butylene oxide with a polymerizable group at one end; fluorinated monomers…). These compounds take part in the free radical polymerization process themselves and anchor to the particle surface by a permanent covalent bond. Although the benefits of using this kind of surfactants has been pointed out in a number of studies, they are still not available at a competitive price, and polymer manufacturers are rather unwilling to use them.[41]

Protective Colloids

They are water-soluble polymeric emulsifiers added to the system in 1-10%/wt, to aid latex steric stabilization. There are natural and synthetic colloids, the most commonly used are hydroxyl-ethyl-cellulose and polyvinyl alcohols (the latter are often included in PVAc formulations).

Preservatives (biocides)

In order to inhibit the biological growth while the products remain in their containers, low amounts (less than 1%wt) of some toxic materials are post added to the emulsion. In the past, copper and tin compounds have been used. Nowadays halogenated compounds are preferred, even though some may produce measurable yellowing when exposed to UV light. Commonly methyl benzisothiazolinones, chloromethylsothiazolines, barium metaborate and formaldehyde donors, such as 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride, are used.

Sequestering agents

These are sometimes added to the emulsions in order to remove the metal ions (such as those present in hard water), preventing them from precipitating any anionic surfactants. The most commonly used are sodium hexametaphosphates.

Coalescents and co-solvents

Within emulsion coatings, films form by evaporation of water and coalescence of the remaining polymer. It is to remember that for the polymer to form a coherent film it must be of sufficiently high molecular weight and the temperature must be above the so called *minimum film formation temperature* (MFFT). This temperature is mainly governed by the Tg (even if somewhat lower, due to the plasticizing effect of

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[41] Aramendia, *et al*. 2003; Guyot, Graillant and Favero*,* 2003; Guyot, 2004; Hayes, Golden and Smith, 2007; Hellgren, Weissenborn and Holmberg, 1999; Klimenkovs, *et al.* 2003; Pich *et al.*, 2005; Samakande, Hartmann and Sanderson, 2006; Silber *et al.*, 2002; Summers and Eastoe, 2003; Tan, *et al.*2005.

surfactants, additives and residual water). Most emulsion polymers are too hard to coalesce by themselves at normal temperature. This is why coalescing solvents are often added to temporarily soften the polymer particles during film formation, aiding final film integrity. They are slow evaporating solvents with some solubility in the polymer phase.

The smaller the polymer droplets, the higher is the shear rate needed for coalescence, and the larger the amount of coalescent used.

In early formulations diethylene glycol performed both as antifreeze agent and plasticizing solvents. For acrylic polymers, propylene glycol is usually preferred, while its use with vinyl acetate polymers is less ccommon (because of the absorption of the glycol into polymer particles).

Other coalescents are: dialkyl succinates, methyl and butyl cellosolve, carbitols, ester alcohols, benzoate esters, glycol ethers, glycol ether esters and *n*-methyl-2-pyrrolidone. The drawbacks of coalescing agents remaining in the paint film for long time are odor and dirt pick-up. As the film formation occurs, they slowly diffuse to the surface and evaporate, increasing the hardness and block resistance of the film.

Wetting Agents

Since the surface tension of many polymers used in coating industry is relatively high, further surfactants are added to the emulsions in order to allow a proper wetting of different surfaces. The formation of continuous good films actually needs that the surface tension of a coating is lower than the critical surface tension of the substrate. If it is not so, some defects, as *cratering* may occur. Surfactants with highly branched tails or with two different tails are often used for this purpose (e.g. sodium bis(2-ethylhexyl)sulfosuccinate; surfactants with acetylenediol as polar head group). To enable aqueous systems to spontaneously spread on very hydrophobic surfaces some *superspreaders* are sometimes used (e.g. ethoxylated silicone-based surfactants).

Freeze / Thaw Stabilizers

Within waterborne emulsions, the formation of ice crystals may disrupt the stability of the dispersion thus causing permanent damage through polymer coagulation. The simplest way to prevent freezing is to depress the freezing point of the water. For this reason, slight amounts (2-10%/wt) of low evaporating solvents are commonly added to waterborne products. Generally, ethylene or propylene glycols are used. Many non-ionic emulsifiers also act as freezing point depressant.

1.2.1.3 Pigments [42]

Roughly speaking, there are two types of pigments:

- colored pigments absorb a portion of the light which falls upon them, thus reflecting to the eye a given group of wavelengths that determine the color;
- white pigments may absorb some light and convert it into heat, but they do not select any particular wavelength and return to the eyes an appearance of white.

According to their nature, pigments may be further classified in inorganic or organic. A detailed description of the pigments which are most commonly used in modern paints goes far beyond the purposes of this thesis. While referring the reader to more specialized literature,[43] only some relevant concepts are following reviewed.

Since 1971, the nomenclature of pigments has been fully standardized and listed in the *Colour Index* (C.I.) published by the Society of Dyers and Colourists. Each pigment is given a C.I. name, consisting of two letters and a number which correspond to color and type of pigment respectively.[44] In addition, a C.I. number makes it possible to look up the chemical composition of the pigment. In this thesis, all the pigments are referred to, according to this system.

The main purpose of including some pigments in a coating is that of hiding the underlying surface. Within works of art, the decorative value of the paint is also of primary importance too.

The hiding power of a coating is related to its ability to reflect light. This depends upon many factors:

- pigment particles size (which usually ranges between 0.2 and 20 μm);[45]
- pigment concentration;
- pigment dispersion in the film (with shape affecting pigments' packing);
- the difference in the refractive index of the pigment and its surrounding medium.

As far as the last aspect, the *hiding power* of the white pigments is proportional to the square of the difference in the refraction index of the pigments and their surrounding medium. The refractive indexes of the synthetic resins used as paint binders are around 1.4 ÷1.6 whereas most prime white pigments (such as basic carbonate white lead, zinc oxide, zinc sulfide, titanium dioxide…) have a refractive index higher than 1.5.

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[42] Holmberg, 2003: 153; Learner, 2004: 24-29; Perera, 2004; Radcliff, 1964

[43] Barnett, Miller and Pearce, 2006; Kalsbeek, 2005; Keijzer, 1988; Keijzer, 1989; Keijzer, 1990a; Keijzer, 1990b; Keijzer, 1999; Picollo, *et al.* 2007; Quillen Lomax and Learner, 2006; Quillen Lomax, Schilling and Learner, 2007; Sonoda, Roioux and Duval, 1993; Sonoda, 1999

[44] For instance, Titanium White C.I. name is PW6 (PW: Pigment White), while its constitution number is 77891.

[45] According to Learner, 2004: 24. According to Holmberg, 2003: 153, the pigment size for maximum scattering is the wavelength of the light within the particle (about 0.2÷0.4μm).

A special group of white pigments is that of the *extenders* or fillers,[46] which are generally used to extend the hiding power of the other pigments. Their refractive indexes are quite close to those of the binding media, but higher than the that of air (1.0). For this reason, if they extend outside the vehicle film into the air they improve the hiding power of the film. This property is often used when formulating matt paints. They are also used in order to reduce the tinting strength of certain synthetic pigments (notably the phthalocyanine ones).[47]

Since in normal condition (within the vehicle film), the hiding power of the extenders is poor, they are often add to the paints in order to fill the coating volume (thus lowering costs), with a minimal impact on the other performances.

Some of them are also used to control the rheological properties of the paints or to improve the mechanical and stability properties of the resulting film (*reinforcing agents*).[48] Extenders may be above 44 µm in size. They usually have low specific gravities (thus reducing the tendency to settle),[49] and do not react with the other components of the paint.

Some typical extenders are: silicate pigments (such as silica, kaolin, talc, mica…) barium sulfates (barytes and Blanc Fixe), calcium sulfates (gypsum and anhydrite), calcium carbonates (of natural origins or precipitate types), magnesium carbonate and double carbonate of calcium and magnesium (dolomite).

Finally, it is important to remember that the properties of an organic coating are influenced by the type of pigment and the *pigments volume concentratio*n (PVC), defined as:

$$PVC = [V_p/(V_p+V_b)] \times 100$$

where V represent the volume, p and b subscripts represent the pigment(s) and binder(s), respectively.

The *critical pigment volume concentration* (CPVC) represents: '*the PVC corresponding to the random tightest possible packing pigment particle and the minimum amount of binder necessary to fill the interstices between particles*'.[50]

Above this value the paint layers become discontinuous and its properties change substantially.

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[46] The word extender refers to the fact that these pigments are used to extend the hiding power of other pigments. The word filler is used for expressing a more negative meaning, implying adulteration. Sometimes the word *inerts* is also used referring to these pigments.

[47] Learner, 2004.

[48] It has been proved that a micaceous magnesium silicate increases the resistance of outside house paints to the weathering agents. An alkaline extender as calcium carbonate is often used to improve the stability of vinylacetate polymers.

[49] Except the barite which has a density of around 4.5, extenders' density is around 2.5÷3.0. Radcliff, 1964:58.

[50] Perera, 2004: 248. The potential effects of pigmentation on the properties of the coatings are deeply reviewed in this paper. Further information in Steward, Hearn and Wilkinson, 2000: 248-251

1.2.1.4 Paint additives [51]

As previously pointed out, when adding the pigments to the emulsion binders, a number of further additives are introduced in the system.
The main of these additives are: wetting and dispersing agents, humectants, defoamers, thickeners and preservatives. The latest ones, although typically included in the base emulsions, are further supplied to avoid dilution as water and other components are added.

WETTING and DISPERSING AGENTS

In order to formulate good hiding power paints, the pigments need to be finely dispersed in the waterborne vehicle.
Pigments are usually supplied as flocculates and agglomerates of primary particles, separated by cavities filled with air and water.

The first step of the dispersion process is to wet these agglomerates, using some compounds which are able to adsorb onto pigments' surface, to remove the air and to help breaking-up the flocculates. This purpose is achieved thanks to wetting agents, usually oligomeric non-ionic surfactants, as alkylphenol ethoxylate and fatty alcohol ethoxylates having a hydrophobic chain length of 10-12 carbon atoms and an ethoxylate chain of 6-8 EO units. Sometimes acetylenic diols, alkylaryl sulfonates and sulfosuccinates are used as well.

The second step is to disperse the pigments through the medium and to maintain the stability of this dispersion.
The stabilization of the pigments is achieved using dispersing agents, which work through electrostatic or steric hindrance mechanism. For this purpose, low molecular weight surfactants or polymeric dispersants (polyelectrolytes) are usually employed.
The choice of the most suitable dispersant depends upon the pigment and the vehicle typology. In waterborne paints, electrostatic repulsion is usually the most important stabilizing mechanism.

To disperse hydrophilic INORGANIC PIGMENTS (as oxides and extenders), polyelectrolyte compounds are often used. The surface charge of the inorganic pigments is related to the oxide typology and the pH of the vehicle. The introduction of an ionic dispersant onto the oxide surface alters the balance of surface charges, altering the isoelectric point of the pigment particle and thus affecting its dispersion stability (for any given pH, adding the ionic dispersant may improve or reduce the stability, depending on whether the charge will increase or decrease).
For this purpose, anionic dispersants are usually employed. Among these dispersants there are inorganic and organic compounds. The typical inorganic dispersants are polymeric phosphates which, at relatively low concentrations, stabilize a variety of

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[51] The information comes from the literature reported at note 35 and from: Holmberg, 2003

inorganic pigments acting both through acid-base interactions (with oxide or hydroxide pigments) or chemisorption at pigments' surfaces (e.g. calcite, barite…). Generally calcium or potassium salts of oligophosphates with two to six phosphate units are used.[52]

Among the anionic organic dispersants instead, polyacrylic acids, styrene-maleate copolymers or low molecular weight[53] polyacrylates are used, with sodium and ammonium salts of polyacrylic acids (2,000 to 20,000 MW) as the most common choice. Sodium salts of lignin sulfonates and aryl alkyl sulfonates are occasionally used.

The dispersants used for stabilizing the more hydrophobic ORGANIC PIGMENTS belong to two classes: anionic surfactants providing electrostatic stabilization,[54] and non-ionic surfactants, providing steric stabilization.[55] As far as the first typology, alkyl benzene sulfonates are probably the most commonly used.

As far as the second typology instead, even though alkylphenol ethoxylates (APE) have been the first choice for a long period of time, because of environmental concerns, they have been gradually replaced by fatty alcohol ethoxylates.

It is to remember that non-ionics with 10-30 EO units in the ethoxylate chain are required to provide adequate steric stabilization of the dispersion.

Regardless of the pigment, mixtures of the two dispersant typologies (anionic and non-ionic) are often used because, as the film formation process occurs, the contribution due to the electrostatic repulsive forces from the anionic surfactant decreases and the non-ionic surfactants may provide steric stabilization around the pigment particles, continuing to secure pigments' dispersion as the system becomes less fluid. The optimum ratio of anionic: non-ionic surfactant is 25:75.[56] Additive manufacturers usually supply these mixtures of surfactants for aqueous paint applications as blends.

Sometimes, monoethanolamide ethoxylates of polyunsaturated fatty acids or zwitterionic surfactants (like lecithin) are used.

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[52] Phosphates were more often seen in the early 1960s. Some limits in their use are: at high pH they may become hydrated, and thus less effective (because not highly charged), causing unexpected rheological changes of the formulation; they are water soluble in the dried coating and make it permeable to moisture; being particularly sensitive to fungi attack may cause a certain blooming of the film; they have been proved to be the cause of some frosty crystalline deposits occurring on the surface of aged paint films.

[53] The use of oligomeric products is due to the need of controlling the viscosity of the system. The best-known dispersants are the Orotan polyacrylate salts (Tamol™ in the U.S., e.g: the sodium polyacrylate olefin polymer Tamol™ 731). Croll, 2007: 20

[54] In this case, the stabilization is supposed to derive from the anionic surfactant forming electron donor-acceptor complexes with pigment surfaces that contain electro deficient groups.

[55] For being effective this kind of stabilization needs: the complete coverage of the pigment particle surfaces with surfactants; the adsorbed surfactant being strongly anchored to the pigment surfaces (lowering desorption by collision); the adsorbed layer being large enough to prevent particles flocculation; interaction of the layer with the dispersing medium, extending into it and becoming solvated.

[56] Thetford, 2003:127

HUMECTANTS

In emulsion paints, pigments act as non-deformable particles, similar to monomers of high Glass Transition temperature. For this reason, during the film formation process, the polymer binding particles must deform more than in clear coatings.

Slow water losses help the polymer particles to flow into each other and around the pigments.
In order to slow the evaporation rate of water, high boiling water soluble liquids are added to the emulsion. Ethylene and propylene glycols are the most commonly used humectants. Other humectants are butyl carbitol and hexylene glycol. The latter, dissolving in the polymer particles during the last stage of the film formation, acts as a temporary plasticizer (reducing the Tg of the binder), thus acting as coalescing agent also.

DEFOAMERS

In coating and paint industry, foaming is an unwanted phenomenon. Since emulsions contain a certain amount of surfactants, they have the inherent tendency to foam. Defoamers or antifoaming agents are a group of surface-active compounds used at different stages of the manufacturing process to prevent the formation of a foam or to destroy a foam already formed. They are very hydrophobic compounds that spread at air/liquid interface, allowing air to release.
In the past, mixtures of solvents (alcohols and ketones) were used. These mixtures were later replaced by alcohol ethoxylates (with 2 or 3 EO units). Nowadays, typically mineral oils, silicone oils (as polydimethylsiloxanes or other high molecular weight polysiloxanes carrying organic substituents) or perfluorinated hydrocarbons are used. One of the drawbacks of using this kind of compounds is that they are likely to produce film defects (craters, fisheyes…).
To prevent foaming formation and to aid wetting, non-ionic effective surfactants are sometimes used, such as molecules with large hydrophobic anchor groups that, being strongly adsorbed on pigments' surface, are less likely to be adsorbed at the air/liquid interfaces (typical examples of these surfactants are di- and tristyrenated phenol ethoxylates, or *o*-phenylphenolethoxylates). Other oligomeric non-ionic effect surfactants, working as wetting and defoaming agents at the same time are: acetylene diols, silicones and fluoro surfactants.

THICKENERS

Different colloids are used to impart the right rheology to waterborne paints, thus improving their handling properties and minimizing the occurrence of application problems as spattering, sagging, appearance of brush marks due to poor leveling, etc...

Thickeners work through multiple hydrogen bonds, causing chain entanglement, looping and/or swelling which leads to volume restrictions. Some of them work also as protective colloids.

For many years, cellulose ethers (as hydroxyl-ethyl cellulose -HEC-, methylcellulose and carboxymethyl cellulose -CMC-) have been a very cost-effective and straightforward method for modifying the viscosity of emulsion paints. They are compatible with a wide range of ingredients and can be purchased in different grades of molecular weights (from less than 100,00 Da to over a million Da). High MW ethers lead to high viscosities while present in fairly low concentrations. In paint formulations often two cellulosic thickeners of different molecular weights are included. Some limitations in using this kind of products are due to the fact that they slowly dissolve and equilibrate in solution, and can be attacked by microbes and mildew in the dried coating.

Polysaccharides such as xanthan and guar gums are also used.

Other thickeners are alkali-swellable polyacrylate emulsions, which add considerably viscosity upon neutralization with an appropriate base. The use of an acrylic thickeners rather than cellulosic colloids is preferred for vinyl acetate finishes.

In addition, in the 1980s the so called *associative thickeners* were introduced.

These are block copolymers consisting of hydrophilic backbones modified with hydrophobic domains. The most common ones are: hydrophobically modified ethylhydroxyethylcellulose (HM-EHEC), and hydrophobically modified ethoxylate urethane (HEUR). The overall molecules of these thickeners have a hydrophobic domain group at each end of their molecules. These domains associate with the binder to form transient networks, which can be destroyed by shear. Limitations in the use of these thickeners are their cost and tendency to phase separate.

Sometimes, inorganic thickening agents, mainly bentone clays (including bentonites, smectites and attapulgites) and fumed silicas, are used.

1.2.2 Film Formation Process [57]

In order to properly understand the properties of the paint films coming from emulsion products, the salient features regarding the film formation process have to be considered.

The precise mechanisms involved in this process are still items of debate. Nevertheless, the film formation can be tentatively described by a simplified model encompassing three main stages: evaporation of water and particle concentration; particles deformation; coalescence (figure 1.2-2).

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[57] Keddie, *et al.*, 1995; Learner, 2004: 14-15; Song, Hourston and Pang, 2000; Steward, Hearn and Wilkinson, 2000.

In the wet state, the solid high molecular weight polymer particles are dispersed in water and stabilized by the surrounding layer of surfactants. As the product is applied, water evaporation (mainly proceeding from top to bottom and from edges to center) leads to the concentration and compaction of the polymer particles.

When the polymer fraction reaches about the 60-70%/v, the polymer particles are packed in a highly ordered state, with interparticular capillary channels still filled by water. As the evaporation goes on, the particles are gradually brought into contact and caused to deform to a polyhedral, progressively space-filling shape (forming the so called *honeycomb* structure). At this point the polymer chains diffuse across the particles boundaries (*coalescence*), finally leading to an isotropic continuous film.

Even if influenced by a number of factors (dispersion properties, film thickness, environmental conditions and support typology) the first steps of the film drying process usually run out in several hours.[58] The coalescence may instead require very long periods of time.[59]

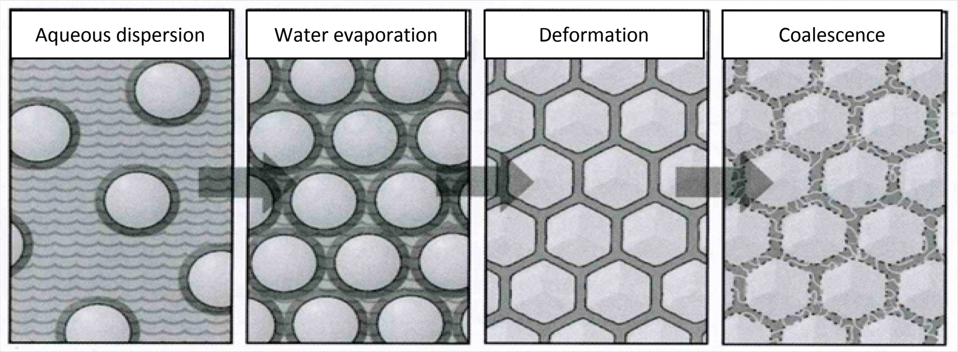

Fig. 1.2-2: Schematic representation of the three stages which lead to the film formation of an emulsion product (image adapted from Zumbühl *et al.*, 2007: 258)

In the attempt of identifying the forces which overcome the resistance of the polymer particles to deform and coalesce, a number of theories have been proposed. Each one of these takes into account the relative weight of different contributions coming from van der Waals, gravitational, capillary, electrostatic, elastic surface and interface forces.[60]

Unquestionably, the film formation is favored if the forces which oppose particles deformation are minimized. This is essentially obtained by properly choosing the polymers and by lowering their glass transition temperatures (using coalescents).[61]

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[58] Zohrevand and te Nijenhuis, 2006.

[59] The honeycomb structure was still detected after 3 months from the film casting. Zumbühl *et al*, 2007

[60] Scalarone*, et al*, 2007

[61] Referring also to the concept of *Minimum Film Formation Temperature* (MFFT), previously mentioned while describing the types of coalescents.

In addition, well-dispersed emulsions of small size particles are expected to produce better films because of the tightly packed arrangement of particles produced before coalescence.
Moreover, the slower is the drying process, the more coherent will be the final film. For this reason all those parameters affecting the evaporation rate of water have to be taken in consideration (ranging from temperature, to relative humidity, substrate porosity…).

Paint films show heteromorphic microstructures, with a network of pigments [62] and additives being retained in the system and preventing a proper coalescence.
In the field of polymer coating science, the fate of the surfactants during the drying process has been well explored, as well as their potential role in affecting the film properties. These aspects will be reviewed in the following section.

1.2.3 Decay processes affecting emulsion paint murals

The decay processes affecting contemporary murals arise from a number of reasons.

First of all, murals are part of an architectural support which may suffers for structural failures, freeze-thaw cycles, capillary rising damp and other processes.
The concurrence of these phenomena leads to many decay typologies (such as cracks, water infiltrations and salt efflorescence), which worsen the stability of the overlaying paint films.

Further problems are related to the chemical and physical compatibility between the inorganic supports and the paint layers (e.g. binder or pigment degradation due to an alkaline pH, paint lifting due to potential decrements in the water vapor permeability of the supports…).

All these aspects are exacerbated, because outdoor murals are often subjected to extreme weathering conditions, encompassing prolonged direct sunlight exposure and heavy rains. These conditions have been reported to cause severe breakdown of the binders and fading of the pigments after as little as ten years.[63]

Notwithstanding the concurrence of all these factors, the first approach to understand the decay typologies which affect mural paintings is to study the properties of the paints themselves. For this reason, two of the main decay processes influencing the durability of emulsion paints are reviewed, and tentatively set in the context of mural works of art.

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[62] Among the studies concerning the influences of inorganic pigments on polymer interdiffusion; Kobayashi, Rharbi and Winnik, 2001.

[63] Reiner, 2003.

1.2.3.1 Phase-separation processes

As extensively described in the previous section, emulsion paints consist of a multitude of additives. With the exception of few volatile compounds, all the others remain in the dry film, possibly affecting its properties and response to environmental conditions.

Since the 1990s, a number of studies have been carried out in the attempt of exploring the fate of the surfactants during the emulsion drying process and the role played by these additives in preventing a proper film coalescence. These studies firstly considered the properties of clear coatings, consisting of anionic surfactants, mainly characterized by sulfate and sulfonate hydrophilic heads.[64]

As the film formation develops, depending upon the solubility of the surfactants in the latex polymer and to their relative surface energies, these additives may either dissolve in the polymer particles (thus exerting a certain plasticization) or form a continuous membrane at the interface between polymer particles.[65]

In a number of cases, it has been however proved that the surfactants tend to migrate from the water-particle interface, redistributing within the film or desorbing towards film interfaces.[66]

In order to understand this migration process, the surfactant solubility in water has to considered. Since the surfactants try to remain in water as long as possible, and water recedes from top to bottom, at the beginning of the drying process they are mainly driven toward the support (where there are higher amounts of residual water).[67]

At this point, two processes may occur:

- as the film formation goes on and the permeability of the upper layers is gradually reduced, the surfactants may remain trapped in the lower part of the film and potentially aggregate in reverse micelles [68]
- the large molecules of the surfactant adsorbed at particle-water interface prevent the contact and coalescence of the polymer particles. For this reason, the surfactants which were initially driven toward the substrate, may later diffuse through a skin of not coalesced but fully deformed particles, reaching the film-air

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[64] All the studies referred in the following notes were carried out on this kind of coatings. The main results of these studies have been reviewed by Lee, *et al*. 2006.

[65] Tzitzinou, *et al.*, 1999

[66] This phase separation process has been firstly reported for p(BMA), p(2-EHA) and p(EA-MAA) films (Tzitzinou, *et al.*, 1999). Gundabala, Zimmerman and Routh (2004) elaborated a mathematical model for predicting the distribution of the surfactants within the film.

[67] This initial direction of the migration also relates to the tendency of the surfactants to lower the polymer-support interfacial tension (Urban, 1997). This relation between substrate surface tension and surfactants mobility is however reduced for non-ionic surfactants (Evanson and Urban 1991b).

[68] This excess of surfactant is possibly the cause of the poor coalescence detected close to the substrates (Urban, 1997). This mechanism was proved to prevail in silicone based films (Mallgol, *et al.*, 2002)

interface. The process leading to this surfactant surface exudation could also relate to the capillary transport performer by water.[69]

Regardless of the dominant migration mechanism, surfactant diffusion primarily upon three factors:

- the polymer-surfactant affinity (the mobility of the anionic surfactants is for instance reduced by the interaction with certain monomers, such as acrylic acid) [70]
- the Glass Transition temperature of the polymer (the lower is the Tg the higher is the mobility of the surfactants, and the more the surface exudation is favored)
- surfactant type and structure (the higher their molecular weight, the lower is their mobility).

A number of other factors may influence the diffusion process.
A film water uptake, was for instance proved to promote the surfactant mobility.[71]
This mobility is moreover encouraged by high temperatures (at least higher than polymer Tg).[72] In addition, different water evaporation rates have been seen to result in different morphologies of the exuded layers (fast evaporation leads to patchy layers while slow evaporation to uniform monolayers).[51]

The redistribution of the surfactant starts and the very beginning of the film formation process but it is followed by slow changes with time, which are influenced by many factors. As a result, the presence of the surfactant within the bulk film or at its interfaces may significantly alter the final performances of the film itself.
It was for instance proved that the surfactant migration toward the support alters the adhesion properties of the film.[73] The surface exudation instead, causes appreciable changes of film wettability (leading to films which are more prone to dirt pick up and which are more sensitive to polar solvents, such as water).[74]
In addition, the surfactants which remain within the bulk film, substantially increase the moisture absorption and the water sensitivity of the film.[75]

For these reasons, the surfactants and their migration processes have become one of the concerns related to conservation of acrylic emulsion paints.[76]

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[69] Belarui, *et al.*,2003; Mallgol, *et al.*, 2002

[70] Evanson, Thorstenson, and Urban 1991

[71] Since surfactants are water soluble, they follow the water penetrating the polymer network. In addition, as water diffuse through the film, it plasticizes the polymer particles, thus further improving the potential mobility of the surfactant. Urban, 1997

[72] Mallgol, *et al.* 2002

[73] Chrameau, Kients and Holl, 1996

[74] Scalarone, *et al.*, 2007

[75] Zhorehvand and te Nijenhuis, 2006

[76] Jabowsky, *et al.* 2003

Since the turbidity of some acrylic binder films was firstly related to the presence of a poly(ethyleneoxide) compound,[77] an ever increasing attention was directed to the potential role played by paints additives in affecting the properties of modern and contemporary works of art. In the attempt of exploring these aspects, a number of studies have been recently carried out on both, laboratory samples and real canvas paintings. [78,79]
The non-ionic polyethoxylate (PEO)[80] type surfactants were identified in a number of artists' grade waterborne paints. It was moreover confirmed that these surfactants tend to spontaneously desorb from acrylic paint layer, leading to small rounded crystals or translucent layers at the paint-air interface.

As already seen for clear coatings, even when dealing with emulsion paints the exudation process is influenced by a number of factors:

- brands reasons, possibly related to the nature of the polymer binder and the amount of the included surfactants (Talens® paint films, based on a p(EA-MMA) formulation were more prone to the process than Liquitex® films, consisting of a p(*n*BA-MMA) emulsion) [81]
- type of surfactant (PEO-based compounds presenting 20-40 ethoxylate units in the hydrophilic head are thought to be more likely to exude)
- pigment type (organic and iron based pigments require higher amounts of surfactant; Cadmium pigments may catalyse some photo-degradation process of the exuded surfactant)[78]
- environmental conditions (the exudation is enhanced by dark storage and raised temperature)[78]
- substrate type (the exudation is reduced when the paint is applied on porous substrates)[82]
- application of share forces.[78]

The changes to the bulk films, due to typical cleaning treatment and removal of the exuded surfactants has been also evaluated. Even though these aspects are still under

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[77] Whitmoreand Colaluca, 1995; Whitmore, Colaluca and Farrell, 1996

[78] The reader is referred to the comprehensive review by Ormsby and Learner, 2009

[79] Non-ionic PEO surfactants have been detected on the surface of some works of art dating from the 1960s and 1970s. Ormsby, *et al.* 2008; Ormsby, *et al.*, 2009

[80] Mainly identified as Triton®X-405 and X-305: Ormsby and Learner, 2009

[81] Ormsby, *et al.*, 2009

[82] When comparing the results gathered from a number of samples differing only for the support type, it was proved that the amount of the exuded PEO-type surfactant was higher for those samples cast onto Teflon supports rather than those cast on more porous acrylic primed cotton canvas. Ormsby, *et al.*, 2007

evaluation, it seems that usual cleaning treatments have a negligible effect on the mechanical properties of the paint films but may induce relevant changes in their optical and morphological properties.[83] It was moreover pointed out that the exudation process continues after previous cleaning treatments.

Until now, poor attention has been instead directed to the occurrence of the exudation process in mural paintings. Nevertheless, the leaching of paints water-soluble components has been reported as one of the degradation processes which potentially affect contemporary murals.[84]

In this context the phase-separation, may be influenced by a number of aspects related to the chemical composition of the paint layers but also to the properties of the inorganic, porous support and the role played by water. As already pointed out, most of the murals are exterior works, directly exposed to rain, or painted on supports affected by water infiltrations and rising damp. On one hand, the presence of the hydrophilic additives in the bulk film is expected to enhance the water permeability of young paint layers.[85] On the other hand, the liquid water is expected to promote the phase-separation process, driving the hydrophilic paint components towards both, the paint surface and the paint-support interface.

1.2.3.2 Photooxidative processes [86]

ACRYLIC RESINS

Since their introduction in the coating industry, acrylic polymers were considered *extremely resistant* to light-induced changes. This definition may however lose its meaning when shifting to works of art, whose durability should be higher than the 50 years usually considered as an acceptable life expectation for quality industrial products.[87]

In the past years the aging properties of solvent-borne acrylics used in the conservation and paint manufacture fields have been widely investigated.[88]

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[83] A part form the results reported by Orbsby and Learner, 2009; the reader is also referred to the AFM evaluations reported by Kampakasali, *et al.* 2011, and to Silva's PhD dissertation (2011).

[84] Golden, 2003. Essay presented during the symposium *Mural Painting and Conservation in the Americas* (May 16-17, 2003, Los Angeles)

[85] Whitmore, Morris and Colaluca, 2007.

[86] A part from the texts referred in the following notes: Boyatzis, Charalambous and Kotoula, 2007; Down, *et al.*, 1996; Jablowsky, *et al.* 2003; Jones, *et al.*, 2005

[87] Golden, 2003

[88] Due to our interest toward the stability of the acrylic products under outdoor conditions, only the results coming from the experimentations carried out using high energy wavelengths are here reviewed. It is however to remember that, upon UVA light exposure, the durability of an acrylic emulsion medium was

When testing acrylic and methacrylic homopolymers upon artificial solar light irradiation (Xenon light source filtered for λ < 295 nm), it was proved that, both types of resins may undergo chain scissions of the side ester groups and cross-linking reactions of the polymer backbone. The first type of reaction leads to the loss of volatile molecules, and is the predominant degradation process for both types of resins. It is especially pronounced for polymer characterized by short alkyl side groups.[89]

It was moreover pointed out that, acrylate units are much more reactive than the methacrylates ones towards photooxidative processes (due to the presence of the more labile tertiary hydrogen atoms). While testing the stability of acrylic co-polymers, it was confirmed that the oxidation processes firstly involve the acrylate units and proceeds through formation of hydroxyl groups and new carbonyl functionalities (among which γ-lactone structures due to intramolecular back-biting processes).[90]

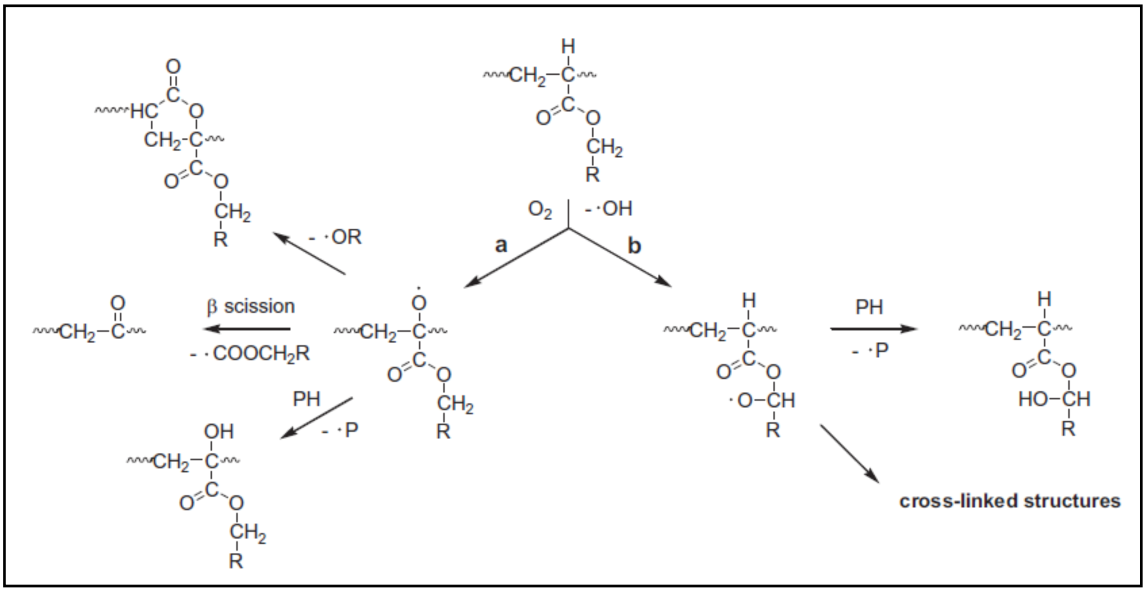

Fig.1.2-3: Simplified mechanism of oxidation of acrylic copolymers (adapted from Lazzari, *et al.*, 2011: 119)

The length of the alkyl side group was also proved to influence the main degradation pathway of these resins. Butylacrylates are less stable and more prone to cross-linking than acryletes presenting lower structural units. As a matter of fact, the oxidation of the butyl groups leads to unstable secondary hydroperoxides which are rapidly photolysed

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confirmed to be very high (showing considerable tensile strength after exposure to an UVA dose equivalent to 5,000 years in a museum). Whitmore and Colaluca, 1995

It was also pointed out that, during the early stages of the ageing, this type of medium undergoes a certain discoloration (particularly pronounced in the case of dark storage conditions), which rapidly reverses as the light exposure is extended (Whitmore, Colaluca and Morris, 2002; Morris, Whitmore, Colaluca, 2003; Smith, 2007). This type of discoloration is thus not expected when dealing with outdoor conditions.

[89] Chiantore, Trossarelli, Lazzari 2000

[90] Chiantore and Lazzari, 2001;Lazzari *et al.*, 2011

to alkoxy radicals, thus promoting an extensive cross-linking.[91] This degradation typology could be due to an higher flexibility of the relatively long butyl side chains, which favor macroradicals recombination.[75]

All the trends described as far as the photooxidative processes of solvent-born acrylic resins were confirmed to affect acrylic waterborne products as well.[92] It was however noticed that, when dealing with emulsions, these degradation reactions develop more rapidly. This behavior was tentatively related to the surfactants molecules, the degradation of which could influence the overall stability of the acrylic resins.[93]

The photostability of the exuded PEO-type surfactants was tested as well, suggesting that they undergo early degradation processes, developing via scission reactions (ethylene oxide chain cleavage and formation of ester and formate groups) and release of volatile fragments (such as acidic compounds, ethylene glycols and CO_2).[94]

The role played by the pigments in influencing the stability of the acrylic binders have been also evaluated. It was suggested that, the inclusion of some pigments acting as physical UV absorbers may stabilize the polymer binder. This effect was recently proposed for some white pigments, such as Rutile (TiO_2).[95] The same pigments have been reported to accelerate the degradation of the binders. Other pigments seemed instead to catalyze the degradation processes of the binder (e.g. Cobalt Blue).[77]

In the context of mural paintings it would be interesting to evaluate the influence due to the support. Previous studies[96] have actually pointed out that, when applied on stones (Carrara and Proconnessium marbles) and aged simulating outdoor conditions, solvent-born acrylic resins are prone to harsh degradation. Besides the well known photooxidative processes, the polymers undergo the hydrolysis of the ester sides chain due to the alkaline environment produced by the calcium carbonate, water and CO_2 system which originates at the marble-resin interface.

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[91] Scalarone, Chiantore and Learner, 2005

[92] Stability tests carried out for a p(*n*BA-MMA) waterborne clear coating confirmed a major degradation trend toward cross-linking. (Smith,2007)

[93] Lazzari, *et al.*, 2011

[94] Scalarone, Chiantore and Learner, 2005; Scalarone, *et al.*, 2007. These results were gathered upon exposure to a Xenon lamp light, filtered for $\lambda<295$ nm. When simulating 'indoor sunlight' (Xenon arc source filtered by a window glass, thus including a small UV-A component of the spectrum) the same surfactants turned out to be quite stable. Smith, 2007

[95] Jablowsky, 2003. Spathis, Karangiannidou and Mogoula (2003) suggested an improvement in the photostability of Paraloid films added with Anatase (TiO_2) pigment toward UV irradiation. This effect was tentatively due to the pigments acting as UV absorbers, because not in contact with atmospheric oxygen and water. Studying the stability of styrene-acrylic resins added with TiO_2 pigments (rutile and rutile/anatase mixtures) Paplianka, Andrikopoulos ad Varella (2010) assessed that, these pigments may play a protective role against moist heat environments but lower the UV-light stability (especially in the mixture of rutile/anatase forms).

[96] Favaro, *et al.*, 2006; Favaro, *et al.*, 2007

Finally, if compared to pure acrylic resins, the styrene-acrylic copolymers are generally reported to be less stable, because of the development of concurrent phenyl ring opening reactions.[97] It was also assessed that styrene-acrylic artists' emulsion paints are more prone to yellowing rather than pure acrylic formulations.[98]

VINYL RESINS

In the past years the aging properties of poly(vinyl acetate) homopolymer resins have been also investigated.

The main degradation processes reported for PVAc polymers are acetate hydrolysis and photooxidative reactions affecting the polyolefin backbone.

These latter processes evolve through a series of radicals and reactive intermediates (such as carboxylic acids, peracids, ketones and lactones) which lead to chain-scissions and cross-linking reactions.[99]

The acetate hydrolysis instead has been reported to proceed both, through homolytic or heterolytic mechanisms. In both cases it leads to the release of acetic acid and the formation of poly(vinyl alcohol). Fears were reported as far as the potential role of acetic acid in promoting further degradation mechanisms.

In the context of mural paintings the acetate hydrolysis process is possibly favored because of the alkaline environment produced, for many substrates, in presence of water.[100]

Upon exposure to light sources involving 254 nm radiations, poly(vinyl acetate) resins were reported to undergo both, chain scission and cross-linking processes accompanied by the release of volatile compounds (mainly acetic acid, but also CO, CO_2 and CH_4).[101]

The nature of these volatile compounds is in agreement with a Norrish type II mechanism, consisting of the development of an excited carbonyl group upon light absorption (figure 1.2-4).

Both degradation mechanisms were reported to increase when the temperature is above the Tg of the polymer.

The potential influence of the pigments on the stability of poly(vinyl acetate) resins has been recently evaluated, while exposing different paint formulations to $\lambda \geq 300$ nm (thus simulating indoor conditions). It was proved that the metal ions present in the tested pigments (TiO_2 in the Rutile form, Fe_2O, PbO and ZnO) do not worsen the photochemical

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[97] Croll, 2007; Papliaka, Andrikopoulos ad Varella, 2010.

[98] Learner, Chiantore, Scalarone, 2002.

[99] Ferreira, *et al.*, 2007.

[100] Golden, 2003.

[101] Ferreira, Melo, Ramos, 2010.

stability of the polymer.[87] On the other hand, the ageing condition used for this study did not promote a significant degradation of the binders, either the solvent-borne nor the emulsion one.

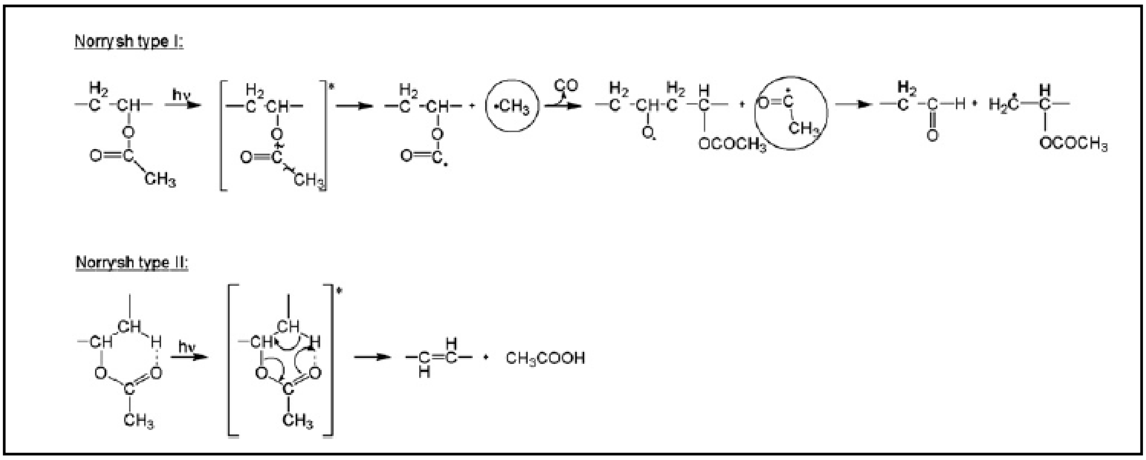

Fig.1.2-4: The photodegradation pathways for PVAc and the possible intermediate which lead to the release of volatile fragments such as acetic acid, CO and CH_4 (adapted from Ferreira, Melo and Ramos, 2010:454)

It was however proved that, commercial poly(vinyl acetate-co-vinyl versatate) emulsion paints exposed to a light source simulating indoor natural daylight, were prone to degradation mechanisms affecting both, the polymer and the non-ionic PEO-type surfactants. In this case the polymer was reported to undergo chain-scissions, acetate hydrolysis and side-chain reactions resulting in a loss of methyl groups.[102]

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[102] Doménech-Carbó, *et al.*, 2011

1.3 Inpainting contemporary murals

As previously pointed out (section *1.1. Theory and practice in the conservation of contemporary murals*), the conservation of contemporary murals poses a number of practical and ethical concerns. In this context, those issues concerning the retouching are still an open question.[103]

Leaving out the theoretical reasoning that lays behind the choice of retouching or not contemporary murals (the actual meaning and implications of this kind of treatment…), the second part of this PhD thesis was developed with the aim of evaluating the suitability of different materials for inpainting acrylic/vinyl mural works of art.

Since the meaning of these paintings is often related to their image and aesthetic value, the first aspects to consider when choosing a retouching medium, is the ability of this medium to match the colour and texture of the area to inpaint.[104]
As previously discussed, in the majority of the cases, the original surfaces of contemporary murals are based on acrylic and vinyl emulsion paints. The soft sheen, the dense pigmentation and the presence of modern colours are some of the aspects which complicate the possibility of matching the surface qualities of these paints.[105]

Besides having adequate *visual properties*, a suitable retouching medium should satisfy a number of further technical criteria. Some of these are directly related to the use of the medium *in practice*: versatility in matching different surface characteristics (matt, gloss or semi-gloss surfaces; totally smooth areas as well as bodied brushstrokes...); ease of handling; minimal adaptation of the medium to achieve the desired qualities (avoiding the incorporation of additives...).
Other criteria are instead related to *compatibility* [106] and *stability* issues.

First of all, a proper medium should be soluble in solvents which do not affect the original paint layers, thus lowering the potential damaging during both application and removal.

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[103] Actually, the literature dealing with the inpainting issues of both, mural works of art and contemporary works of art, is scarce. As far as the first aspect: Ropret *et al.* 2007
As far as the second aspect, a general review is given by Chiantore and Rava, 2005: 136-147. In the same text, the authors present same cases studies which can be considered as examples of the possible approach to follow when treating (and inpainting) contemporary works of art. Among these *Who is afraid of Red, Yellow and Blue* and *Cathedra*, by Barnett Newman (Chiantore e Rava, 2005: 287-293). The treatment of Klein's *Blue Monochrome (IKB4)*, was moreover reported by Haiml, 2007.

[104] A preliminary selection was based on the results reported by Sims, *et al.* 2010 ; Smithen, 2007

[105] Sims et *al.* 2010

[106] In conservation, the need of preserving the original material substance of the work of art is one of the most important principles to follow. The materials used for the treatments should not present any potential of damaging this original substance. Broadly speaking, the higher are the similarities between the properties of original and treatment materials, the lower is the risk of damage.

It should be also characterized by a high stability to the environmental conditions it will be exposed to (in the case of out-door paintings, direct sunlight and rain).
In order to limit the risks and costs of frequent re-treatments, it is preferable to use materials resistant to discoloration and surface changes. Moreover, the higher is the durability of the materials the better is their expected *reversibility*.[107]
Nevertheless, recalling the *compatibility* concept, the ageing rates of original and retouching materials should be as similar as possible. If the materials used for a treatment are much more stable than the original ones, the potential risk of damaging the original material substance of the work of art increases.

Finally, since *discernibility* is another important goal to achieve, the possibility to visually discriminate between original and treated areas was also considered.
For traditional works of arts, the discernibility is achieved through well-established strategies (*rigatino*, *tratteggio*, etc…)[108], that do not generally suit the conservation of contemporary paintings (where, again, the meaning could be strongly linked to aesthetic values).

For these reasons, different methods for achieving discernibility should be developed.

It is supposed that, when examining the surface of a painting under UV light (λ 365 nm, typical emission wavelength of a Wood's lamp), areas painted with binders differing as far as their chemical composition (e.g. oil and watercolor) or their age (the original and more recent inpainted areas), could be descriminated.
On the contrary, when dealing with contemporary works of art, the differences between original and inpainted areas are expected to be slight or negligible.
Usually, the original paint layers did not suffer from a prolonged ageing before being inpainted, and the composition of the original paints and the retouching materials is often similar (even if not exactly the same).
For these reasons a strategy to enhance the differences perceived when comparing original and inpainted areas under UV light, was studied.

Some molecular lanthanide compounds (e.g. the β-diketonate complexes) are known for efficiently absorbing near-UV wavelengths and, as a consequence of energy transfers from the ligands to the metal centre, for emitting characteristics narrow bands in the visible region (with the emission wavelength depending on the lanthanide centre).
If a proper amount of a suitable lanthanide complex is added to a retouching formulation, the discernibility of the inpainted area under the UV-light is expected to improve.

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[107] Reversibility is another important conservation principle. It implies the possibility of removing the materials used during a treatment without affecting the original material substance of the work of art, at anytime.

[108] A more comprehensive review of the theories concerning the inpaintig issues of traditional works of art (with respective references) in Perusini, 2004:72-81.

Even though quite promising, the use of these complexes for conservation purposes needs to be thoroughly tested.
One of the aims of the experimentation dealing with the inpainting issues of contemporary murals was to preliminary evaluate the pros and cons of using this kind of materials (e.g. assessing their influence on the visual and stability properties of the paint layers, assessing their stability to the ageing conditions, etc…).

Since the innovative potential of this application, the main features related to the lanthanide complexes and their luminescence properties are reviewed.

1.3.1 Luminescent lanthanide complexes [109]

Due to their peculiar luminescent properties, the rare-earth (lanthanide) compounds have been playing a prominent role in different applications, ranging from lighting and light conversion industry to biomedical, sensing areas and optical imaging.
An abundant scientific literature have been published in this field and, for more information, the reader is referred to proper comprehensive reviews.[110]
The aim of this section is to summarize some basic notions concerning the principles of lanthanide elements (e.g. the electronic properties which originate their optical features), and the photophysical properties of lanthanide complexes. The attention is mainly focused on the β-diketonates of the Europium(III) ion, actually used during the experimentation.

The electronic configuration of the elements belonging to the lanthanide series range from $[Xe]4f^0$ for Lanthanum (La) to $[Xe]4f^{14}$ for Lutetium (Lu). The progression of the fourteen 4f electrons is perfectly regular in the lanthanide trivalent ions (Ln^{3+}), leading to the constancy of their physical-chemical properties such as the oxidation state (all of them show a stable +3 oxidation state), the redox potential and the ionic radii (steady decrease from La^{3+} to Lu^{3+}).
The peculiar luminescent properties of these ions are one of their most attractive features. Upon irradiation with UV light indeed, many of them show specific emissions falling in the visible or near-infrared spectral region. These emissions are due to intraconfigurational f-f transitions inside the partially filled 4f shell. Since the 4f electrons are well shielded from their environment by the $5s^2$ and $5p^6$ orbitals, the ligands in the first and second coordination sphere perturb the electronic configuration of the trivalent ions only to a limited extent. This is the reason why the luminescence is

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[109] Luminescence is the spontaneous emission of light from atoms, molecules or crystals under non-thermal excitation. It could be further defined depending on the method of excitation. When originating from the absorption of an electromagnetic radiation, as in this case, the term *photoluminescence* (PL) is actually more appropriate. The words photoluminescence and luminescence may be found through the text referring to the same process.

[110] Richardson 1982; Hasegawa, Wada and Yanagida 2004; Binnemans 2009; Armelao *et al.* 2010

characterized by long lifetime excited states (microseconds to milliseconds) and narrow-band emissions depending on the specific lanthanide ion, but largely independent from the environment.

The Europium(III) ion[111] emits in the visible red spectral range. Its most characteristic electronic transitions are those shown in the following table.[112]

Eu(III) Electronic Transitions	Emission Spectral Regions
$^5D_0$-$^7F_0$	579-581 nm
$^5D_0$-$^7F_1$	585-600 nm
$^5D_0$-$^7F_2$	608-630 nm

Tab. 1.3-1: Some of the allowed electronic transitions of the Eu(III) ion together with the related emission spectral regions.

The intensity of the luminescence is proportional to both, the luminescence quantum yield [113] and the amount of light absorbed. When dealing with trivalent lanthanide ions, only a limited amount of radiation is absorbed by direct excitation in the 4f levels,[114] thus resulting in a weak luminescence.

A well-established strategy to overcome this problem is turning to molecular lanthanide complexes, exploiting the so-called *antenna effect* (or *sensitization*).

Several organic chromophores ligands are actually characterized by intense ultraviolet absorption bands.[115] If properly exciting these absorption bands, higher amounts of light can be absorbed by the complex and, as the excitation energy is transferred from the ligands to the lanthanide metal centre, an emission at the wavelengths of the lanthanide is produced.

The sensitization process develops through the following steps: population of the lowest-laying singlet excited state (S) of the organic ligand; intersystem crossing (ISC) to its triplet level (T); energy transfer (ET) to the Ln^{3+} centre.

After this indirect excitation by energy transfer, the lanthanide ion may undergo radiative transitions (line-like photoluminescence), or may be deactivated by

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[111] Atomic number: 63. Electronic configuration: $[Xe]4f^6$. Electronic ground level of the trivalent ion: $^7F_0$

[112] Melby *et al.,* 1964: 5122

[113] The *luminescence quantum yield* (ф) is the ratio between the number of emitted photons and the number of absorbed photons per time unit.

[114] The molar absorption coefficients (ε) of the transitions in the absorption spectra of the trivalent lanthanide ions are about 1-10 M^{-1} cm^{-1}, Armaleo *et al.*, 2010: 489

[115] Typical chromophores are aromatic or hetero-aromatic highly π-conjugated systems characterized by high molar absorption coefficients (ε about 10^4-10^5 M^{-1} cm^{-1}), Armaleo *et al.*, 2010: 489
Typical excitation wavelengths are above 350 nm. As far as this specific experimentation a Wood's lamp is used (main emission at 360 nm).

nonradiative processes. One of the main causes of deactivation is the *vibronic coupling* with the ligands and/or other molecules.[116]

As shown in Figure1.3-1, many other photophysical processes occur at the same time in a molecular lanthanide complex (*internal conversions*, *molecular fluorescence*, *molecular phosphorescence*).

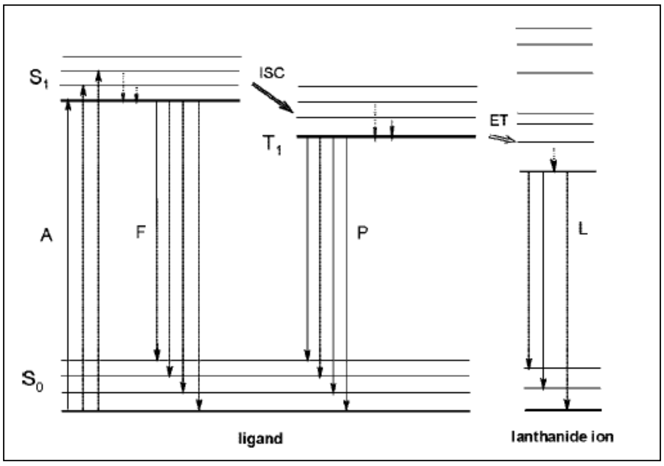

Fig.1.3-1: Schematic representation of the phothopysical processes occurring in lanthanide(III) complexes. S= singlet, T= triplet, A= absorption, F= fluorescence, P= phosphorescence, L= lanthanide-centered luminescence, ISC= intersystem crossing, ET= energy transfer. Dotted vertical lines indicate non radiative transitions while full vertical lines radiative transitions. (adapted from Binnemans 2009: 4285)

For the aim of this thesis, it is only important to remembered that:

- the luminescence of Ln^{3+} is only possible from certain energetic levels (*resonance levels*)
- the luminescence of the complex is a function of the relative positions of these levels and the lowest triplet level of the complex (which relates both to the ligands used and temperature)
- the emission of the Ln^{3+} is possible only if the nonradiative deactivation and the other photopysical processes are minimized

For these reasons, particular care should be paid when choosing the antenna chromophore. For instance, a short distance between the sensitizers and the cations promotes a fast energy transfer, so that chromophores which directly coordinate the metal centre are preferred (e.g. aza-aromatic compounds or phenolate aromatics).

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[116] The presence of high frequency vibrational oscillators (such as OH, NH and CH groups) in the proximity of the lanthanide ion favor the thermal dissipation of the energy, resulting in the quenching of the luminescence. The lower is the excited state energy of the lanthanide ion, the more the deactivation process is favored. When inserting a lanthanide complex into a matrix (which, in the case of a paint layer, could be particularly composed), the luminescence could be significantly reduced.
In addition, it is to remember that the quenching of the luminescence could relate to the concentration of the lanthanide ions in the matrix (*cross-relaxation*, *up-conversion* and *energy trap processes*). As far as this point: Miyakawa and Dexter 1970; Zhang *et al.*, 1998

It should be also remembered that, because of the already discussed shielding, the 4f electrons are scarcely available for covalent interaction with the ligands. The lanthanide-ligand interactions are therefore electrostatic and the geometry of the complexes relates to steric factors rather than electronic ones. In addition, due to their small size, the lanthanide ions have an high surface positive charge density, and strongly coordinate ligands having highly electronegative donor sites.

Depending on the steric demand of the ligand, the coordination numbers of the trivalent lanthanide cations are in the 3÷12 range (with 8 and 9 being the most commonly observed).

The complex formation result from the attraction between the ligands and the Ln^{3+} and is associated with their partial or total desolvation.

In order to increase the thermodynamic stability of the complex, the cation-ligand interaction has to be maximixed. For this reason, anionic ligands are usually recommended (e.g. carboxylates, phosphinates, phosphonates and β-diketonates).

The most common (and investigated) luminescent lanthanide organic complexes are those coming from the coordination of the Ln^{3+} ions with β-diketone ligands (1,3-diketones such acetylacetone, benzoyltrifluoroacetone, benzoylacetone, etc…).

The popularity of these complexes is due to their excellent luminescent properties, as well to some practical reasons. In fact, many β-diketone ligands are commercially available, and the synthesis of the corresponding lanthanide complexes is relatively easy.

There are three main types of lanthanide (III) β-diketonates cmplexes: *neutral tris complexes*, *Lewis base adducts of the tris complexes* and *tetrakis complexes*.

The first ones are six-coordinate complexes, characterized by three β-diketonates ligands for each Ln^{3+} (general formula$[Ln(\beta\text{-dike})_3]$).

The lanthanide ion can further expand its coordination sphere by oligomer formation (with bridging β-diketonate ligands) and by adduct formation with Lewis bases (such as water; 1,10-phenanthroline; 2,2'-bipyridine; tri-*n*-octylphosphine oxide…). The general formula of these complexes is $[Ln(\beta\text{-dike})_3L]$, where L=a mono or bidentate N- or O-donor ligand.

The *tetrakis complexes* are finally formed arranging four β-diketonate ligands around a single Ln^{3+}. These complexes are anionic and the electric neutrality is achieved by a countercation (general formula $[Ln(\beta\text{-dike})_4]^-$).

As far as the experimentation dealing with the discernibility of inpainted areas, an *adduct of an* Eu(III) *tris complex* was chosen. This complex is based on three dibenzoylmethane ligands and 1,10-phenanthroline, $[Eu(DBM)_3phen]$.

Figure 1.3-2 shows the photoluminescence (PL) spectra of two different $Eu(DBM)_3phen_x$, 0.5 wt% doped in poly(methylmethacrylate), on excitation with λ_{ex} 266 nm (iv: Eu $Eu(DBM)_3phen_{1.0}$; v: Eu $Eu(DBM)_3phen_{1.5}$). The spectra on the left (570÷730 nm) point out the enhancement in the fluorescence intensity of the Eu(III) with respect to the other complexes (iii: Eu(DBM)$_3$·2H$_2$O; vi: Eu(Phe)$_3$·2H$_2$O). Among the emission bands, the dominant one is that related to the $_5D_0f_7F_2$ transition, at 612 nm.

The spectra on the right (290÷530 nm) point out the decrement in the fluorescence intensity corresponding to dibenzoylmethane and 1,10-phenanthroline (i: Phen; ii: DBM), suggesting the combined role played by the two ligands in causing the enhancement of intensity of Eu(III).

Figure 1.3-3 presents the excitation spectra (PLE) of the same complexes. Even though the maximum of luminescence is observed by 380 nm excitation, the excitation by a Wood’s lamp (365 nm) is expected to promote an appreciable luminescence as well.

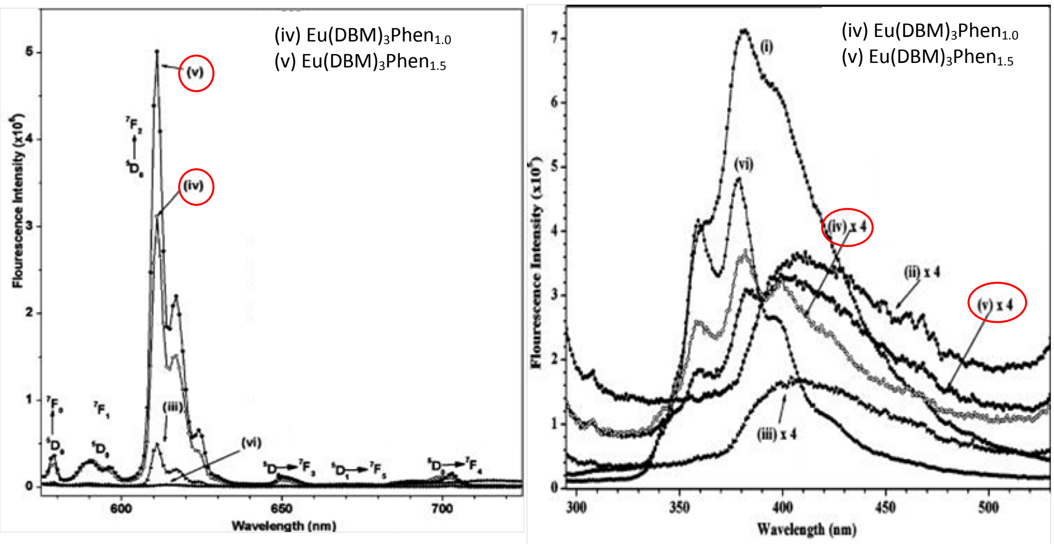

Fig.1.3-2: PL spectra of Eu(DBM)$_3$phen$_{1.0}$ (iv) and Eu(DBM)$_3$phen$_{1.5}$ (v) complexes doped in pMMA (0.5 wt%), on excitation with λ_{ex} 266 nm. The comparison spectra are those of: Phen (i), DBM (ii), Eu(DBM)$_3$·2H$_2$O (iii) and Eu(Phen)$_3$·2H$_2$O (vi). (adapted from Singh, *et al.*, 2010: 13046)

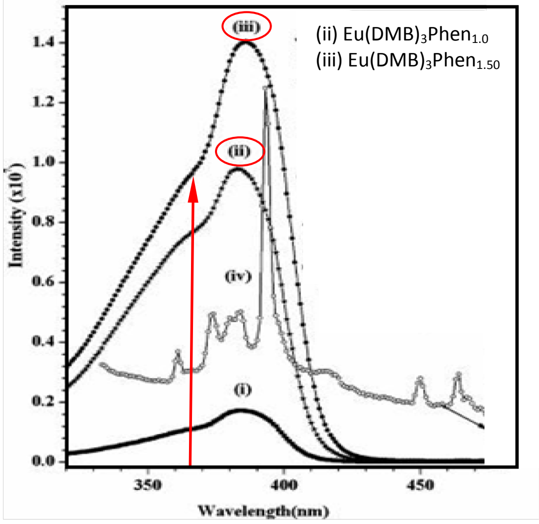

Fig.1.3-3: PLE spectra of Eu(DBM)$_3$phen$_{1.0}$ (ii) and Eu(DBM)$_3$phen$_{1.5}$ (iii) complexes doped in pMMA (0.5 wt%). The comparison spectra are those of: Eu(DBM)$_3$·2H$_2$O (i), EuCl$_3$·6H$_2$O (iv). The arrow points out the luminescence intensity promoted by 365 nm excitation. (adapted from Singh, *et al.*, 2010: 13047)

Chapter 2

EXPERIMENTAL

This chapter presents the experimental method. It is divided in four main sections: *2.1 Selection of the materials* (where the materials used for the experimentation are presented, focusing on the reasons of their choice); *2.2 Casting procedure* (where the preparation of the samples, as both free-films and mock-ups, is described); *2.3 Ageing condition*s (where the procedure used for carrying out the rising damp and UV-light stability tests are described); *2.4 Investigation techniques* (where the analytical techniques used during the experimentation are briefly presented).
Due to the considerable number of samples and to the complexity of the casting procedure, the structure and the main contents of the chapter are summarized in the following schemes. The first one deals with the study of artists' emulsion paints, the second one with the evaluation of the retouching materials and methods.

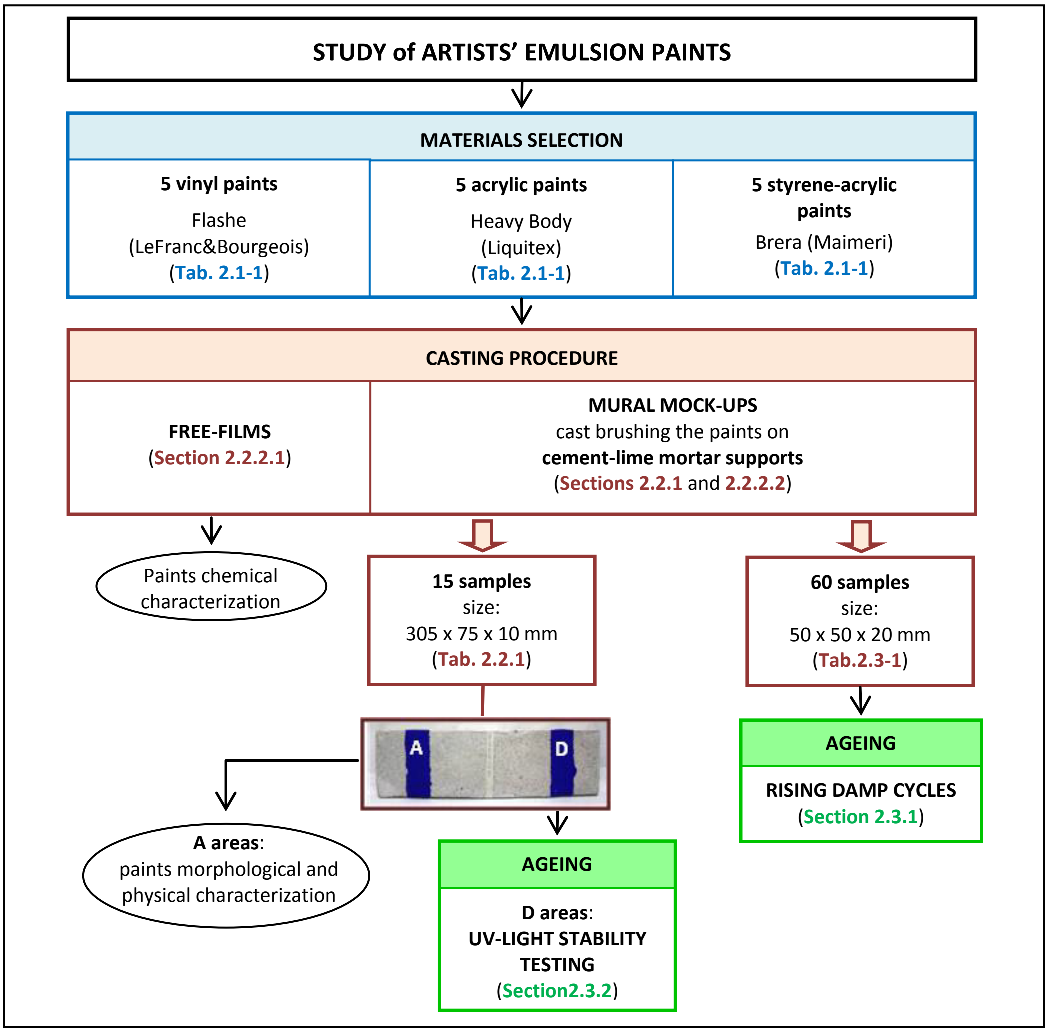

Fig. 2-1: Scheme summarizing the experimental method used to study the artists' emulsion paints.

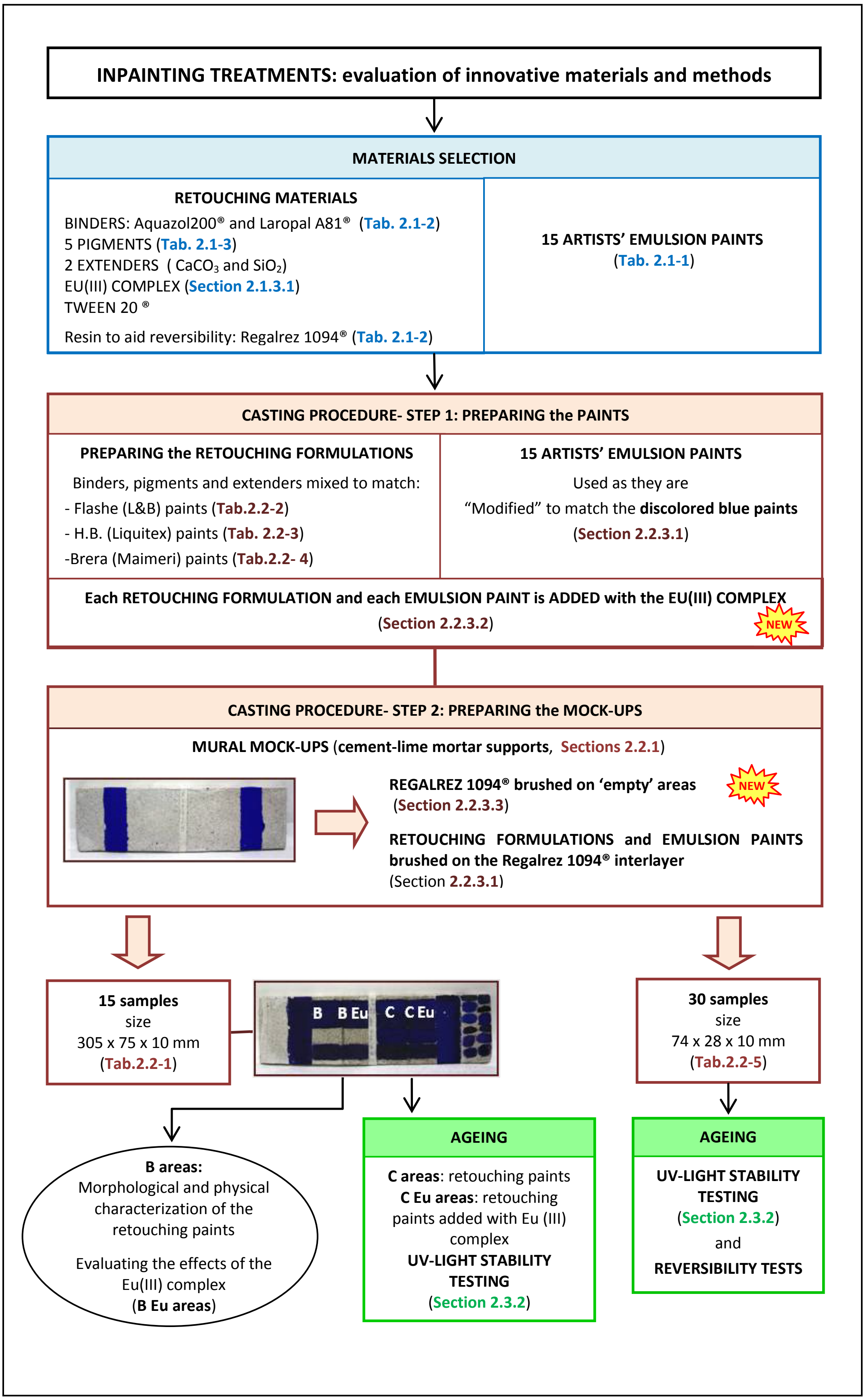

Fig. 2-2: Scheme summarizing the method used to carry out the experimentation dealing with inpainting.

2.1 Selection of the materials

2.1.1 The support

In the context of mural painting, the support is a fundamental aspect to consider. It actually influences the morphological and physical-chemical properties of the paint layers applied on it, and it could play an active role in promoting the decay processes of the paintings.
Modern and contemporary murals could be created on different supports such as brick walls, cement surfaces, lime and cement-lime plasters, carrying or not a finishing layer (which can act as a ground for the paint).

In the attempt of finding out the best trade-off between the selection of a representative support typology and the need of working with materials that allow good reproducibility while casting the samples, a cement-lime mortar was chosen.
The supports were prepared using a widespread product in the home-building field, called Malta Bastarda (GrasCalce).
The cement-lime mortar was not characterized before use. All the pieces of information regarding its properties were deduced from the technical data sheet of the product and are reported in *Appendix 1*.

2.1.2 Artists' emulsion paints

The experimentation was planned considering some emulsion paints that could be used by contemporary artists when creating their murals.

As previously described in the *Introduction* (*1.2.1 The chemistry of emulsion paints*), the most common polymer binders used for manufacturing waterborne paints are: vinyl copolymers, acrylic copolymers and styrene-acrylic copolymers.[1] Considering our area of interest (Italy), the use of this kind of paints was also confirmed by a number of characterization surveys carried out on 20th century murals.[2]

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[1] This was furthermore confirmed by an Italian household paints manufacturer (Umberto Dainese, San Marco Group S.p.a.; personal communication, spring 2010).

[2] The use of a vinyl paint was confirmed in the mural works: *Occupazione delle terre e lotta per lo sviluppo di Fiano Romano* (by Ettore de Conciliis and Rocco Falciano, Fiano Romano, 1970-72); *Senza Titolo* (by Maurizio Matrone, MACAM, 1987); *Senza Titolo* (by Gian Franco Asveri, MACAM, 1991).
The use of an acrylic paint was assessed in the mural works: *Fuga in Egitto* (by Renato Guttuso, Varese, 1983); *Senza Titolo* (by Armando Testa, MACAM, 1988); *Capriccio* (by Salvo, MACAM, 1986); *Pane bianco quotidiano: fantasmagoria* (by Concetto Pozzati, MACAM, 1986); *Senza Titolo* (by Gian Franco Asveri, MACAM, 1991); *Senza Titolo* (Ugo Nespolo, MACAM, 1986).

For this reason, the first choice was to include in the study three paint brands encompassing these three binder typologies.

In addition, since one of the aims of this research was to study the surfactants' phase-separation process, the selection included some paints which were likely to undergo this decay typology. Apart from the Titanium White paints, the others were thus chosen because consisting of some inorganic (Ultramarine Blue and Mars Yellow) and organic pigments (Phthalocyanine Green and Quinacridone Red) that require high amounts of dispersing agents (surfactants).[3]

Artists usually opt for industrial cheaper paints to create mural paintings.
However, considering the huge choice of industrial paints present on the market and the limits in properly characterizing their formulations (known for containing a multitude of additives and for being susceptible to frequent undeclared changes), it was preferable to use some professional grade artists' paints, that have been partially studied during previous research projects.[4]
The three paint brands included in this study were: the vinyl Flashe® (LeFranc&Bourgeois), the acrylic Heavy Body (Liquitex®) and the styrene-acrylic Brera (Maimeri®).

The full list of the selected 15 paints is given in table 2.1-1. For each paint, the commercial name and the general composition declared in the manufacturers' catalogs are reported.[5]

The use of a styrene-acrylic paint was assessed in the mural works: *Archeologia della Notte* (Franco Guerzoni, MACAM, 1989); *Senza Titolo* (Ugo Nespolo, MACAM, 1986); *Tuttomondo* (by Keith Haring, Pisa, 1989).

Gurgone, *et al.* 2005; Chiantore, Ploeger and Rava, 2006; Ferriani, Marell and Rava, 2008. Preliminary results of the COPAC project (Preventive Conservation of Contemporary Art in Tuscany), presented by Colombini *et al.* (SCIBEC-INSTM Pisa, Italy) and: A. Rava, *Rescue of a Mural Painting by Keith Haring in Pisa*, oral communication presented at the *Modern and Contemporary Mural* conference (Valencia, May 4-5, 2012)

[3] The surfactant exudation was actually reported for synthetic organic and iron-based pigments (Ormsby and Learner, 2009).

[4] Learner, 2004; Ormsby, *et al.* 2009; Doménech-Carbó, *et al*. 2011; Hoogland and Boon 2009a/b; Silva, *et al.* 2010. More pieces of information can be also read in Silva's PhD thesis (2011).

[5] http://www.lefranc-bourgeois.com/beaux-arts/produits-acryliques-vinyliqueflashe.html
http://www.maimeri.it/CGIDEV2P/SIT030.PGM?VARIA=ENAC001&V4=Acrylic%20colours&VX=
http://www.liquitex.com/WorkArea/DownloadAsset.aspx?id=1484
(accessed 24/11/2011)
All the products were purchased in September 2010, in Venice, Italy.

COMMERCIAL BRAND	COMMERCIAL NAME	COMPOSITION DECLARED by the MANUFACTURER	
		Pigment	Other components
Flashe® (LeFranc&Bourgeois)	001-White	PW6-PW5	Long molecular chain vinyl resins in emulsion
	043-Ultramarine Blue	PB29	
	302-Yellow Ochre	PY42	
	388-Ruby Red	PV19	
	512-Armor Green	PG7	
Heavy Body (Liquitex®)	432-Titanium White	Titanium Dioxide (PW6)	Acrylic polymer emulsion
	380-Ultramarine Blue (Green Shade)	Complex Silicate of Sodium and Aluminum with Sulfur (PB29)	
	332-Transparent Raw Sienna	Synthetic Iron Oxide Yellow (PY42)	
	110-Quinacridone Crimson	Gamma Quinacridone Red (PV19)	
	317-Phthalocyanine Green (Blue Shade)	Chlorinated Copper Phthalocyanine (PG7)	
Brera (Maimeri®)	018-Titanium White	Titanium Dioxide (PW6)	Emulsion of acrylic resin, preservatives, surfactants and UV filters
	390-Ultramarine	Sodium Polysulphide-Aluminosilicate (PB29)	
	131-Yellow Ochre	Synthetic Iron Oxide (PY42)	
	256-Primary Red Magenta	Quinacridone (PV19)	
	321-Phthalo Green	Chlorinated Phthalocyanine (PG7)	

Tab. 2.1-1: List of the 15 artists' grade waterborne paints included in the study (the commercial name and the general composition, as declared in the manufacturer's catalogue, are reported).

2.1.3 Retouching materials

The experimentation concerning the inpainting issues of contemporary murals, was planned considering different retouching materials.

These encompassed the commercial paints described in the previous section and further retouching paints, that were especially formulated by adding two synthetic resin binders with proper amounts of powder pigments.

The selection of the binders was driven by the idea of using highly stable resins, which are soluble in a range of solvents which do not affect the slightly aged vinyl, acrylic, and styrene-acrylic reference paint layers.
Keeping to specialized literature,[6] Aquazol200® and LaropalA81® resins were selected.

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[6] As far as Laropal A81®: Borgioli and Cremonesi, 2005:146-149; Borgioli, 2008; de la Rie, *et a*l. 2002.
As far as Aquazol200®: Appolonia, *et al*. 2009; Arslanoglu, 2005; Bernardini, 2009; Borgioli and Cremonesi, 2005: 171-172; Fasce and Carnasciali, 2009; Gagné, 2007; Shelton, 1996; Ventikou (web

In order to reduce the absorption of the retouching materials into the support (thus pursuing reversibility), the influence of a resin interlayer between the mortar and the inpainting layers was evaluated. After some preliminary testing, Regalrez® 1094 resin was selected for this purpose.

The chemical composition of the three resins, together with the details about the preparation of their solutions, are shown in Table 2.1-2.

RETOUCHING RESINS	CHEMICAL COMPOSITION	PREPARATION DETAILS
AQUAZOL 200®	poly(2-ethyl-2-oxazoline) polymer	Solvent: deionized water Concentration: 20% w/w
LAROPAL A81®	urea-aldehyde polymer	Solvent: mixture of hydrocarbon solvents with low aromatic content (Shellsol D40: Shellsol A mixture, volume ratio 1:1) Concentration: 40% w/w
REGALREZ 1094®	hydrogenated hydrocarbon oligomer	Solvent: Shellsol D40 Concentration: 40% w/w

Tab. 2.1-2: The synthetic resins selected for the retouching trials: Aquazol 200® and Laropal A81® resins were used as retouching paint binders; Ragalrez 1094® was used to enhance the reversibility of the treatments. The details concerning the formulation of the resins' solutions are also given.

In order to match the colour of the reference paint areas, Aquazol200® and LaropalA81® resins were added with variable amounts of powder pigments.

The five finely-ground pigments (Maimeri®) used for this purpose are listed in Table 2.1-3 where, together with the commercial names, some technical information is reported as declared in the manufacturer's catalog.[7]

While inpainting contemporary works of art, a satisfactory aesthetic result should consider the color properties of the paint layers, as well as their texture properties.

To gain satisfactory texture matches, calcium carbonate ($CaCO_3$) and Micronized Silica LO-VEL 27 (SiO_2) extenders were thus included in some of the formulations.

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reference accessed 2010); Wolbers, McGinn and Duerbeck, 1998; Wolbers, 2008. Further literature is referenced in these texts.

[7] http://www.maimeri.it/CGIDEV2P/SIT030.PGM?VARIA=ENRE101 (accessed 01/12/2011)
The pigments were all purchased in Spain (May 2011).

In order to improve pigments' dispersion in the binding media, low amounts of Tween20® non-ionic surfactant (a polyoxyethylene(20)sorbitan monolaurate) were added.

A proper description of the formulation of the retouching paints is given later in the text, in the section related to the casting procedure (*2.2.2.1 Retouching formulations*).

All the details concerning the materials (ranging from properties to purchasing) are presented in *Appendix 1*, focusing the attention on the properties of the three resins.

COMMERCIAL NAME	CHEMICAL COMPOSITION	LIGHTFASTNESS	TRANSPARENCY	RESISTANCE to LIME
018 Titanium White	Titanium Dioxide (PW6)	+++	opaque	+++++
392 Ultramarine Deep	Sodium Polysulphide-Aluminosilicate (PB29)	+++	semi-opaque	+++++
102 Mars Yellow	Synthetic Iron Oxide (PY42)	+++	opaque	+++++
212 Quinacridone Rose	Quinacridone (PV19)	+++	Semi-opaque	+++++
321 Phthalo Green	Chlorinated Phthalocyanine (PG7)	+++	transparent	+++++

Tab. 2.1-3: List of the pure powder pigments used to prepare the retouching formulations. Referring to Maimeri® catalogue, the commercial name and the chemical composition of the pigments are reported, together with the information regarding their lightfastness (+++ corresponding to the maximum), transparency and resistance to lime (+++++ corresponding to the maximum).

2.1.3.1 The Europium (III) complex

Another aim of the study concerning the inpainting issues of contemporary murals was to assess a strategy to improve the discernibility of the treated areas under UV light.

As already reported in the *Introduction* (section *1.3.1. Luminescent lanthanide complexes*), many β-diketones Eu(III) complexes are known for their excellent luminescence properties. The popularity of these complexes is also due the fact that different β-diketone ligands are commercially available, and the synthesis of the corresponding lanthanide complexes is relatively easy. Even if the pure β-diketones complexes are expected to decay quite fast when exposed to photo-oxidative conditions, they are supposed to show an acceptable stability when embedded in a polymeric matrix (in this case, the paint layers).[8]

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[8] Bortoluzzi *et al.* 2011; Liu *et al.* 2003; Liu *et al.* 2004

For these reasons a [Ln(β-dike)$_3$L] complex was chosen as the most appropriate candidate to firstly assess the potentiality of the use of luminescent compounds in the cultural heritage field.

The [Eu(DBM)$_3$phen] is expected to efficiently absorb the UV light (main excitation λ 365 nm) and to result in a strong red light emission, typical of the central cation (main Eu(III) emission at 612nm).

The diketonates method of Melby *et al.*[9] was applied for the Europium(III) complex synthesis. The method is based on the interaction between an Europium salt (in this case Europium nitrate pentahydrate), a β-diketone (dybenzoylmethane) and a neutral ligand (1,10-phenanthroline) in ethanol solution, in presence of a small amount of sodium hydroxide (NaOH).

Europium (III) nitrate pentahydrate ($Eu(NO_3)_3 \cdot 5H_2O$, 99.9%), dibenzoylmethane (DBM, 98%) and 1,10-phenanthroline (Phen, 99%) were purchased from Aldrich and used as received. All the other chemicals and solvents, obtained either form Aldrich or Carlo Erba, were reagent grade and used as received.

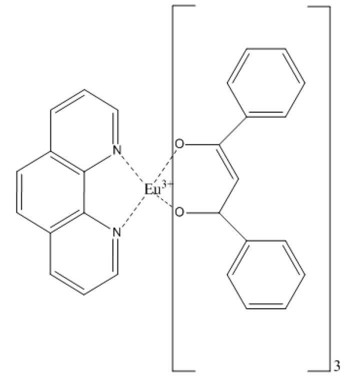

Fig.2.1-1: The molecular structure of the Eu(DBM)$_3$phen complex

2.2 Casting Procedure

2.2.1 The support

In order to simulate mural works of art, several cement-lime mortar supports were cast.

The mortar mixing was carried out according to the technical data sheet of the factory blended product (using clean potable water, approximately 3 L per 25 Kg bag).

Since mock-ups differing in dimensions were required, different moulds were used for shaping the mortar supports. Some samples measuring 50mmX 50mmX20mm, others

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[9] Melby *et al.* 1964: 5124

measuring 305 mmX75 mmX10mm and further measuring 74mmX 28mmX10mm were cast.

All the supports were left to cure at laboratory conditions (T 20±2°C, R.H. 60±5%) for approximately one year. Just before painting, all loose particles, dirt and dust were removed and the supports were further conditioned in a oven (T 60°C), until reaching a constant weight (Δm% calculated weighting samples every 24h ≤ 0.01%).

Since alkaline conditions are known to possibly affect the stability of both, polymer binders and pigments, the surface pH of the mortar supports was evaluated.

In all the cases, the pH was around 8.

2.2.2 Artists' emulsion paints

2.2.2.1 Free-Film samples

To allow a better chemical characterization of the emulsion paints, some free-film samples were cast. The artists' emulsion paints were thus diluted with distilled water (paint and water in a ratio of 4:1, by weight) and applied on Mylar® sheets. The samples were then prepared by drawing-down a spatula, using 6 tape stripes to control paint layers' thickness, and resulting in 300 mm long and 50 mm wide films. The samples were left to dry at laboratory conditions (20±2°C, R.H. 50±5%) for six months before testing, showing a final average thickness ranging between 100÷150 µm.

2.2.2.2 Mural painting mock-ups

The mock-ups simulating mural paintings were prepared brushing the 15 artists' emulsion paints listed in Table 2.1-1 (section 2.1.2 *Artists' emulsion paints*) on the mortar supports.

The paints were slightly diluted with distilled water (paint water ratio 4:1, by weight) and brushed over the supports until reaching a fresh paint weight in grams of 500g/m^2. Previous casting trials suggested that such an amount of paint would result in dry films with a thickness of approximately 200±50 µm.

A range of mock-ups differing in shape and size were required, in order to suit specific ageing conditions or experimental set ups:

- 60 samples measuring 50mmX50mmX20mm were cast to perform the rising damp cycles (the full list of the samples in section 2.3.1, Table 2.3-1)
- 15 samples measuring 305mmX75mmX10mm were cast to carry out the morphological and physical characterization of the paint layers, to study the response of the paints to UV-light exposure, and to subsequently test the properties of the retouching materials.

Figure 2.2-1 shows one of these 15 samples. The surface was divided in 4 areas: A and D areas were painted with the artists' emulsion paints (and used for the characterization and the UV ageing respectively); B and C areas were subsequently painted using the retouching formulations. The full list of these samples is given in Table 2.2-1.

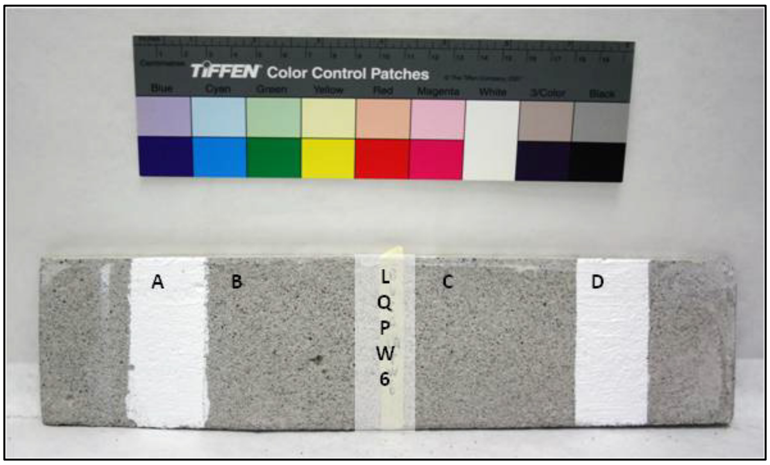

Fig.2.2-1: LQPW6 sample cast brushing the Titanium White Heavy Body paint (Liquitex®) on one of the cement-lime mortar supports measuring 305 mm X 75 mm X 10mm. A area (on the left) was considered as a 'reference' (morphological and physical characterization of the paint layer) while D area (on the right) was later exposed to UV-light. B and C areas were subsequently painted, to carry out the experimentation concerning the evaluation of retouching paints.

ID cod	Description	Planned Testing
FLPW6	White-Flashe®(LeFranc&Bourgeois)	A areas: morphological and physical characterization of emulsion paint layers (LM, SEM-EDX, Colorimetric Measurements) D areas: UV-light stability testing of emulsion paint layers (400h+400h, respectively before and after the application of the retouching paints) B areas: chemical, morphological and physical characterization of different retouching paints (FTIR spectroscopy, LM, SEM-EDX, Colorimetric Measurements) C areas: UV-light stability testing of the same retouching paints used to inpaint B areas (400h)
FLPB29	Ultramarine Blue Flashe®(LeFranc&Bourgeois)	
FLPY42	Yellow Ochre Flashe®(LeFranc&Bourgeois)	
FLPV19	Ruby Red-Flashe®(LeFranc&Bourgeois)	
FLPG7	Armor Green Flashe®(LeFranc&Bourgeois)	
LQPW6	Titanium White-Heavy Body (Liquitex®)	
LQPB29	Ultramarine Blue (Green Shade) Heavy Body (Liquitex®)	
LQPY42	Transparent Raw Sienna Heavy Body (Liquitex®)	
LQPV19	Quinacridone Crimson Heavy Body (Liquitex®)	
LQPG7	Phthalocyanine Green (Blue Shade) Heavy Body (Liquitex®)	
BRPW6	Titanium White-Brera (Maimeri®)	
BRPB29	Ultramarine-Brera (Maimeri®)	
BRPY42	Yellow Ochre- Brera (Maimeri®)	
BRPV19	Primary Red Magenta-Brera (Maimeri®)	
BRPG7	Phthalo Green-Brera (Maimeri®)	

Tab. 2.2-1: Full list of the mock-ups cast brushing the artists' emulsion paints on cement-lime mortar supports (measuring 305 mm X 75 mm X 10mm)

2.2.3 Inpainting treatments

The study of the properties and stability of the retouching formulations was carried out using the samples listed above, in Table 2.2-1.

After exposing D areas to 400h of UV-light, B and C unpainted areas were divided into several sections to paint using different retouching materials.

While B inpainted areas were considered as reference, C areas were later exposed to UV ageing.

2.2.3.1 Retouching formulations

The first aim of the study dealing with the inpainting issues of contemporary murals was to evaluate the quality of the aesthetic match that can be reached, between treated and original areas, when working with different retouching paints (formulated using powder pigments and Aquazol200® or Laropal A81® resins as binders).

After the preliminary ageing of the 'reference' emulsion paints, most of the samples did not show a significant discoloration of D areas. For this reason, the proper balance between the organic and the inorganic components to use for formulating the retouching paints was assessed referring to the color and texture of A unaged areas.[10]

In order to finally detect the best retouching formulations' recipes, preliminary testing was required. A number of formulations were prepared, by adding low quantities of binding media (less than 0.50 g) with controlled amounts of powder pigments and extenders (weighted using a technical balance, 0.01 g precision).

When inpainting the mock-ups, bigger amounts of paints were needed, and higher amounts of the retouching formulations were prepared on the basis of the components' weight ratios assessed in the previous tests.

The components included in each formulation, together with their weight ratios, are shown in the following tables (Tab.2.2-2; Tab.2.2-3 and Tab. 2.2-4). The amounts of the binders and of the inorganic components are expressed as percentages of the weight expected for the dry film.[11] To simplify the reading of the recipes, the ratio between the different inorganic components is also expressed as parts by weight (pbw). The conversion between different units of measurement implied a certain approximation.

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[10] The only samples that showed a significant discoloration of D areas were the blue ones (FLPB29, LQPB29 and BRPB29). It was no relevant to assess the ratios of the pure resins and pigments required to perfectly match the properties of the discolored areas. As a matter of fact, it is reasonable to suppose that, when preparing a paint using pure pigments and resins it would be always possible to adjust the amounts of the components, until reaching the desired quality match.

[11] For example, in the case of the Aquazol200® formulation used to inpaint the FLPW6 sample: 0.05g of Titanium White Pigment and 0.25g of Calcium Carbonate were added to 0.30g of the binder solution.
The percentages in weight were calculated considering that Aquazol200® resin is only the 20%w/w of the solution (0.30g of solution = 0.06g of resin and 0.24g of water).

ID cod	**AQUAZOL200® FORMULATIONS**			**LAROPALA81® FORMULATIONS**		
	Binder's amount (%w/w)	**Inorganic Components** (%w/w and weight ratio between these components)		**Binder's amount** (%w/w)	**Inorganic Components** (%w/w and weight ratio between these components)	
		PIGMENTS	EXTENDERS		PIGMENTS	EXTENDERS
FLPW6	17%	PW6 (~14%; 1pbw)	$CaCO_3$ (69%; 5pbw)	30%	PW6 (~12%; 1pbw)	$CaCO_3$ (58%; 5pbw)
FLPB29	15%	PB29 (34%; 1pbw)	$CaCO_3$ (51%; 1.5pbw)	25%	PB29 (~21%; 1pbw)	$CaCO_3$ (54%; 2.5pbw)
FLPY42	15%	PY42 (~8%; 1pbw)	$CaCO_3$ (77%; 10pbw)	27%	PY42 (~7%; 1pbw)	$CaCO_3$ (66%; 10 pbw)
FLPV19	16%	PY42 (~1%; 0.33pbw); PV19 (~3%; 0.67pbw)	$CaCO_3$ (80%; 20 pbw)	22%	PY42 (~1%;0.33 pbw); PV19 (~2%; 0.67pbw)	$CaCO_3$ (75%; 26 pbw)
FLPG7	14%	PG7 (~10%; 1pbw)	$CaCO_3$ (76%; 8 pbw)	28%	PG7 (~2%; 1pbw)	$CaCO_3$ (70%; 30 pbw)

Tab. 2.2-2: The components included in the Aquazol200® and the Laropal A81® formulations used to inpaint Flashe®(LeFranc&Bourgeois) samples. The amounts of binders, pigments and extenders are expressed as percentages of the weight expected for the dry film (considering the actual concentration of the resins in the solutions). The ratio between the different inorganic components is also expressed as parts by weight. The meaning of samples' Identification Codes and of powder pigments' Color Indexes have been already explain in the text.

ID cod	**Aquazol200® Formulations**			**LaropalA81® Formulations**		
	Binder's amount (%w/w)	**Inorganic Components** (%w/w and weight ratio between the components)		**Binder's amount** (%w/w)	**Inorganic Components** (%w/w and weight ratio between the components)	
		PIGMENTS	EXTENDERS		PIGMENTS	EXTENDERS
LQPW6	48%	PW6 (~24%; 5pbw)	$CaCO_3$ (~24%; 5pbw) SiO_2 (~4%; 1pbw)	71%	PW6 (~18%;1.7pbw)	SiO_2 (~11%; 1pbw)
LQPB29	62%	PB29 (19%; 1pbw) PV19 q.s.	SiO_2 (19%; 1pbw)	48%	PB29 (~35%;14pbw) PV19 q.s	$CaCO_3$ (~15%; 7pbw) SiO_2(~2%;1pbw)
LQPY42	56%	PY42 (~34%; 6pbw) PB29 (~5%; 1pbw) PV19 (~5%; 1pbw) PG7 q.s.	-	71%	PY42 (~22%; 6pbw) PB29 (~3.5%;1pbw) PV19 (~3.5%;1pbw) PG7 q.s.	-
LQPV19	48%	PV19 (~10%; 2pbw)	$CaCO_3$ (~37%; 8 pbw) SiO_2 (~5%; 1pbw)	57%	PV19 (~6%; 2pbw)	$CaCO_3$ (~34%; 12 pbw) SiO_2(~3%;1pbw)
LQPG7	71%	PG7 (29%;)	-	83%	PG7 (17%)	-

Tab. 2.2-3: The components included in the Aquazol200® and the Laropal A81® formulations used to inpaint Heavy Body (Liquitex®) samples. The amounts of binders, pigments and extenders are expressed as percentages of the weight expected for the dry film (considering the actual concentration of the resins in the solutions). The ratio between the different inorganic components is also expressed as parts by weight. The meaning of samples' Identification Codes and of powder pigments' Color Indexes have been already explain in the text. The abbreviation q.s. (*quantum sufficit*) indicates a negligible amount that cannot be exactly quantified.

ID cod	Aquazol200® formulations			LaropalA81® formulations		
	Binder's amount (%w/w)	**Inorganic Components** (%w/w and weight ratio between these components)		**Binder's amount** (%w/w)	**Inorganic Components** (%w/w and weight ratio between these components)	
		PIGMENTS	EXTENDERS		PIGMENTS	EXTENDERS
BRPW6	38%	PW6 (~20%; 5pbw)	$CaCO_3$ (~38%;10pbw) SiO_2 (~4%; 1pbw)	69%	PW6 (~17%;1.25pbw)	SiO_2 (~14%; 1pbw)
BRPB29	59%	PB29 (23%; 1.3 pbw) PV19 q.s.	SiO_2 (18%; 1pbw)	74%	PB29 (~15%; 1.3pbw) PV19 q.s.	SiO_2 (~11%; 1pbw)
BRPY42	40%	PY42 (16%; 4pbw)	$CaCO_3$ (40%; 10pbw) SiO_2 (4%; 1pbw)	50%	PY42 (10%; 4pbw) PB29q.s.	$CaCO_3$ (37.5%; 15 pbw) SiO_2 (2.5%; 1pbw)
BRPV19	67%	PV19 (~13%;2pbw) PY42 q.s.	$CaCO_3$ (~13%; 2 pbw) SiO_2 (~7%; 1pbw)	43%	PV19 (~5%; 2pbw) PY42 q.s.	$CaCO_3$ (~49.5%; 24 pbw) SiO_2 (~2.5%; 1pbw)
BRPG7	63%	PG7 (~25%; 2pbw)	SiO_2 (~12%; 1pbw)	74%	PG7 (~15%; 1.3pbw)	SiO_2 (~11%; 1pbw)

Tab. 2.2-4: The components included in the Aquazol200® and the Laropal A81® formulations used to inpaint Brera (Maimeri®) samples. The amounts of binders, pigments and extenders are expressed as percentages of the weight expected for the dry film (considering the actual concentration of the resins in the solutions). The ratio between the different inorganic components is also expressed as parts by weight. The meaning of samples' Identification Codes and of powder pigments' Color Indexes have been already explain in the text. The abbreviation q.s. (*quantum sufficit*) indicates a negligible amount that cannot be exactly quantified.

On the basis of the real pros and cons of mixing the pure binding media with powder pigments (in terms of handling properties, aesthetic results, time, costs, etc…), the use of commercial paints turned out to be worth considering.
For this reason, some of the unpainted areas were filled in using the same artists' emulsion paints used for casting the samples. Flashe, Heavy Body and Brera paints were diluted and brushed over the mortar supports, following the same procedure described in section 2.2.2.2 *Mural painting mock-ups*.

The potential of matching discolored paint areas when using the artists' emulsion paints was considered. While inpainting the blue samples (the only one that suffered a significant discoloration after 400h of UV ageing), the use of artists' emulsion paints, "modified" in order to better match the properties of discolored D areas, was thus included.
For this purpose, the Flashe® Ultramarine Blue paint was diluted with distilled water (paint: water ratio of 2:1, by weight) and added with a slight amount of Calcium Carbonate extender (5% by weight), Heavy Body® Ultramarine Blue and Brera® Ultramarine paints were only diluted with distilled water (paint: water ratio of 2:1, by weight).

Figure 2.2-2, shows the LQPB29 sample after inpainting and allows a better visualization of the procedure followed to cast the samples used to evaluate the properties of the retouching paints.

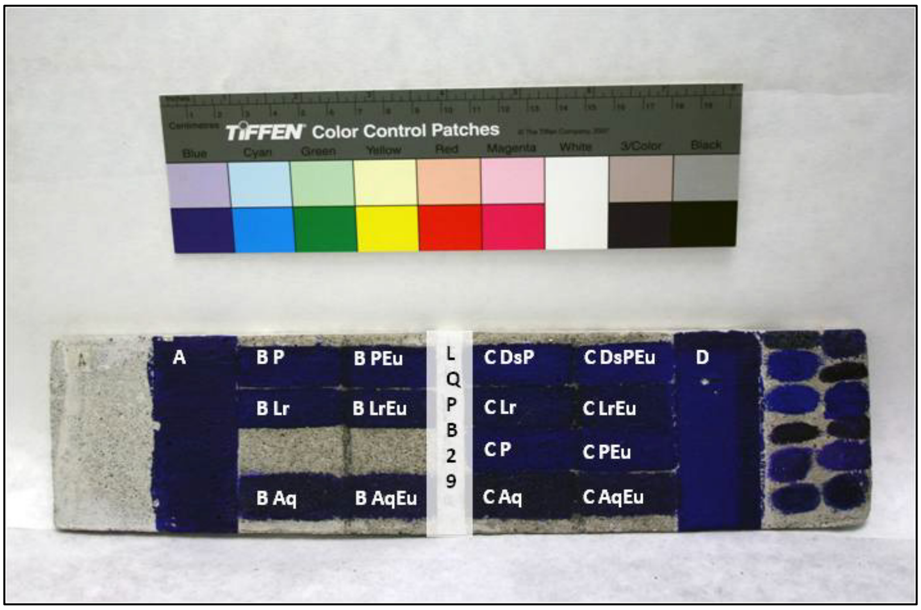

Fig 2.2-2:LQPB29 sample after inpainting. A: reference commercial paint. D: commercial paint after 400h of UV ageing (discoloration is appreciable). B: reference inpanted areas. C: inpanted areas that will be exposed to UV ageing. P: emulsion paint. DsP: emulsion paint modified to match the discolored D area. Lr: LaropalA81® formulation. Aq: Aquazol200® formulation. Eu: formulation added with 2%w/w of the Europium(III) complex. On the right, the results of some preliminary tests carried out to assess the composition of the best retouching formulations.

Summarizing:

- B and C areas of each sample were inpainted using 3 different methods: the artists' emulsion paint (P), a retouching formulation based on Laropal A81® binder (Lr) and a retouching formulation based on Aquazol 200® binder (Aq)
- in order to evaluate the possibility of matching the properties of discolored areas using artists' emulsion paints, the blue samples were treated with an additional method: "modified commercial paints"(DsP)
- the retouching paints were formulated according to the recipes previously shown in tables 2.2-2; 2.2-3 and 2.2-4)

2.2.3.2 Discernibility Issues

In the attempt of enhancing the discernibility of the inpainted areas, the effect gained when adding the retouching formulations with an UV luminescent pigment was evaluated. Each inpainted area was so replicated, adding a certain amount (2% by weight) of the laboratory synthesized complex ($Eu(DBM)_3Phen$) into the retouching paints (see Figure 2.2-2, areas marked with the Eu abbreviation).

2.2.3.3 Reversibility Issues

In order to reduce the absorption of the retouching materials into the support (and so pursuing a better reversibility), the influence of a resin interlayer between the mortar and the paint films was evaluated.
The results of the preliminary testing carried out with different resins (Aquazol200®, LaropalA81®, Plextol B500® and Regalrez 1094®) are not displayed here.

Considering the pros and cons of working with all these products, Regalrez 1094® turned out to be the most promising one: being soluble in non-polar solvents (like Shelsoll D40) it can be applied over the mortar support without affecting the surrounding paints; it is also supposed to have a certain durability[12] and so to maintain its solubility properties with ageing (and this could finally improve the reversibility of the inpainting treatment).

Being characterized by a low molecular weight, Regalrez 1094® tends to be absorbed into the mortar support instead of coating its surface with a proper film. Nevertheless, qualitative examinations suggested that, reiterating the application of the resin , slight changes in the surface properties of the mortar are achieved. These changes, which probably relate to a low consolidating effect, do not strongly interfere with the wettability of the mortar (the different paints are easily brushed on the "treated" surface) but they actually reduce the absorption of the retouching materials in the support (enhancing the reversibility).

For all these reasons, before inpainting, the Regalrez 1094® solution was brushed over B and C areas until reaching a fresh resin weight in grams of 250g/m^2. The supports were then left to dry at laboratory conditions (20±2°C and R.H. 50±5%) for at least 72h before applying the different retouching materials.

In order to assess the reversibility of the retouching materials, some qualitative solubility test were planned. For this reason, thirty mock-ups measuring 74mm X 28mm X10 mm were cast (their full list is given in Table 2.2-5). By way of example, one of this samples in shown in Figure 2.2-3.

The samples were painted according to the previously described method:

- application of the Regalrez 1094® interlayer
- application of the retouching paints, consisting of: the artists' emulsion paints, the Aquazol200® formulations and the LaropalA81® formulations (all of which added or not with the luminescent complex).

The solubility of the retouching materials was assessed after exposing the samples to UV-light, considering different times of exposure (0h, 200h and 400h).

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[12] As stated in: Blackman, 2007; Borgioli and Cremonesi 2005: 150-157; Whitten, 1995.

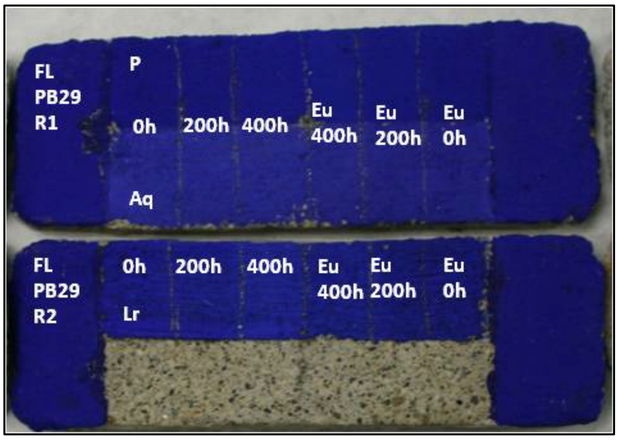

Fig.2.2-3: The Ultramarine Blue Flashe® samples prepared to assess the reversibility of the retouching methods (P: emulsion paint; Aq: Aquazol200® formulation; Lr: LaropalA81® formulation; Eu: 2%w/w of Europium (III) complex). The solubility of the materials was assessed after different times of UV exposure (0h, 200h, 400h). On the right and on the left, areas painted with the reference artists' emulsion paints.

ID cod	Description
FLPW6_R1	White-Flashe®(LeFranc&Bourgeois), Emulsion Paint and Aquazol200® paint
FLPW6_R2	White-Flashe®(LeFranc&Bourgeois), Laropal A81® paint
FLPB29_R1	Ultramarine Blue Flashe®(LeFranc&Bourgeois), Emulsion Paint and Aquazol200® paint
FLPB29_R2	Ultramarine Blue Flashe®(LeFranc&Bourgeois), Laropal A81® paint
FLPY42_R1	Yellow Ochre Flashe®(LeFranc&Bourgeois), Emulsion Paint and Aquazol200® paint
FLPY42_R2	Yellow Ochre Flashe®(LeFranc&Bourgeois), Laropal A81®paint
FLPV19_R1	Ruby Red-Flashe®(LeFranc&Bourgeois), Emulsion Paint and Aquazol200® paint
FLPV19_R2	Ruby Red-Flashe®(LeFranc&Bourgeois), Laropal A81® paint
FLPG7_R1	Armor Green Flashe®(LeFranc&Bourgeois), Emulsion Paint and Aquazol200® paint
FLPG7_R2	Armor Green Flashe®(LeFranc&Bourgeois), Laropal A81® paint
LQPW6_R1	Titanium White-Heavy Body (Liquitex®), Emulsion Paint and Aquazol200® paint
LQPW6_R2	Titanium White-Heavy Body (Liquitex®), Laropal A81® paint
LQPB29_R1	Ultramarine Blue Heavy Body (Liquitex®), Emulsion Paint and Aquazol200® paint
LQPB29_R2	Ultramarine Blue (Green Shade)-Heavy Body (Liquitex®)
LQPY42_R1	Transparent Raw Sienna Heavy Body (Liquitex®), Emulsion Paint and Aquazol200® paint
LQPY42_R2	Transparent Raw Sienna Heavy Body (Liquitex®), Laropal A81® inpainting
LQPV19_R1	Quinacridone Crimson Heavy Body (Liquitex®), Emulsion Paint and Aquazol200® paint
LQPV19_R2	Quinacridone Crimson Heavy Body (Liquitex®), Laropal A81® inpainting
LQPG7_R1	Phthalocyanine Green Heavy Body (Liquitex®), Emulsion Paint and Aquazol200® paint
LQPG7_R2	Phthalocyanine Green (Blue Shade) Heavy Body (Liquitex®), Laropal A81® paint
BRPW6_R1	Titanium White-Brera (Maimeri®), Emulsion Paint and Aquazol200® paint
BRPW6_R2	Titanium White-Brera (Maimeri®), Laropal A81® paint
BRPB29_R1	Ultramarine-Brera (Maimeri®), Emulsion Paint and Aquazol200® paint
BRPB29_R2	Ultramarine-Brera (Maimeri®), Laropal A81® paint
BRPY42_R1	Yellow Ochre- Brera (Maimeri®), Emulsion Paint and Aquazol200® paint
BRPY42_R2	Yellow Ochre- Brera (Maimeri®), Laropal A81® paint
BRPV19_R1	Primary Red Magenta-Brera (Maimeri®), Emulsion Paint and Aquazol200® paint
BRPV19_R2	Primary Red Magenta-Brera (Maimeri®), Laropal A81® paint
BRPG7_R1	Phthalo Green-Brera (Maimeri®), Emulsion Paint and Aquazol200® paint
BRPG7_R2	Phthalo Green-Brera (Maimeri®), Laropal A81® paint

Tab. 2.2-5: Full list of the mock-ups cast for carrying out the reversibility test

2.3 Artificial ageing conditions

2.3.1 Rising damp cycles

The delamination of the synthetic paint layers from the inorganic support is one of the most common decay typologies which affect contemporary murals.[13]

This phenomenon is mainly due to the properties of the support itself, which is often affected by rising damp and crystallization of water soluble salts. Nevertheless, the adhesion properties of the paint layers could be influenced by the presence of surfactants at the support-film interface.[14]

In order to evaluate the actual causes of delaminations, a number of samples were subjected to rising damp cycles.

Sixty mortar supports (about 50mm X 50mm X 20mm) were cast and painted as described in the 2.2.2.2 section (*Mural painting mock-ups*). For each one of the 15 artists' emulsion paints, four samples were prepared. Among these three were aged, while the last one (the reference) was stored at laboratory conditions (T 20±2°C, R.H. 50±5%). The full list of the samples is given in Table 2.3-1.

Because the water absorption and the overall ageing process could be influenced by the properties of the mortar, two unpainted supports were also included in the test.

The porosity of the supports was also evaluated in terms of mass density: since the supports are characterized by similar mass densities (ranging between 1.9 and 2.1 g/cm^3) they are supposed to absorb water in a similar way.

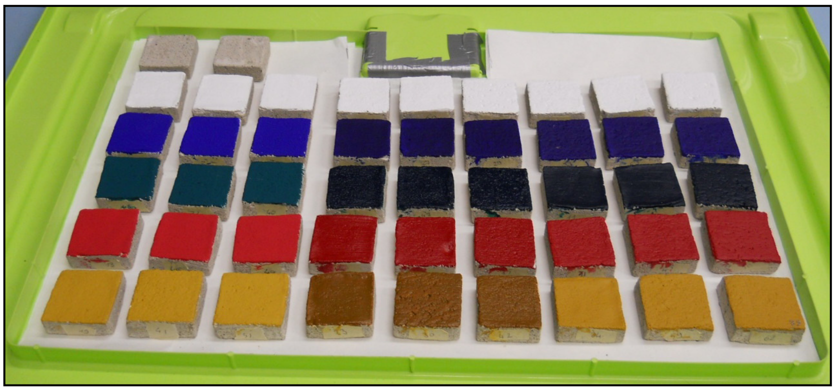

Fig.2.3-1: The complete set of the 45 samples subjected to the ageing cycles simulating the absorption of water into the support through capillary rise mechanism.

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[13] Many murals painted in Dozza, as well as those at M.A.C.A.M. (Museo di Arte Contemporanea all' Aperto di Maglione) are actually affected by this decay typology. Some examples are the works by: Masi (Dozza, 1981); Bardeggia (Dozza, 1985); Dorigo (M.A.C.A.M., 1989); Asdrubali (M.A.C.A.M., 1988); Asveri (M.A.C.A.M., 1991); Tedeschi (Dozza, 1993); Donzelli (Dozza, 1997); Rousset (Dozza, 2000); Zamboni (Dozza, 2005).

[14] Charmeau, Kients, and Holl, 1996.

ID Cod	**Description**	**Dimensions (cm)***	**Weight of mortar supports (g)****	**Mass Density of mortar supports (g/cm^3)**	**Casting period**
RRD_FLPW6	White Paint Flashe®	4.9 X 5.0 X 2.1	99.33	1.9	06/2010
1RD_FLPW6		4.9 X 5.0 X 2.0	96.11	2.0	06/2010
2RD_FLPW6		5.0 X 5.0 X 1.9	93.76	2.0	06/2010
3RD_FLPW6		4.8 X 5.0 X 2.0	98.31	2.1	05/2010
RRD_FLPB29	Ultramarine Blue Paint - Flashe®	4.8 X 5.0 X 2.0	95.62	2.0	06/2010
1RD_FLPB29		5.0 X 5.0 X 2.0	93.44	1.9	05/2010
2RD_FLPB29		4.8 X 5.0 X 2.0	97.96	2.1	05/2010
3RD_FLPB29		4.9 X 5.0 X 2.0	97.74	2.0	07/2009
RRD_FLPY42	Yellow Ochre Paint - Flashe®	5.0 X 4.9 X 2.0	99.63	2.0	07/2009
1RD_FLPY42		5.0 X 5.0 X 1.9	90.58	1.9	05/2010
2RD_FLPY42		5.0 X 5.0 X 1.9	100.63	2.1	07/2009
3RD_FLPY42		5.0 X 5.2 X 1.9	97.70	2.0	07/2009
RRD_FLPV19	Ruby Red Paint Flashe®	5.0 X 5.0 X 1.9	97.67	2.1	07/2009
1RD_FLPV19		5.0 X 5.0 X 2.0	95.95	1.9	06/2010
2RD_FLPV19		4.9 X 4.9 X 1.9	91.51	2.0	07/2009
3RD_FLPV19		5.0 X 5.1 X 1.9	97.57	2.0	07/2009
RRD_FLPG7	Armor Green Paint - Flashe®	5.0 X 5.0 X 1.8	92.90	2.1	07/2009
1RD_FLPG7		4.8 X 5.0 X 2.0	90.73	1.9	05/2010
2RD_FLPG7		4.9 X 4.9 X 1.9	90.71	2.0	07/2009
3RD_FLPG7		4.8 X 5.0 X 1.9	92.69	2.0	07/2009
RRD_LQPW6	Titanium White Paint -Heavy Body	5.0 X 5.1 X 2.0	106.52	2.1	07/2009
1RD_LQPW6		4.7 X 4.9 X 2.0	99.82	2.2	07/2009
2RD_LQPW6		5.0 X 4.9 X 2.0	107.57	2.2	07/2009
3RD_LQPW6		4.8 X 5.0 X 1.9	95.76	2.1	07/2009
RRD_LQPB29	Ultramarine Blue Paint-Heavy Body	4.7 X 5.0 X 2.0	91.87	2.0	06/2010
1RD_LQPB29		4.9 X 5.0 X 2.0	98.85	2.0	05/2010
2RD_LQPB29		4.9 X 5.0 X 2.0	95.30	1.9	05/2010
3RD_LQPB29		4.9 X 4.9 X 1.9	95.48	2.1	07/2009
RRD_LQPY42	Transparent Raw Sienna Paint-Heavy Body	5.0 X 5.0 X 2.0	99.47	2.0	05/2010
1RD_LQPY42		5.0 X 5.0 X 1.9	88.53	1.9	05/2010
2RD_LQPY42		5.0 X 5.1 X 1.9	97.46	2.0	07/2009
3RD_LQPY42		4.7 X 4.9 X 1.9	90.39	2.1	07/2009
RRD_LQPV19	Quinacridone Crimson Paint-Heavy Body	5.0 X 4.9 X 2.0	96.68	2.0	06/2010
1RD_LQPV19		5.0 X 5.0 X 2.0	97.68	2.0	06/2010
2RD_LQPV19		4.8 X 5.0 X 1.9	85.53	1.9	05/2010
3RD_LQPV19		4.8 X 5.0 X 19	94.79	2.1	07/2009
RRD_LQPG7	Phthalocyanine Green Paint-Heavy Body	4.8 X 5.0 X 1.8	86.53	2.0	07/2009
1RD_LQPG7		4.7 X 5.0 X 1.9	94.30	2.1	07/2009
2RD_LQPG7		4.9 X 4.9 X 1.9	88.15	1.9	07/2009
3RD_LQPG7		4.9 X 5.0 X 1.9	92.64	2.0	07/2009

Tab. 2.3-1: Part of the samples subjected to the rising damp cycles. RD = rising damp, RRD= reference rising damp (indicating samples that were not subjected to the ageing). The other abbreviations refer to the artists' emulsion paint used for the casting (brand name and pigment type). The dimensions and weights of the conditioned unpainted supports are show together with their mass densities. *Error 0.1 cm ** Error 0.01g

ID Cod	Description	Dimensions (cm)*	Weight of mortar supports (g)**	Mass Density of mortar supports (g/cm^3)	Casting period
RRD_BRPW6	Titanium White Paint -Brera	5.0 X 5.0 X 2.0	96.25	1.9	05/2010
1RD_BRPW6		4.9 X 5.0 X 1.9	92.76	2.0	07/2009
2RD_BRPW6		5.0 X 5.0 X 1.9	95.84	2.0	07/2009
3RD_BRPW6		5.0 X 5.0 X 2.0	103.19	2.1	07/2009
RRD_BRPB29	Ultramarine Paint-Brera	5.0 X 5.0 X 2.1	104.59	2.0	06/2010
1RD_BRPB29		4.9 X 5.0 X 1.9	89.27	1.9	07/2009
2RD_BRPB29		5.0 X 5.0 X 1.8	90.80	2.0	07/2009
3RD_BRPB29		5.0 X 4.7 X 1.9	93.04	2.1	07/2009
RRD_BRPY42	Yellow Ochre Paint-Brera	5.0 X 5.0 X 2.0	102.34	2.1	07/2009
1RD_BRPY42		4.9 X 5.0 X 1.9	90.21	1.9	05/2010
2RD_BRPY42		5.0 X 5.0 X 1.8	89.37	2.0	07/2009
3RD_BRPY42		5.0 X 4.8 X 2.1	105.13	2.1	07/2009
RRD_BRPV19	Primary Red Magenta Paint Brera	4.9 X 5.0 X 2.0	92.48	1.9	06/2010
1RD_BRPV19		4.9 X 5.0 X 2.0	96.91	2.0	07/2009
2RD_BRPV19		5.0 X 5.0 X 1.9	97.17	2.1	07/2009
3RD_BRPV19		5.0 X 5.1 X 1.9	99.39	2.1	07/2009
RRD_BRPG7	Phthalo Green Paint-Brera	5.0 X 5.0 X 2.0	100.34	2.0	05/2010
1RD_BRPG7		5.0 X 5.0 X 2.0	103.17	2.1	06/2010
2RD_BRPG7		5.0 X 5.0 X 2.0	99.16	2.0	07/2009
3RD_BRPG7		5.0 X 4.9 X 1.9	95.25	2.1	07/2009

Tab. 2.3-1: Part of the samples subjected to the rising damp cycles. RD = rising damp, RRD= reference rising damp (indicating samples that were not subjected to the ageing). The other abbreviations refer to the artists' emulsion paint used for the casting (brand name and pigment type). The dimensions and weights of the conditioned unpainted supports are show together with their mass densities. *Error 0.1 cm ** Error 0.01g

After painting, the samples were left to dry under laboratory conditions for 24h and further conditioned in a temperature and R.H. controlled environment (T=20±2°C, R.H.= 50±5%) until reaching a constant weight (Δw % ≤ 0.01%, weighting the samples every 24h).

As shown in figure 2.3-1, the rising damp cycles were carried out by placing the back of each sample in contact with some filter paper, soaked with distilled water. The samples were left to absorb the water (simulating the rising damp mechanism) for 2 hours, then placed over a grating and left to dry at laboratory conditions for 24h (or 72h).
Before starting a new cycle, the samples were carefully examined and pictures were taken (using both normal and raking light). Before and after each cycle, the samples were weighted (using a technical balance, 0.01 g precision) in order to roughly evaluate the water absorption and evaporation processes. A total of 20 cycles were carried out.

At the end of the ageing, the chemical composition of the paint surfaces was assessed using Mid-Near FTIR Reflection Spectroscopy. MIR active thermography was instead used for detecting the paint layer delaminations. When affected by this decay typology, the paint layer was completely peeled from the support, and the support-paint layer interface was studied using different FTIR spectroscopy techniques.

2.3.2 UV-light stability testing

Many contemporary murals are outdoor works of art, directly exposed to sunlight. Depending on materials sensitivities and variations of light spectrum, this direct exposure could cause different decay typologies (e.g. loss of physical properties, chalking, cracking, peeling, fading, etc…).

In order to evaluate the UV-light stability of the artists' emulsion paints and of the retouching paints included in the study, some accelerated weathering tests were carried out.

Laboratory accelerated weathering tester are designed to simulate natural sunlight, providing fast, repeatable and reproducible results. The light sources used for this kind of tests are typically compared to what is called the solar Maximum condition (global, noon sunlight at normal incidence, on the summer solstice), corresponding to the most sever condition met in outdoor service.

When using a QUV tester, the aim is not to reproduce the full spectrum of sunlight but just its damaging effects. For this reason different fluorescent lamps can be used, with primary emissions confined to the UV portion of the spectrum.

In our case, the UVA-340 lamps were chosen because designed to enhance correlation with natural exposure, simulating the sunlight from about 370 nm to the cut-off of 295 nm (figure 2.3-2).[15]

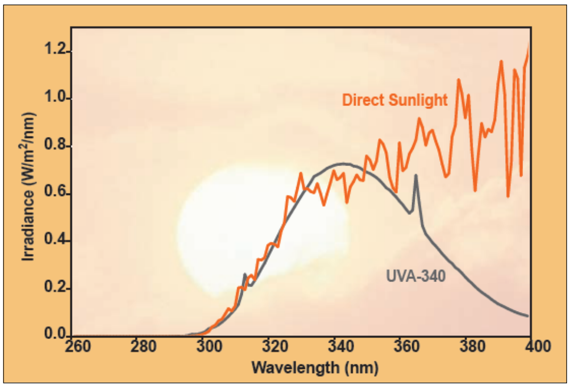

Fig. 2.3-2:The UVA-340 spectrum is the best available simulation of sunlight in the UV region, where most of the damage to materials occurs.[16]

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[15] This lamps are often used in industry tests for evaluating plastics and coatings performances (they were for instance used by Butler, Fellows and Gilbert, 2005). In the field of conservation science a number of different sources of artificial UV light have been used, encompassing mercury high-pressure lamps and fluorescent lamps (with primary emission confined in the UVA or UVB range). In order to simulate indoor museum conditions, a Xenon light source filtered for λ< 295 nm is commonly used. This topic has been briefly review by Pintus, Wei and Schreiner, 2012. The reader is also referred to: Feller, 1994.

The samples included in the UV ageing trials are:

- the 15 samples listed in table 2.2-1 (section *2.2.2.2 Mural painting mock-ups*), used for testing the stability of both, the emulsion paints (D areas) and the retouching formulations (C areas)
- the 30 samples listed in table 2.2-5 (section 2.2.3.3 *Reversibility Issues*), cast for evaluating the reversibility of the retouching formulations while carrying out the ageing.

All the samples were subjected to UV-light exposure in a QUV-Basic Dycometal chamber, equipped with UVA-340 lamps (Q-Panel Lab Products). During the ageing, the temperature was maintained at a constant value of 45°C.

The emulsion paints were exposed for a total of 800h, while the retouching paints were exposed only for 400h. Since it was not possible to control the exact irradiance of the lamps during the tests, no correlations between exposure time and real ageing can be drawn, assuming any reciprocity laws.

All the samples were periodically monitored for chemical (FTIR spectra collected every 100h) and physical changes (colorimetric measurements were carried out every 200h, while the paint layer morphology was studied through Light Microscopy and Scanning Electron Microscopy every 400h).

2.4 Investigation techniques

This section presents the analytical techniques used for the study. While focusing on technical aspects and working conditions, the theoretical notions concerning the working principles of each technique are intentionally left out. As a matter of fact, most of these techniques are commonly used in the field of conservation science and do not need further explanations.[17]

The selection of the techniques suited the need of characterizing the materials included in the study from both, the chemical (FTIR spectroscopy, Thermogravimetric Analysis, Energy Dispersive X-ray analysis) and physical (Light and Scanning Electron Microscopy, Colorimetric Measurements and Mid-IR active Thermography) points of view.

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[16] http://www.q-lab.com/documents/public/96770b50-5fa3-4d67-92c2-552952e7722c.pdf (08/06/2012)

[17] The information concerning different analytical techniques (FTIR spectroscopy, LM, SEM-EDX and TGA) can be found in specialized literature: Ciliberto and Spoto 2000 (eds.); Stuart 2007; Volpin and Appolonia, 1999.

In addition, since the study of real mural paintings should be carried out *in situ* (limiting the sampling as much as possible), the selection included also some non-invasive techniques which allow to perform the analysis using portable instrumentations. Apart from Colorimetric Measurements, Mid-Near FTIR reflection spectroscopy was used to monitor the exudation process of the surfactants, while Mid-IR active thermography was used to detect the delaminations of the paint layers.

The experimentation was mainly carried out in Venice and Valencia, taking advantage of the facilities of Ca' Foscari (D.A.I.S. laboratories) and UPV (IRP, *Laboratorio de Analisis Físico-Químico y Control Medioambiental de Obras de Arte*) universities. This is the reason way different instrumental set ups are sometimes described. The use of the specific set-ups will be stated through the text.

2.4.1 Fourier Transform Infrared (FTIR) spectroscopy [18]

FTIR spectroscopy analysis were performed using different instrumental set-ups.

The characterization of the reference paints and of the samples taken from real case studies was carried out using a Perkin Elmer Spectrum 100 spectrometer, equipped with an Attenuated Total Reflection (ATR) accessory (diamond crystal). The spectra were collected in the 4000÷400 cm^{-1} range, with a total of 32 scans and a resolution of 4 cm^{-1}. Data were processed using OMNIC32 software.[19]

To characterize the paint water extracts and some of the reference materials (powder pigments, extenders, pure resins…), as well as to monitor the chemical changes occurring during the UV ageing of both reference and retouching paints, a Vertex 70 Fourier Transform Infrared spectrometer (Bruker Optik GmbH) was used.
This instrument was equipped with an Attenuated Total Reflection accessory (diamond crystal) and a fast recovery deuterated triglycine sulfate (FR-DGTS) temperature-stabilized coated detector. The spectra were collected in the 4000÷500cm^{-1} spectral range, with a total of 32 scans and a resolution of 4 cm^{-1}. Data were processed using OPUS software, version 5.0.

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[18] More details about the specific use of FTIR spectroscopy in the field of conservation science in: Derrick, Stulik and Landry, 1999; Adrover Gracia, 2001

[19] These FTIR analysis were carried in collaboration with Arcadia Ricerche s.r.l. (Marghera-Venice).

2.4.1.1 Mid-Near FTIR reflection spectroscopy [20]

As pointed out in previous publications,[21] Mid-Near reflection spectroscopy is one of the most appropriate analytical techniques for monitoring the surface exudation of emulsion paints surfactants. In addition, the use of this portable technique, perfectly suits the need of investigating mural paintings *in situ*, through a non-invasive approach.

The reflection spectra acquired on real painting surfaces are however affected by large distortions in the shape and position of the bands and, while interpreting these spectra some basic notions have to be considered.

In spectroscopy there are three classifications of external reflection measurements: transmission-reflection (the so-called transflection), specular reflection and diffuse reflection.

Specular reflection occurs on optically flat objects, which reflects the predominant amount of radiation at an angle equal and opposite to the incident radiation. It is governed by Fresnel's law and depends upon *absorption coefficient* (k) and *refractive index* (n).

Diffuse reflection occurs on rough surfaces, when radiation penetrates the sample and is backscattered (e.g. by pigments or inorganic particles) over a wide range of angles. The perfectly diffuse scatter (Lambertian) exhibits a cosine response to the incident radiation. This kind of phenomenon is ruled by Kubelka-Munk's law and depends on *absorption coefficient* (k) and *scattering coefficient* (s).

When analyzing a material using reflection spectroscopy both of these components are collected, with a ratio that depends on the roughness of the surface of the sample.

The specular component generally appears in the reflection spectra as first-derivative-like features, hindering the band centre location. In addition, the very strong bands (characterized by high absorption coefficients, $k>>n$) appear as inverted, as a consequence of the *reststrahlen effect*. This is the most evident distortion typology which affects reflection spectra and it is usually seen when studying minerals or polymer compounds.[22]

In diffuse reflection spectra instead, the intensities of the absorption bands at high wave numbers increase with respect to conventional absorption spectra. This effect is observed because shorter wavelength radiation has less penetration power, thus undergoing to less absorption.[23] The near infrared region of diffuse spectra is thus

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[20] This topic was preliminary approached thanks to Kenza Kharim's PhD thesis (2009/10), where lots of specific texts are referenced.

[21] Ormsby *et al.* 2008; B. Ormsby *et al.* 2009

[22] Chalmers, Everall and Ellison, 1996; Korte and Röseler, 2005

[23] Allen, 1992

characterized by positively shaped reflection bands, corresponding to overtones and combination absorptions.

Studying real surfaces, the Kramers-Kroning and Kubelka-Munk algorithms, that are usually applied for correcting the distortions coming from specular and diffuse reflectance to re-create an absorbance spectrum, cannot be used without introducing a large source of error. For this reason, the two components cannot be resolved one from another, and the reflection spectra remain affected by distortions.

The type of the predominant distortion affecting a spectrum is due to a number of factors: particle dimensions; packing density; surface roughness; real refractive, absorption and scattering coefficients; optics geometry and wavelength.
If relating only to the wavelength, it could be said that:

- the 500-1800 cm^{-1} region is dominated by the specular reflection features of fundamental vibrations, which usually result in derivative or inverted shaped bands
- the 1800-3740 cm^{-1} region exhibits competitive specular and diffuse components of reflection. If considering polymer binders, only specular reflection features (e.g. C-H stretching derivative shaped bands) may be used for diagnostic purposes while combination bands and overtones resulting from diffuse reflection should not be used as spectral markers because often prone to variations
- in the 3740-4500 cm^{-1} region the diffuse component of reflection becomes more important. Positive shaped overtones and combination bands, if well resolved, may be used for the characterization of polymer binders
- the 4500-10000 cm^{-1} region, governed by diffuse reflection, shows positive shaped combination and overtones bands of fundamental vibrations that are useful for the characterization of polymer binders.

EXPERIMENTAL SET-UP [24]

Reflection FTIR spectra were collected using a portable Bruker's Alpha FTIR spectrometer (about 7 Kg of weight and an overall dimension of22X30X25 cm^3).
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 (distance between the sample spot and the instrument of 15 mm). The probe, characterized by 23°/23°geometry, was kept perpendicular to the sample surface. The

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[24] Mid-Near FTIR reflection spectroscopy analysis were carried out in collaboration with CNR-ISTM & SMAArt group of Perugia (c/o the Chemistry Department, University of Perugia).

investigated sample area width, as determined by the probe diameter, was either 6 or 3 mm. Interferograms were collected from 7500 to 360 cm^{-1} at a resolution of 4 cm^{-1}, using a gold mirror reference and a scan time of 3 minutes.

The chemical characterization of the mortar-paint layer interface, was carried out through μ-FTIR reflection spectroscopy. A benchtop Jasco FT-IR 4100e spectrometer, coupled to an IMV-400 optical microscope was used, 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 7500-375cm^{-1}.

All the spectral data collected in reflection mode, were processed using OPUS software (version 5.0) and are presented as pseudo absorbance A' [A'=log (1/Reflectance)].

2.4.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis were carried out in order to properly characterize the reference emulsion paints, evaluating the weight ratio between their organic and inorganic components.

The measurements were performed using a NETZSCH STA 409 cell instrument equipped with a TSAC414/3 controller. Samples of approximately 15-20 mg were taken from the free-films specimens and finely ground prior to analysis. The heating was carried out from 30°C to 800°C at 10°C/min, purging the TG head with an air flow of 40 cm^3/min. The analysis of each sample was replicated twice. Data were collected and analyzed using NETZSCH-TA3.5 software and further processed using OriginPro8 software.

2.4.3 Light microscopy (LM)

Light Microscopy examinations were carried out to preliminary evaluate the color and morphological properties of the mock-ups painted with both commercial and retouching formulations. This technique was moreover used to study the samples taken from the real case studies.

For these purposes two microscope were used: an Olympus SZ X9 and a Leica DMR microscopes. In both cases reflected light was used.

2.4.4 Scanning electron microscopy and energy dispersive X-ray microanalysis (SEM-EDX)

The morphology of the mock-ups samples was studied using a Jeol JSM 6300 scanning electron microscope, working in High Vacuum conditions (20 kV accelerating voltage, secondary or back scattered electrons). This Scanning Electron Microscope was operating with a Link-Oxford-Isis X-ray microanalysis system which allowed elemental analysis. To minimize charging effects, samples were carbon coated.

The samples taken from the real case studies were instead examined using a JEOL JSM-5600 LV Scanning Electron Microscope, operating in Low Vacuum conditions (20kV, back-scattered electrons). The EDX analysis were carried out with an OXFORD-Link ISIS Series 300 microanalysis system (Super ATW, 20kv).

2.4.5 Colorimetric measurements [25]

Colorimetric measurements were carried out in order to precisely define the color of the painted surfaces, and to evaluate the color changes induced by UV-light ageing.

The measurements were performed using a CM-2600d portable spectrophotometer (Konica Minolta), set with D65 illuminant (intended to represent average daylight, color temperature 6504°K), small measuring aperture (SAV, ø3mm) and 10°standard observer.

Thanks to a Numerical Gloss Control, simultaneous data with specular component excluded (SCE) and included (SCI) were provided.

In the first mode, only the diffuse reflectance is measured, resulting in a color evaluation correlated to the way the observer sees the color of an object. When using the SCI mode instead, the specular reflectance is included with the diffuse reflectance during the measurement process, allowing the evaluation of the total appearance of the color, regardless of surface conditions.

The reflectance spectra, collected in the 400-700nm range, were also used for calculating the colorimetric values in the CIEL*a*b* color space.

A set of 3 spectra were collected for each point. The number of measured points varied depending to the properties of sample surface (1 point for smaller homogeneous surfaces, 3 points for larger uneven surfaces), with final colorimetric values coming from an average and errors calculated as standard deviations.

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[25] Plain but valuable explanations regarding color communication can be found visiting Konica Minolta website. More details as far as colorimetric measurements applied to Cultural Heritage can be found in: Bacci, Picollo and Radicati, 2001

In order to collect the reflectance spectra of the same areas at different times (monitoring ageing color variations), an especially shaped Mylar® cover was used. The total color difference (ΔE^*_{ab}) was calculated using the following equation:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

When discussing the data, the ΔE^*_{ab} are referred to some threshold values, established on the base of previous measurements. The color variations were therefore classified as: negligible for $\Delta E^*_{ab} < 3$; minor for $3 < \Delta E^*_{ab} < 5$; detectable to naked-eye examination for $\Delta E^*_{ab} > 5$.

Data were processed using Microsoft Excel software.

2.4.6 Mid-IR active thermography [26]

Among non-destructive testing methods, infrared imaging techniques allow the non-invasive examination of large surfaces *in* situ, as well as the mapping of locally investigated features. As suggested in previous publications,[27] Mid-IR active thermography is a powerful technique for assessing the condition of contemporary mural paintings, allowing to precisely locate paint layers' delaminations at suitable resolution (being able to detect sub-surface voids down to sub-millimetric scale) and to assess the degree of adhesion between paint layers and support after consolidation treatments.

For this reason, Mid-IR active thermography was chosen for monitoring the occurrence of paint layer delaminations as the rising damp cycles were carried out.[28]

The final set-up came from systematic laboratory testing, including different materials and defects modeling.[29] The thermographic device was a Nikon LAIRD-S270 camera, based on a cooled PtSi detector (475x442 pixels) with spectral sensitivity in the Mid-IR 3-5 µm (MWIR), -20°C÷250°C temperature range at resolution of 0.2°C.

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[26] Ambrosini, *et al.* 2010; Avdelidis and Moropoulou 2004; Blessey, *et al.* 2010; Gavrilov, *et al.* 2011; Ibarra-Castanedo, *et al.* 2008; Ibarra-Castanedo, *et al.* 2010; Maldague 2000; Maldague 2001; Sabater González and Rodríguez Pedraza 2011; Scudieri, Mercuri and Volterri, 2001

[27] Daffara, *et al.*2011; Melchiorre Di Cresecenzo, *et al.* 2011 (*Publications and conference activity*)

[28] Mid-IR active thermography measurements were carried out using the instrumentation of the CNR-INO, Gruppo Beni Culturali, Firenze.

[29] The results of the preliminary testing have been partially reported in Silvia Scrascia' s master thesis (2009/10).

A sample-thermocamera stand-off distance of 600 mm turned out to provide an acceptable trade-off between size of the smallest resolved feature and field of view (FOV= 155X195 mm; sampled pixel at painting surface of less than 500 µm).

The initial heating or pulse heat stimulation was provided by a controlled IR source (tungsten 500W lamp). The surface of the samples was illuminated orthogonally, varying the pulse length until a significant temperature gradient was reached (maximum gradient of 7°C).

The thermal response decay was stacked in high spatial resolution maps for MATLAB computing.

Chapter 3

RESULTS AND DISCUSSION

The results of the experimentation are presented in this chapter, which is divided into two main sections:

- the first one (*3.1 Study of artists' emulsion paints*) reports on the characterization of the 15 emulsion paints (section 3.1.1) and the evaluation of their stability to different ageing conditions (section 3.1.2)
- the second one (*3.2 Inpainting treatments: evaluation of innovative materials and methods*) reports on the evaluation of the properties (section 3.2.1) and stability (section 3.2.2) of the retouching paints.

The results concerning the different items are properly discussed in the various sections titled *Discussing Results*.

3.1 Study of artists' emulsion paints

3.1.1 Preliminary characterization

3.1.1.1 Chemical characterization

The chemical composition of the artists' emulsion paints included in the study was preliminary assessed.

Since waterborne paints are very complex systems, and their formulations are often varied by paint manufacturers, it was necessary to compare the information deducible from technical data sheets and existing literature with the results of laboratory analysis.

A detailed chemical characterization of these paints requires the use of specific analytical tools and methods, the development of which is still the aim of other research projects.[1]

For this reason, our laboratory investigation was focused only on those aspects considered of primary importance for the purposes of this study:

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[1] This is especially true when dealing with the identification of organic additives: Boon, Hoogland and van der Horst, 2007; Hoogland and Boon, 2009a; Hoogland and Boon 2009b; Ormsby *et al.*, 2008; Silva *et al.*, 2010; Smith, 2005. Recently a Py-GC/MS double shot method was developed in order to allow a combination of thermal desorption for the analysis of the volatile compounds and pyrolisis for the analysis of the polymer (Pintus and Schreiner, 2011)

- Fourier Transform Infrared Spectroscopy analysis were carried out in order to identify the main components of the paint layers (binders, extenders and pigments), and to partially characterize paints' water extracts;
- an evaluation of paints' organic/inorganic components weight ratio was obtaied using Thermogravimetric Analysis (TGA);
- Energy Dispersive X-ray analysis, coupled with Scanning Electron Microscopy examinations (SEM-EDX), contributed to a proper identification of the inorganic components (pigments and extenders).[2]

The results collected from the 5 vinyl paints (Flashe®-L&B), the 5 acrylic paints (Heavy Body-Liquitex®) and the 5 styrene-acrylic paints (Brera- Maimeri) are dealt with separately.

FLASHE® PAINTS (LeFranc&Bourgeois)

FTIR SPECTROSCOPY: CHARACTERIZATION of the PAINT FILMS

The infrared spectra collected from each Flashe® paint layer are presented below, together with a table reporting the main absorption features and their tentative assignments (Tab. 3.1-1).[3]

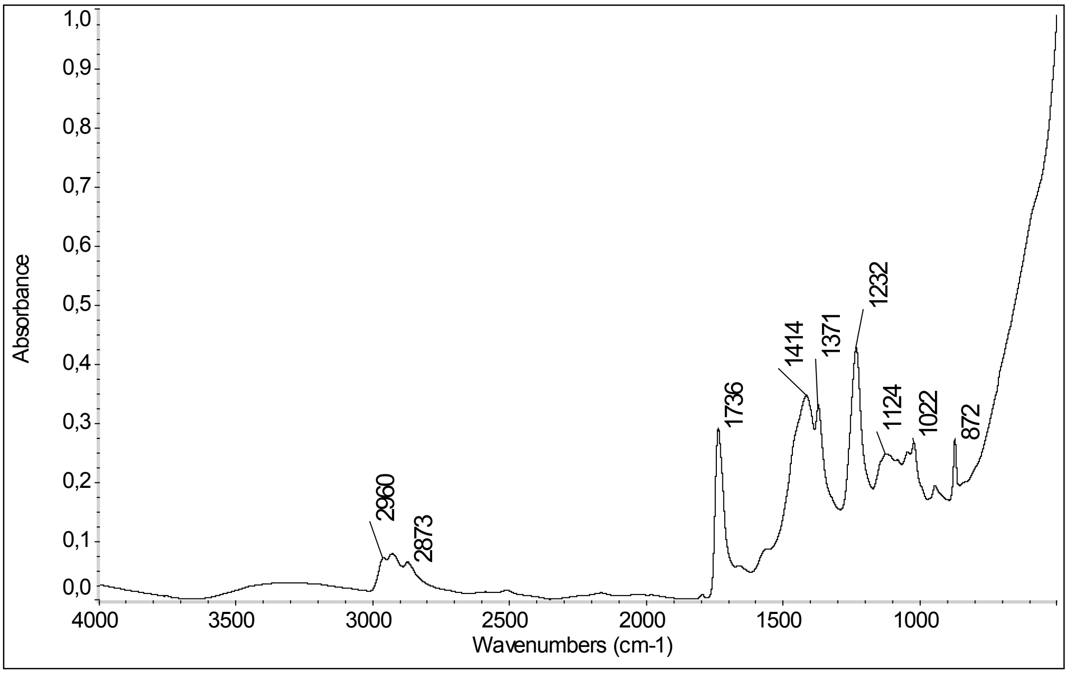

Fig. 3.1-1: FTIR-ATR spectrum from the White paint layer, Flashe® (L&B)

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[2] Even though Energy Dispersive X-ray analysis can be grouped together with the analytical techniques which allow the chemical characterization of the paints, EDX spectra will be shown later in the text, together with the SEM images.

[3] These and the following paints' spectra were collected working on free film samples, using the Perkin Elmer Spectrum 100 instrument. The processing, carried out using OMNIC32 software, included automatic base line correction, automatic smoothing and scale normalization.

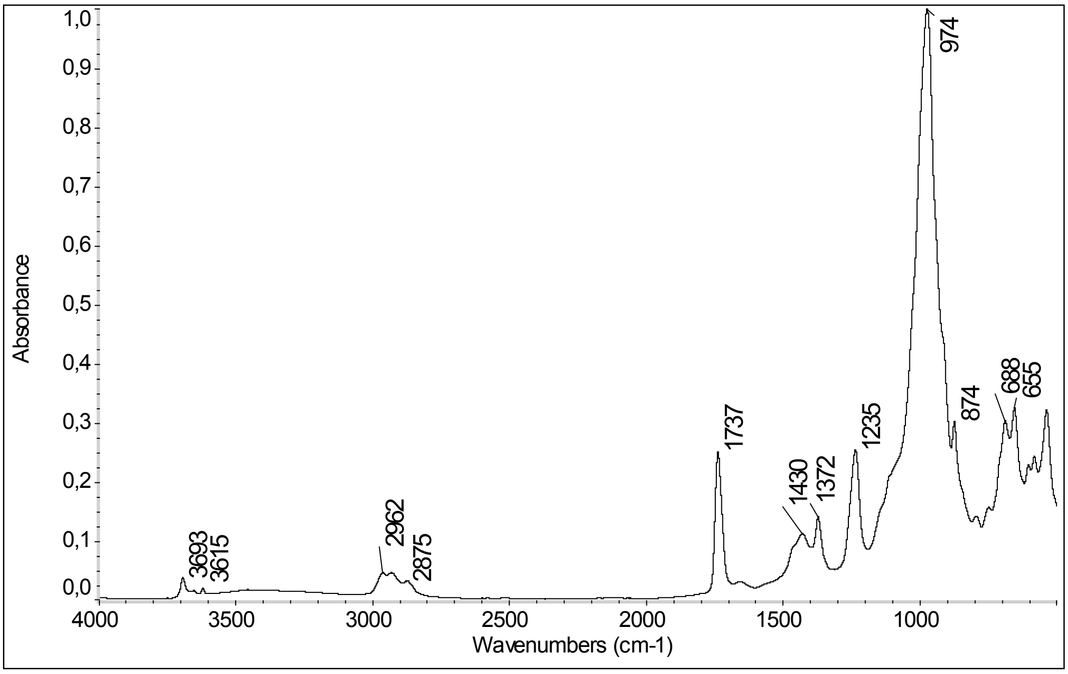

Fig. 3.1-2: FTIR-ATR spectrum from the Ultramarine Blue paint layer, Flashe® (L&B)

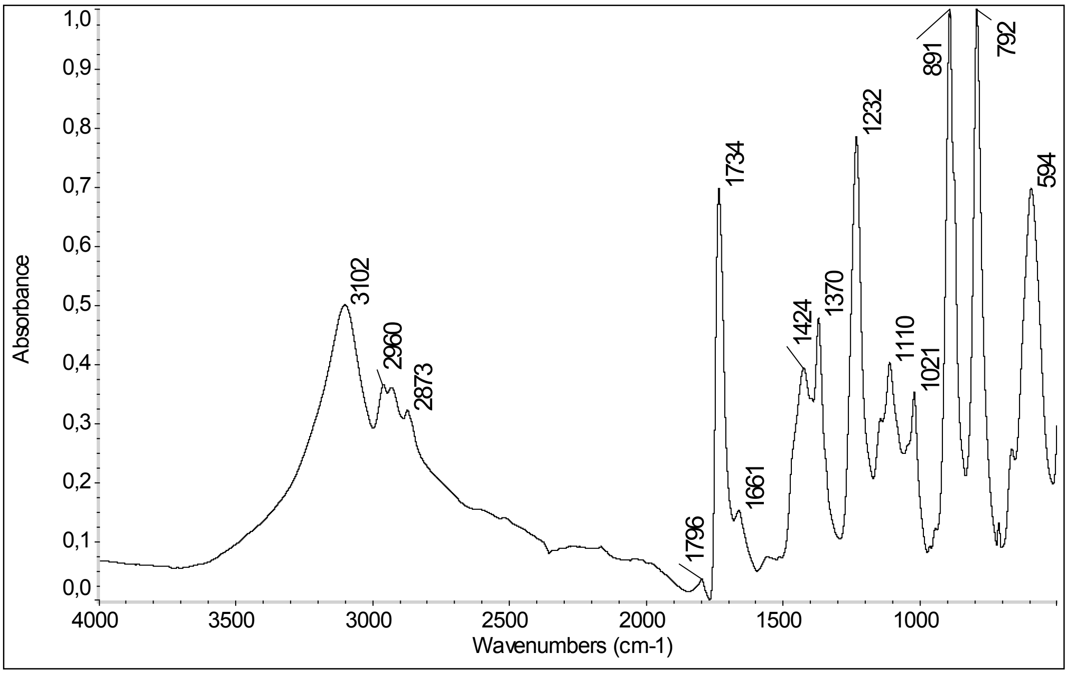

Fig.3.1-3: FTIR-ATR spectrum from the Yellow Ochre paint layer, Flashe® (L&B)

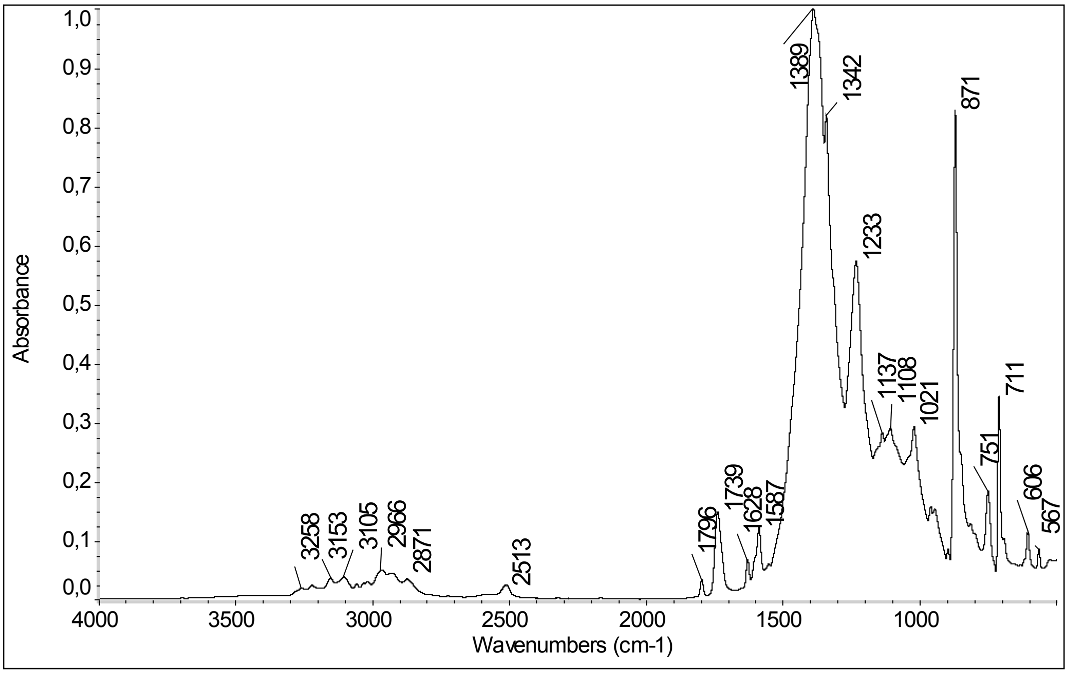

Fig. 3.1- 4: FTIR-ATR spectrum from the Ruby Red paint layer, Flashe® (L&B)

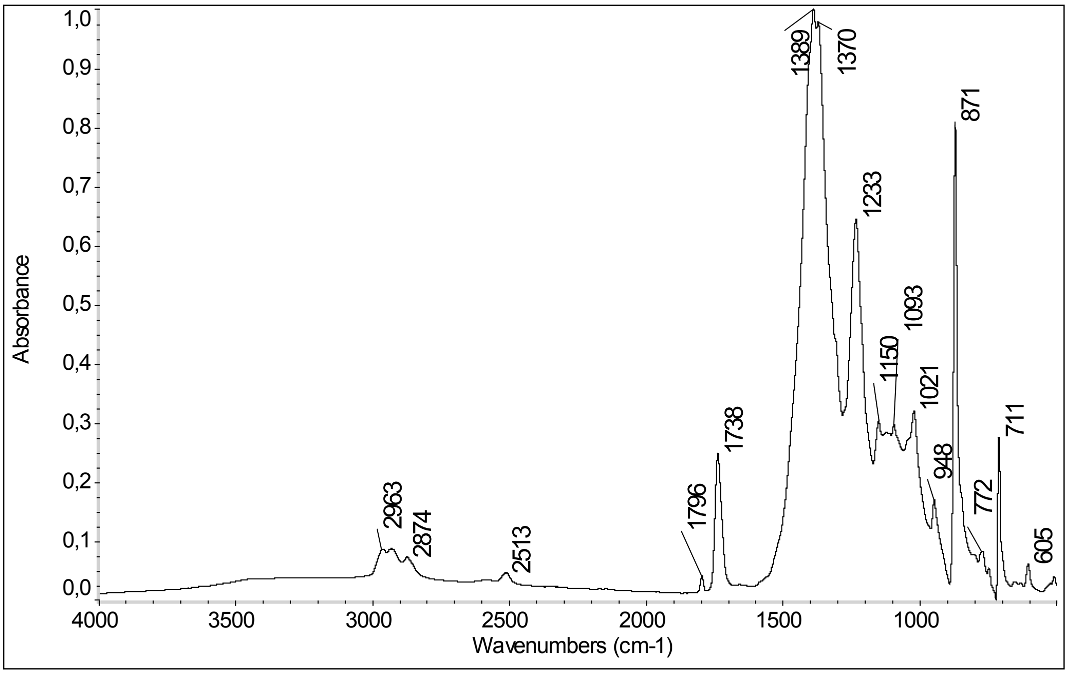

Fig. 3.1-5: FTIR-ATR spectrum from the Armour Green paint layer, Flashe® (L&B)

FLASHE® PAINTS (LeFranc & Bourgeois)					
White	**Ultramarine Blue**	**Yellow Ochre**	**Ruby Red**	**Armor Green**	**Tentative Band Assignments**
-	3693	-	-	-	PB29
-	3652	-	-	-	PB29
-	3620	-	-	-	PB29
-	-	-	3263	-	PV19
-	-	-	3227	-	PV19
-	-	-	3157	-	PV19
-	-	-	3105	-	PV19
-	-	3102	-	-	PY42
-	-	-	3055	-	PV19
-	-	-	3037	-	PV19
2960	2962	2960	2966	2963	Vin. binder
2929	2932	2931	2919	2932	Vin. binder
2873	2875	2873	2871	2874	Vin. binder
-	-	-	2513	2513	$CaCO_3$
1796	-	1796	1796	1796	$CaCO_3$
1736	1737	1734	1739	1738	Vin. binder
-	-	-	1628	-	PV19
1654	-	-	-	-	Add.
-	-	1661	-	-	PY42
-	-	-	1587	-	PV19
1566	-	1557	-	-	Add.
-	-	1514	-	-	Add.
1414	1430	1424	1389	1389	$CaCO_3$/ Vin. binder
1371	1372	1370	-	1370	Vin. binder
-	-	-	1342	-	PV19
1232	1235	1232	1233	1233	Vin. binder
-	-	-	-	1150	PG7
-	-	-	1137	-	PV19
1124	-	1143	-	1124	Vin. binder
-	-	1110	1108	-	Vin. bind. /add
-	-	-	-	1094	PG7
1083	-	-	-	-	PW5
1045	-	-	-	-	PW5
1022	-	1021	1021	1021	Vin. binder
-	974	-	-	-	PB29
-	-	-	960	-	PV19
-	-	-	-	948	PG7
945	-	963	945	-	Vin. binder
-	-	-	897	-	PV19
-	-	891	-	-	PY42
872	874	-	871	871	$CaCO_3$
-	-	792	-	-	PY42
-	-	-	751	-	PV19
-	-	-	-	749	PG7
-	-	712	711	711	$CaCO_3$
-	688	-	-	-	PB29
-	655	-	-	-	PB29
600	-	-	-	-	PW6

Table 3.1-1: FTIR-ATR absorption features (cm^{-1}) of Flashe® paint layers with tentative band assignment (the table continues in the following page).

FLASHE® PAINTS (LeFranc & Bourgeois)					
White	**Ultramarine Blue**	**Yellow Ochre**	**Ruby Red**	**Armor Green**	**Tentative Band Assignments**
-	-	-	606	-	PV19
-	-	-	-	605	PG7
-	-	594	-	-	PY42
-	582	-	-	-	PB29
-	-	-	566	-	PV19
-	537	-	-		PB29

Table 3.1-1: FTIR-ATR absorption features (cm^{-1}) of Flashe® paint layers with tentative band assignment. Vin. binder= p(VAc-VeoVa) absorptions; Add= additive; PW5= Lithopone; PW6=Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Red; PG7= Phathalocyanine Green

As deducible from the FTIR spectra,[4] Flashe® paints consist of a vinyl binder, with absorption features suggesting a poly vinyl acetate-vinyl versatate copolymer (p(VAc-VeoVa)). The main absorptions that can be related to this vinyl binder are:

- C-H stretching absorptions at about: 2962 cm^{-1} (ν_{as} CH_3),2926 cm^{-1}(ν_{as} CH_2),2872 cm^{-1} (ν_s CH_3 partially enhanced by ν_s CH_2 around 2853 cm^{-1});
- C=O stretching band between 1734 cm^{-1} and 1738 cm^{-1};
- fingerprint region absorptions: a fairly sharp band around 1370 cm^{-1} (possibly related to δ_s CH_3), the very strong and typically rounded ν_{as} C-O (of the C-C(=O)-O bond) at about 1240 cm^{-1}, the ν_{as} C-O (of the O-C-C bond) around 1100 cm^{-1}. Other absorptions in the finger print region (and so absorptions related to C-H bending, C-O stretching, C-C stretching and C-H rocking) that could be assigned to the binder (as the main organic component of the paints) are those occurring at: 1124 cm^{-1}, 1021 cm^{-1}, 963 cm^{-1}.

The band around 1436 cm^{-1} that is usually seen in p(VAc-VeoVa) spectra is here partially covered by a strong absorption between 1389 cm^{-1} and 1430 cm^{-1} ascribable to the ν_3 asymmetric stretching of CO_3^{2-}, indicative of calcium carbonate extender ($CaCO_3$). The presence of this inorganic extender is confirmed by other absorptions in the FTIR spectra (ν_1+ν_3 combination band at 2513 cm^{-1}; ν_1+ν_4 combination band at 1796 cm^{-1}, the strong and sharp ν_2 band at 873 cm^{-1}, the less strong but still sharp ν_4 absorption at 714 cm^{-1}).

The spectra mainly show the diagnostic features expected when considering the pigments declared by paints' manufacturer.[5]

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[4] The interpretation was based on: Adrover Gracia 2001; Derrick *et al.* 1999; Farmer (ed.) 1974; Learner 2004; Nyquist and Kagel 1971; Ricci *et al.* 2006; Silverstein, Bassler and Morril, 1981. The data base of the *Infrared and Raman user Group* was considered as well (http://www.irug.org/).

[5] Useful information as far as the pigments was found in: Montagna 1993; Roy (ed.) 1993; West Fitzhugh (ed.) 1997. Further information was acquired looking through: *The Pigment Compendium CD-ROM* Elsevier (2004). Spectra interpretation was based on these texts and the comparison with the reference spectra collected for pure pigments (see Appendix 2). Data are totally consistent with those coming from Energy Dispersive X-ray microanalysis (shown later in the text).

The spectrum of White paint does not show, in the Mid-IR region, any diagnostic absorptions related to the Titanium Dioxide pigment (TiO_2, PW6), which results only in a very broad band at the low wavenumbers end of the spectrum (below 800 cm^{-1}). The absorptions at 1083 cm^{-1} and 1045 cm^{-1} could be instead related to the Lithopone pigment (ZnS-$BaSO_4$, W5), which is also contained in the paint. The typical absorptions reported for Baryte ($BaSO_4$) are: $\nu_1$980 cm^{-1}, $\nu_2$470 cm^{-1} and 439 cm^{-1}, $\nu_3$1100 cm^{-1} and 1042 cm^{-1}, $\nu_4$614 cm^{-1}.

The Ultramarine Blue paint turned out to contain the Ultramarine Blue pigment (PB29), a polysulfide of sodium aluminosilicate ($2Na_2Al_2Si_2O_6 \cdot NaS_2$), in this case of artificial origin. The presence of the pigment was confirmed thanks to some diagnostic features: a very strong and broad absorption around 970 cm^{-1} (overlapping stretching bands for Si-O-Si and Si-O-Al) and other weaker but distinct absorptions around 685 cm^{-1} and 655 cm^{-1} (Si-O bond vibrations). Additional features are: the sharp bands around 3690 cm^{-1} and 3620cm^{-1} (OH- stretching of hydrated aluminum silicates, possibly related to Kaolinite, $Al_2Si_2H_4O_9$)[6]; the absorptions around 794 cm^{-1},580 cm^{-1} and 538 cm^{-1}.

The Yellow Ochre paint contains the Mars Yellow[7] pigment ($FeO(OH)\ H_2O$, PY42), an hydrated iron oxide of synthetic origin, whose spectrum shows the following diagnostic features: a very broad absorption in the O-H stretching region with a maximum observed at about 3100 cm^{-1}; three distinct peaks around 895 cm^{-1}, 795 cm^{-1} and 600 cm^{-1}. Additional features seen in the reference spectrum of this pigment are the absorptions around: 1795 cm^{-1}, 1660 cm^{-1}, 1125 cm^{-1} and 515 cm^{-1}.

The presence of a Quinacridone pigment ($C_{20}H_{12}N_2O_2$, PV19) was confirmed for the Ruby Red paint, with the spectrum displaying a very sharp and intense peak at 1345-1346 cm^{-1} and an intense area of absorption between 1580 and 1630 cm^{-1}.

Finally, the presence of a Phthalocyanine Green pigment ($C_{32}H_3Cl_{13}CuN_8 \div C_{32}HCl_{15}CuN_8$, PG7) was confirmed for the Armor Green paint, with the spectrum showing some of the phathalocyanine diagnostic absorptions. The reference spectrum of this green pigment is usually characterized by: absorptions between 3100÷2800 cm^{-1} (C-H stretching); other absorptions in the 1700÷1550 cm^{-1} region (C=N stretching of the 5 membered ring lactam); other absorptions between 1629÷1420 cm^{-1} (aromatic bands); some sharp diagnostic bands in the 1480÷1300 cm^{-1} (C-H bending) and 1330÷1050 cm^{-1} (C-N stretching) regions. Further absorptions are seen between 950÷900 cm^{-1} and 800÷730 cm^{-1}.

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[6] Sight amounts of Kaolinite were recently detected in other Ultramarine blue based commercial paints. (Pintus, Wei, and Schreiner, 2012). This is moreover consistent with pigment manufacturing procedure (Plesters, 1993).

[7] The name *Mars Yellow* is hereinafter used according to Learner, 2004: 25, referring to a Synthetic Yellow Iron Oxide pigment.

FTIR SPECTROSCOPY: CHARACTERIZATION of PAINTS' WATER EXTRACTS

In order to identify some of the paints additives, FTIR spectroscopy analysis were carried out on paints' water extracts.[8]
After 6 months of natural ageing at laboratory conditions (T about 22±2°C; R.H. 50±5%), samples of the same size and shape (about 0.12g in weight) were removed from each paint free-film and subjected to 24h, 30 ml distilled water extractions. The water fractions were separated and left to dry on Petri dishes.

The infrared spectra collected on the dry residues are shown in figure 3.1-6, together with a table presenting the main absorption features and tentative assignments (Tab. 3.1-2).

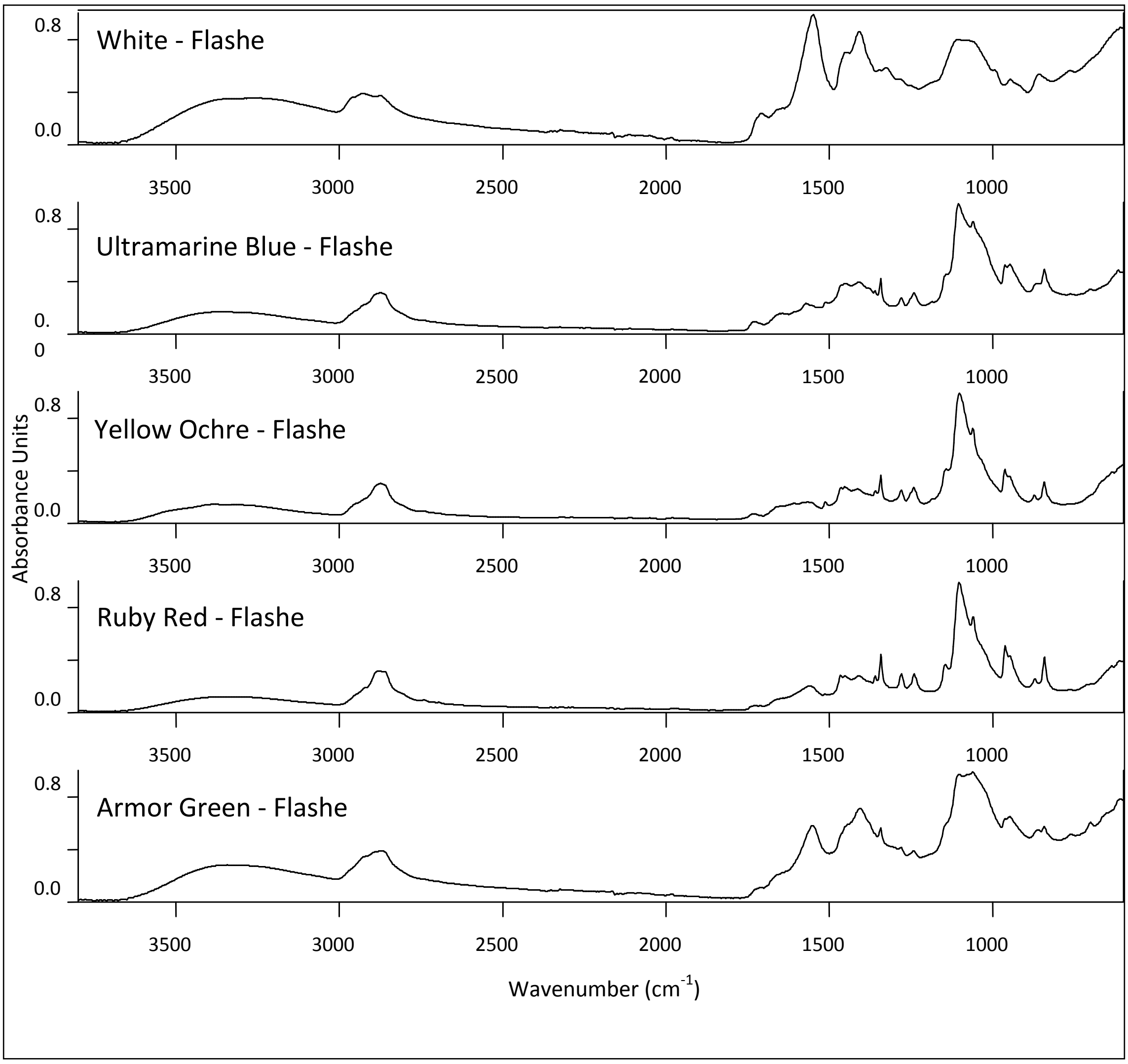

Fig. 3.1-6: FTIR spectra from the Flashe® paints' water extracts.

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[8] The spectra of the water extracts were collected using the Vertex70 FTIR spectrometer (equipped with ATR accessory). The processing, carried out using OPUS software (version 5), included some smoothing and scale normalization.

The spectra from the water extracts of Ultramarine Blue, Yellow Ochre and Ruby Red paints are very similar.

Even though, in the 1500÷1400 cm^{-1} region the spectra are not well readable, the main diagnostic features of an alkylphenol ethoxylate (APE) surfactant were tentativey detected.

As a matter of fact, the C-H stretching region is dominated by the absorptions of the methylene groups (with $\nu_s CH_2$ centered at 2873 cm^{-1} for Ultramarine Blue, 2877 cm^{-1} for Yellow Ochre and Ruby Red) and shows two absorptions related to the C-H stretching vibrations of the methylendioxy group linked to the aromatic ring (2741 cm^{-1} and 2692 cm^{-1} for Ultramarine Blue, 2741 cm^{-1} and 2695 cm^{-1} for Yellow Ochre and Ruby Red).

In addition, the spectra show: a small band at 1512 cm^{-1}; a doublet around 1360 cm^{-1} and 1342 cm^{-1} (1363 cm^{-1} and 1343 cm^{-1} for Ultramarine Blue, 1360 cm^{-1} and 1344 cm^{-1} for Yellow Ochre and Ruby Red) and a sharp peak at 1104cm^{-1}.

In table 3.1-2 other absorptions, falling in the C-H stretching region (3200÷2800 cm^{-1}) and the finger print region (1500÷500 cm^{-1}) are listed. Some of these absorptions, even if less diagnostic, could be assigned to vibrations of the APE surfactant molecule.

Other bands are those at about: 1730 cm^{-1} (1731 cm^{-1} for Ultramarine Blue and Yellow Ochre, 1729 cm^{-1} for Ruby Red); 1640 cm^{-1} (1645 cm^{-1} for Ultramarine Blue, 1644 cm^{-1} for Yellow Ochre); 1560 cm^{-1} (1570 cm^{-1} and 1554 cm^{-1} for Ultramarine Blue, 1567 cm^{-1} for Yellow Ochre, 1561 cm^{-1} for Ruby Red); 1400 cm^{-1} (1408 cm^{-1} for Ultramarine Blue and Ruby Red, 1415 cm^{-1} for Yellow Ochre).

With the exception of the absorption around 1640 cm^{-1}, which may arise from residual water (as suggested even by the band centered at 3400 cm^{-1}), the other ones could be related to a variety of organic additives that are usually included in waterborne paints, such as a polyacid pigment dispersant (like Tamol^{TM}), methenamine derivative preservative (like Dowicil^{TM} 75), phenyl phosphates, phthalates etc…[9]

All these features are less defined in the spectra of White and Armour Green paints, which show a quite broad absorption around 1100 cm^{-1} (that could be referred to the ethoxylate moieties of the surfactants, as well as to the C-O-C stretching of a cellulose ether) and are dominated by two strong absorptions at about 1550 cm^{-1} (1550 cm^{-1} for White and 1554 cm^{-1} for Armour Green) and 1400 cm^{-1} (1411 cm^{-1} for White, 1405 for Armour Green). These latter absorptions could be due to a the stretching of a carboxylate anion, possibly related to an anionic pigment dispersant such as the widespread Sodium polyacrylate.

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[9] This is consistent with the results gained through Py-GC-MS by Silva *et al.* 2010.

FLASHE® PAINTS (LeFranc & Bourgeois)					
White	**Ultramarine Blue**	**Yellow Ochre**	**Ruby Red**	**Armor Green**	**Tentative Band Assignments**
3270	3350	3350	3320	3320	Water
2959	-	2955	-	-	Org. Add
2931	-	-	2926	2926	Org. Add
2877	**2873**	**2877**	**2877**	2871	**APE surf**
-	-	-	2861	-	Org. Add
-	**2741**	**2741**	**2741**	-	**APE surf**
-	**2692**	**2695**	**2695**	-	**APE surf**
1707	1731	1731	1729	1712	Add. Org.
1644sh	1645	1644	1658sh	-	Water
-	-	1612	-	-	Org. Add
-	1570	1567	1561	-	Org. Add
1550	1554sh	-	-	1554	Pol. Disp.
-	**1512**	**1512**	**1512**	-	**APE surf**
-	-	1467	1467	-	APE surf
1449	1454	1454	1454	-	APE surf
1411	-	-	-	1405	Pol. Disp.
-	1408	1415	1408	-	Org. Add.
-	**1363sh**	**1360**	**1360**	-	**APE surf**
1345	**1343**	**1344**	**1344**	1344	**APE surf**
1327	-	-	-	-	Org. Add
1286	1282	1279	1279	1282	APE surf
-	1240	1244	1240	1244	APE surf
-	1140sh	1143	1146	-	APE surf
1110	-	-	-	-	Org. Add
-	**1104**	**1104**	**1104**	**1104**	**APE surf**
1078	-	-	-	1075	Org. Add
-	1059	1062	1062	1062	APE surf
-	962	965	962	962	APE surf
946	949	949	949	949	Org. Add.
-	-	875	872	-	Org.Add.
861	861	-	-	862	Org.Add.
-	842	842	842	842	APE surf
763	758	-	-	762	APE surf
-	703	-	-	700	APE surf

Table 3.1-2: FTIR absorption features (cm^{-1}) of Flashe® paints' water extracts, with tentative band assignment. In bold letters, the most diagnostic absorptions of the alkylphenol ethoxylate surfactant (APE surf). The absorption bands which cannot be univocally referred to a compound, are generally assigned to Organic Additives (Org. Add). Pol. Disp.= polyacrylate dispersant. sh= shoulder

THERMOGRAVIMETRIC ANALYSIS

In figure 3.1-7, the curves resulting from the themogravimetric analysis of the five Flashe® paints are shown.

Most of the curves display three principle mass losses, occurring around 325°C, 455°C and 720°C.

The oxidative degradation of pVAc consists of 3 steps: the deacetylation step (300-400°C) resulting in a polyenic structure; the charring step (400-500°C) resulting in a fully aromatized thermally stable product (the so called char); an ultimate degradation step (above 500°C) characterized by the oxidation of the aromatic structure formed during the previous step. When vinyl acetate is copolymerized with other monomers (e.g: ethylene), the copolymers are reported to degrade according to a 2 steps pattern: after deacetylation (300-400°C), the polymer degrades in a single step (400-500°C). The copolymers do not form a stabilized aromatic structure or char.[10]

The first two mass losses shown by the thermograms could be related to the polymer degradation process, the third one is due to the decomposition of calcium carbonate extender ($CaCO_3$).[11] Some of the samples (White, Ultramarine Blue and Ruby Red paints) show a further mass loss around 260°C, that could be related to the first degradation steps of various organic components.

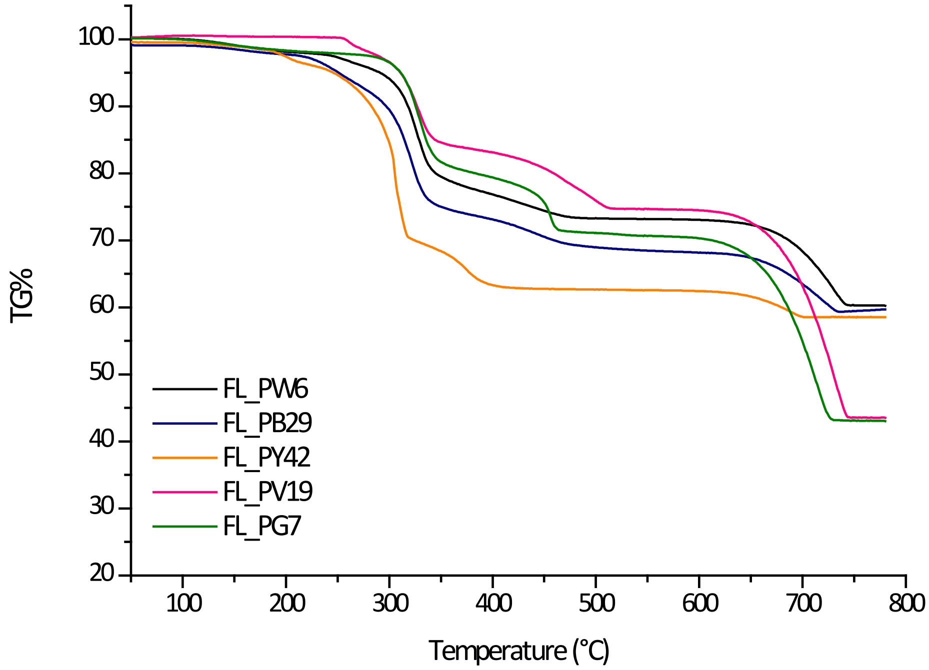

Fig. 3.1-7: TG curves of Flashe® (FL) reference paints (LeFranc&Bourgeois).

Since White and Ultramarine Blue paints consist of pigments that are thermally stable in the scanned temperature range (30-800°C), it is possible to evaluate their organic/inorganic components weight ratio in a reliable way. If considering all the weight losses occurring below 500°C, White paint turns out to contain a 25% by weight of organic materials, while Ultramarine Blue a 29%. If considering only the steps related to binder degradation (those around 325°C and 455°C), White paint loses the 23% of its

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[10] Rimez *et al.*2008.

[11] The decomposition of calcium carbonate has been observed in the 630-800°C range (Nardini *et al.*2007).

weight, while Ultramarine Blue the 24%. The amount of binder turns out to be almost the same in both paints.

Sample	Low Temp. Weight Loss (%)	First step Weight Loss (%)	Second step Weight Loss (%)	Third Step Weight Loss (%)	Residual Weight %	Residues Identification
White (PW6)	1.78 (225÷280°C)	18.63 (280÷385°C)	4.40 (385÷500°C)	12.72 (620÷760°C)	60.00	PW6 - CaO
	1.88 (225÷275)	18.51 (275÷385)	4.20 (385÷500)	12.59 (620÷760°C)	60.20	
Ultramarine Blue (PB29)	4.48 (210÷275°C)	19.26 (275÷385°C)	4.91 (385÷500°C)	8.58 (620÷750°C)	59.23	PB29 - CaO
	5.01 (200÷275°C)	19.10 (275÷385°C)	4.65 (385÷500°C)	8.61 (610÷750°C)	59.84	
Yellow Ochre (PY42)	22.96* (275÷325°C)		6.78 (325÷425°C)	3.98 (590÷720°C)	57.41	Fe_2O_3 -CaO
	21.56* (275÷325°C)		7.10 (325÷425°C)	3.93 (590÷710°C)	58.52	
Ruby Red (PV19)	1.67 (250÷280°C)	14.87 (280÷385°C)	9.10* (385÷540°C)	30.82 (620÷770°C)	41.57	CaO
	2.11 (250÷280°C)	14.63 (280÷385°C)	8.79* (385÷520°C)	30.61 (620÷750°C)	43.55	
Armor Green (PG7)	-	16.99 (275÷385°C)	9.33* (385÷500°C)	26.85 (590÷750°C)	41.57	CaO
	-	17.69 (275÷385°C)	8.82* (385÷500°C)	27.32 (590÷740°C)	43.96	

Tab. 3.1-3: Together with the residual weights (%), the weight losses (%) ascribable to the thermal degradation of paints' main components are shown. Four degradation steps are considered: that occurring below 300°C (not always detected); two degradation steps related to binder degradation; a third step related to extender degradation. Together with the weight losses, the on*set* and end*set* temperatures of the degradation processes are shown. Residual thermally stable chars were analyzed through FTIR spectroscopy. * indicates values influenced by pigment thermal degradation process.

Interpreting the curves of Yellow Ochre, Ruby Red and Armor Green paints instead, the contribution due to the pigments' degradation process has to be considered. Thermogravimetric analysis of reference pigments, actually revealed that Quincridone Red (PV19) and Phthalocyanine Green (PG7) show weight losses in the 450-700°C range. The degradation process of Mars Yellow (PY42) instead, occurs in the 200-400°C range, partially overlapping with the first degradation step of the binder.[12]

As displayed in Table 3.1-3, different paints are characterized by different amounts of the calcium carbonate extender (that is generally higher for paints containing organic pigments, expected to require higher amounts of extenders because having high tinting strength).[13]

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[12] The first degradation step of synthetic α-FeOOH and synthetic γ-FeOOH, have been both observed around 300°C. (MacKenzie 1970)

[13] Learner, 2004

HEAVY BODY (Liquitex®)

FTIR SPECTROSCOPY: CHARACTERIZATION of PAINT FILMS

The infrared spectra collected from each Heavy Body-Liquitex® paint layer are shown below, together with a table presenting the main absorption features and their tentative assignments (Tab. 3.1-4).

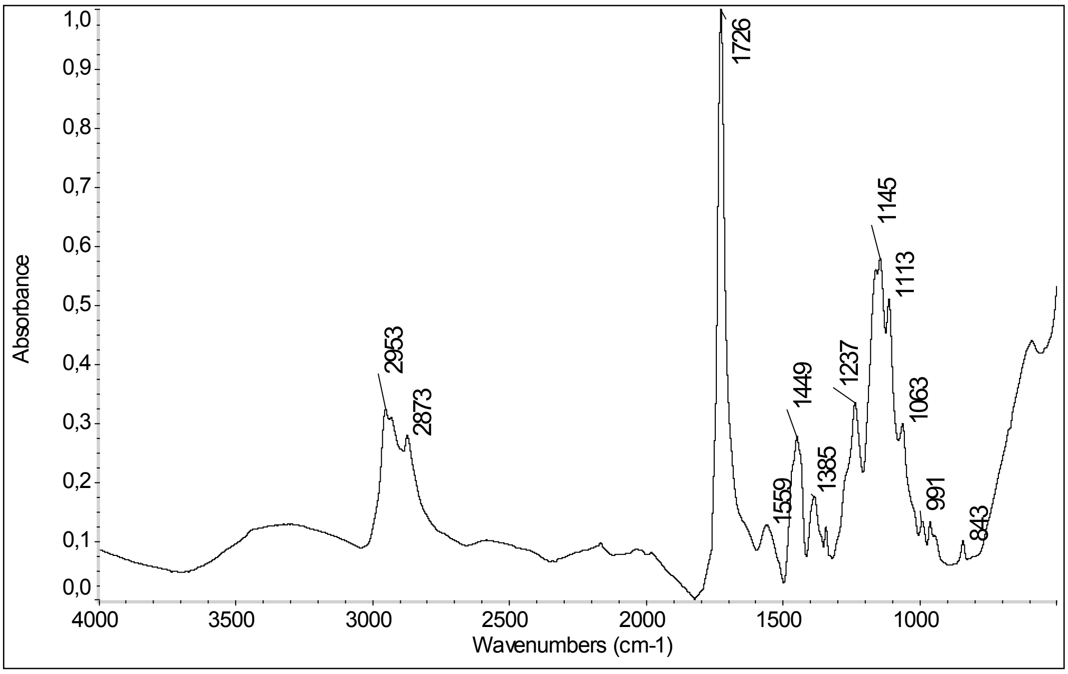

Fig. 3.1-8: FTIR-ATR spectrum from the Titanium White paint layer, Heavy Body (Liquitex ®)

As deducible from the FTIR spectra of the figures, Heavy Body paints consist of an acrylic binder, with absorption features suggesting a poly *n*-butyl acrylate -methyl metacrylate co-polymer (p(nBA-MMA)).

The main absorptions that can be related to this binder are:

- C-H stretching region absorptions, with two main peaks at about 2955cm^{-1} (ν_{as} CH_3) and 2874 cm^{-1} (ν_s CH_3) and a shoulder around 2933 cm^{-1}
- C=O stretching band, between 1726 cm^{-1} and 1730 cm^{-1}
- C-H bending absorptions around: 1452 cm^{-1} (CH_3 asym. bending/ CH_2 scissoring), and 1387 cm^{-1} (CH_3 sym. bending)
- C-O stretching and C-C stretching absorptions at about: 1237 cm^{-1}, 1160 cm^{-1}, 1145 cm^{-1}, 1064 cm^{-1} and 990 cm^{-1}
- C-H rocking absorption around 840 cm^{-1}

All the features related to the pigments' absorptions mainly coincide with those previously discussed for Flashe® paints.

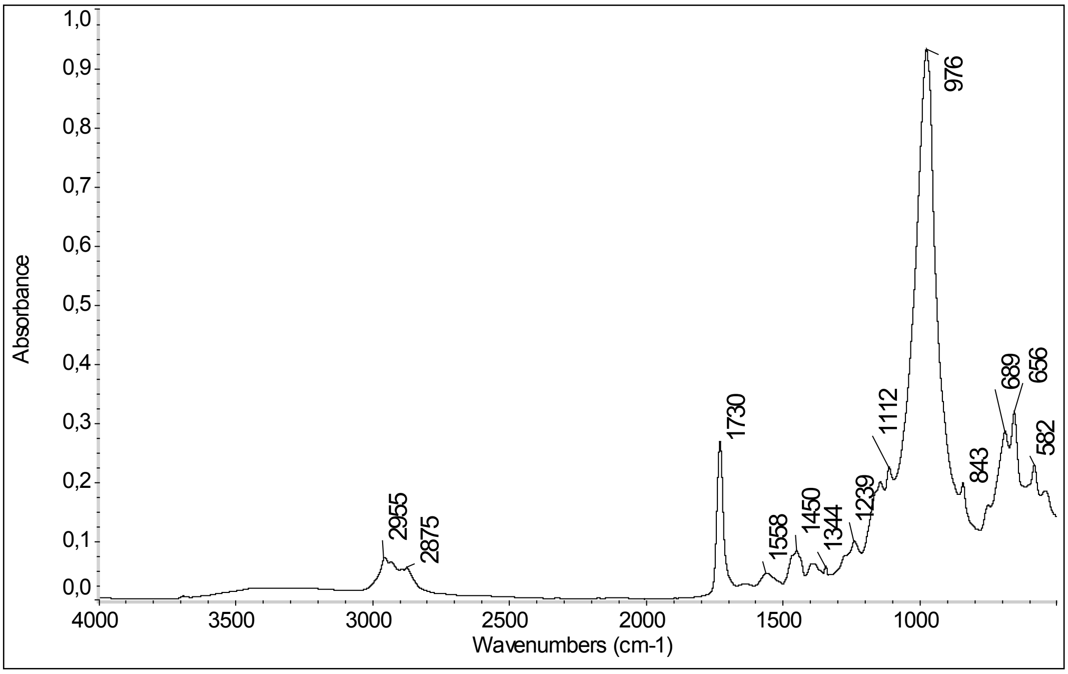

Fig. 3.1-9: FTIR-ATR spectrum from the Ultramarine Blue-Green Shade paint layer, Heavy Body (Liquitex ®)

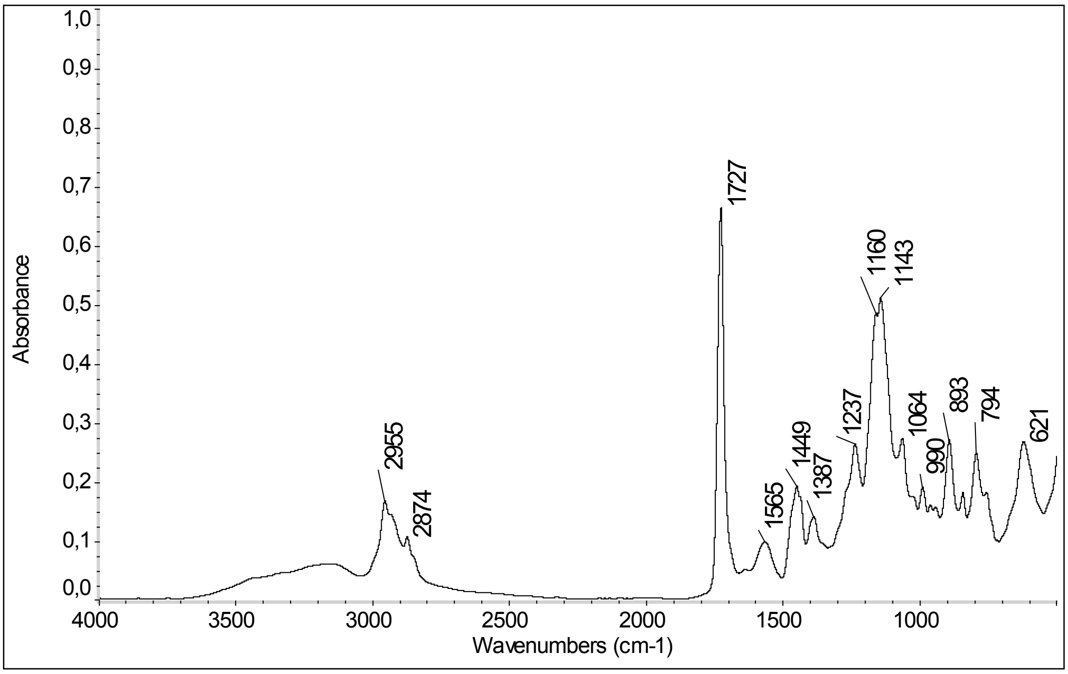

Fig. 3.1-10: FTIR-ATR spectrum from the Transparent Raw Sienna paint layer, Heavy Body (Liquitex ®)

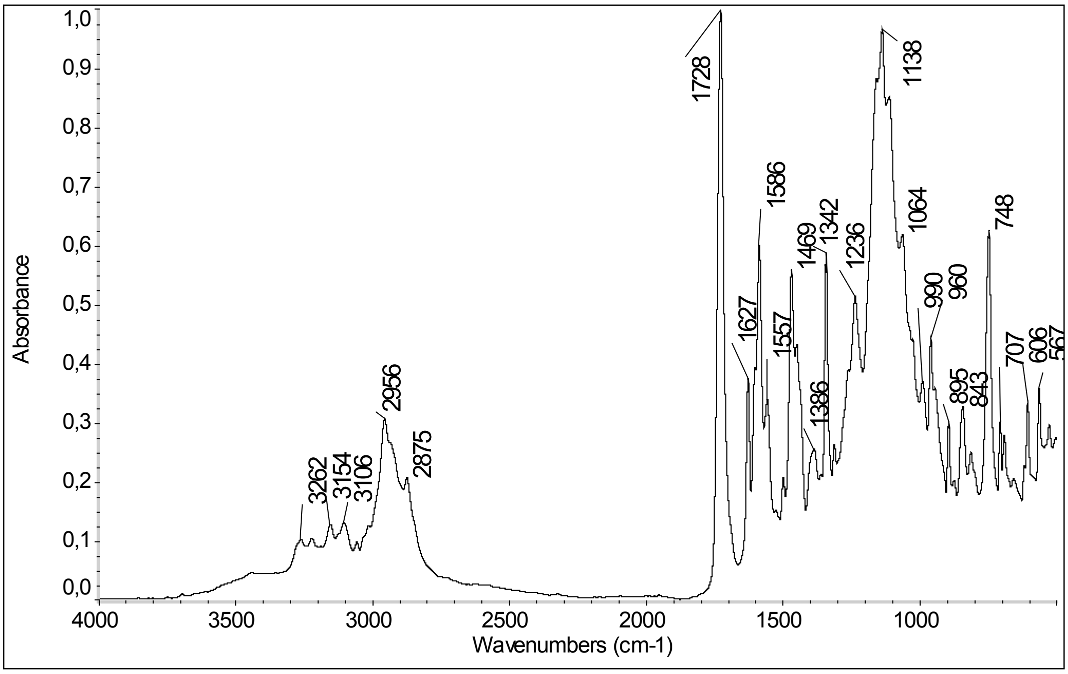

Fig.3.1-11: FTIR-ATR spectrum from the Quinacridone Crimson paint layer, Heavy Body (Liquitex ®)

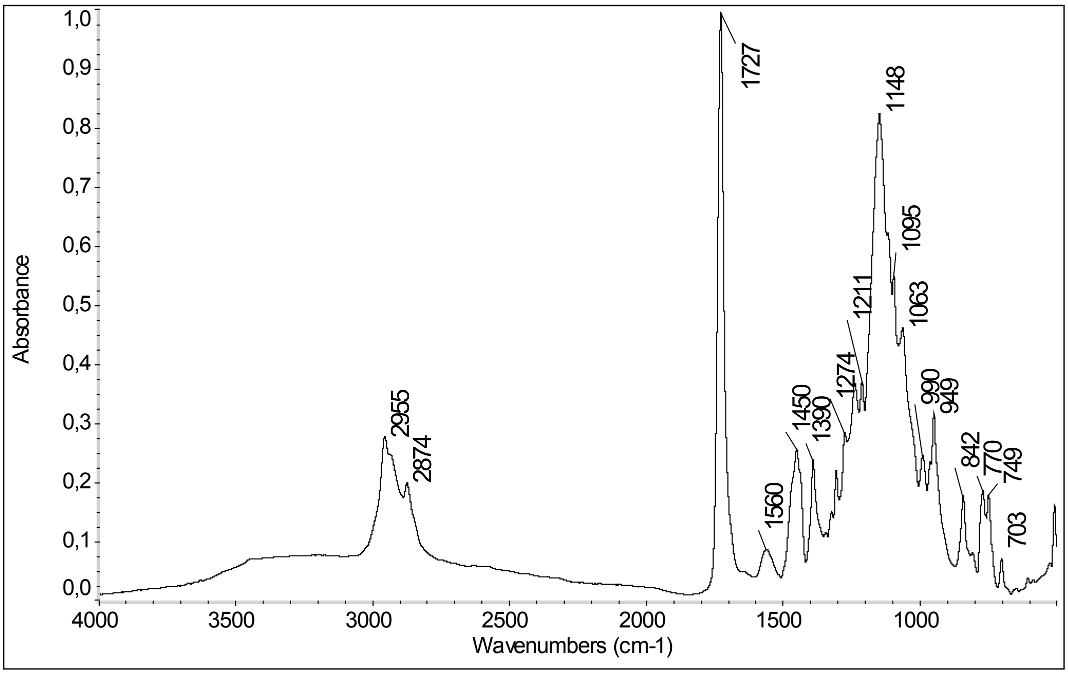

Fig. 3.1-12: FTIR-ATR spectrum from the Phthalocyanine Green-Blue Shade paint layer, Heavy Body (Liquitex®)

HEAVY BODY PAINTS (Liquitex®)					
Titanium White	**Ultramarine Blue- Green Shade**	**Transparent Raw Sienna**	**Quinacridone Crimson**	**Phthalocyanine Green**	**Tentative Band Assignments**
-	-	-	3262	-	PV19
-	-	-	3221	-	PV19
-	-	-	3154	-	PV19
-	-	3130	-	-	PY42
-	-	-	3106	-	PV19
-	-	-	3058	-	PV19
2953	2955	2955	2956	2955	Acr.binder
2933	2933	-	-	-	Acr.binder
2873	2875	2874	2875	2874	Acr.binder
1726	1730	1727	1728	1727	Acr.binder
-	-	1638	-	-	PY42
-	-	-	1627	-	PV19
-	-	-	1587	-	PV19
1559	1558	1565	-	1560	Add.
-	-	-	1557	-	PV19
-	-	-	1498	-	PV19
-	-	-	1469	-	PV19
1449	1450	1449	1450	1450	Acr.binder
1385	1387	1387	1386	1390	Acr.binder
1343	1344	-	-	1344	Add.
-	-	-	1342	-	PV19
-	-	-	-	1322	PG7
-	-	-	1312	-	PV19
-	-	-	-	1305	PG7
				1274	PG7
1237	1239	1237	1236	1237	Acr. binder
-	-	-	-	1211	PG7
1161	-	1160	1158	-	Acr.binder
-	-	-	-	1148	Acr.binder/PG7
1145	1145	1143	-	-	Acr.binder
-	-	-	1138	-	Acr.binder/PV19
1113	1112	-		1117(sh)	Acr.binder/Add.
-	-	-	1109	-	Acr.binder/PV19
-	-	-	-	1095	PG7
1063	-	1064	1064	1063	Acr.binder
991	-	990	990	990	Acr.binder
-	976	-	-	-	PB29
963	-	962	-	-	Acr.binder
-	-	-	960	-	Acr.binder/PV19
-	-	-	-	949	PG7
-	-	-	895	-	PV19
-	-	893	-	-	PY42
843	843	843	843	842	Acr.binder
-	-	-	814	-	PV19
-	-	794	-	-	PY42
-	-	-	-	770	PG7
-	-	-	-	749	PG7
-	-	-	748	-	PV19
-	-	-	707	-	PV19

Table 3.1-4: FTIR-ATR absorption features (cm^{-1}) of Heavy Body-Liquitex® paint layers with tentative band assignment (the table continues in the following page).

HEAVY BODY PAINTS (Liquitex®)					
Titanium White	**Ultramarine Blue- Green Shade**	**Transparent Raw Sienna**	**Quinacridone Crimson**	**Phthalocyanine Green**	**Tentative Band Assignments**
-	-	-	-	703	PG7
-	-	-	691	-	PV19
-	689	-		-	PB29
-	656	-	-	-	PB29
-	-	621	-	-	PY42
-	-	-	606	-	PV19
600	-	-	-	-	PW6
-	582	-	-	-	PB29
-	-	-	567	-	PV19

Table 3.1-4: FTIR-ATR absorption features (cm^{-1}) of Heavy Body-Liquitex® paint layers with tentative band assignment. Acr. Binder= p(*n*BA-MMA); Add= additive; PW6=Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Red; PG7= Phathalocyanine Green

FTIR SPECTROSCOPY: CHARACTERIZATION of PAINTS’ WATER EXTRACTS

The water soluble components of the Heavy Body- Liquitex®paints were investigated, using the same analytical procedure described for Flashe® paints. The spectra of paints’ water extracts are presented in figure3.1-13. The main absorption features, with related tentative assignments are shown in table 3.1-5.

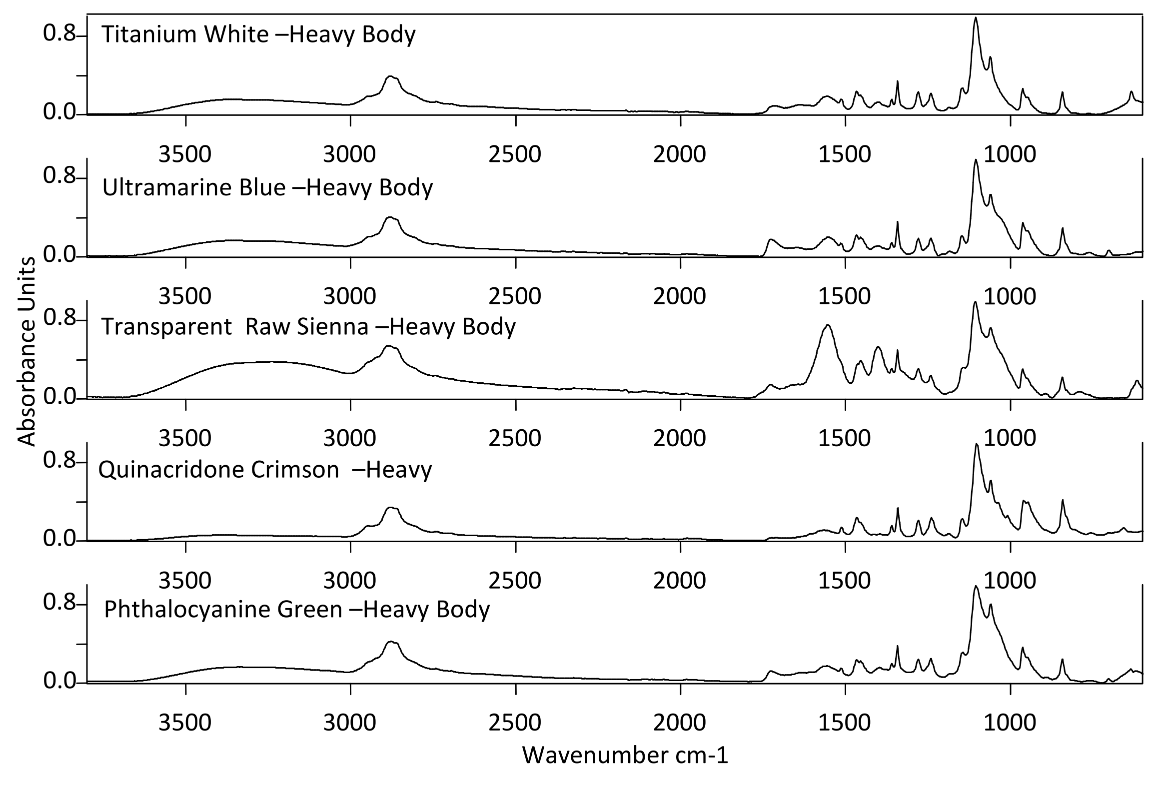

Fig. 3.1-13: FTIR spectra of Heavy Body-Liquitex ® paints’ water extracts.

With the exception of the spectrum acquired for Transparent Raw Sienna, the other spectra present the same diagnostic features. These absorptions are ascribable to some additives that are commonly used in waterborne polymers and paints manufacturing.[14]

An APE surfactant (alkylphenol ethoxylate) was identified by the presence of:

- a characteristic C-H stretching region pattern, dominated by the absorptions of methylene groups ($\nu_s CH_2$ centered at 2881 cm^{-1} for Titanium White, Ultramarine Blue, Quinacridone Crimson and Phthalocyanine Green) and showing two absorptions related to the C-H stretching vibrations of the ($Ar\text{-}O\text{-}CH_2$-) group (at 2741 cm^{-1} and 2694 cm^{-1} for Titanium White, Quinacridone Crimson and Phthalocyanine Green; at 2741 cm^{-1} and 2691 cm^{-1} for Ultramarine Blue)
- the small band possibly related to -C=C- ring stretch, around 1511 cm^{-1} (1512 cm^{-1} for Titanium White and Quinacridone Crimson, 1516 cm^{-1} for Ultramarine Blue and Phthalocyanine Green)
- the doublet around 1360 cm^{-1} and 1342 cm^{-1} (1362 cm^{-1} and 1343 cm^{-1} for Titanium White and Ultramarine Blue, 1359 cm^{-1} and 1342 cm^{-1} for Quinacridone Crimson; 1362 cm^{-1} and 1339 cm^{-1} for Phthalocyanine Green)
- the sharp peak around 1110 cm^{-1} related to the ν_{as} C-O-C (1106 cm^{-1} for Titanium White, Ultramarine Blue and Phthalocyanine Green; 1103 cm^{-1} for Quinacridone Crimson)

In table 3.1-5 other absorptions, falling in the C-H stretching region (3200÷2800 cm^{-1}) and the finger print region (1500÷500 cm^{-1}), are listed. These absorptions, even if less diagnostic, can be assigned to vibrations of the APE surfactant molecule.

Other bands are those at about: 1725 cm^{-1} (1715 cm^{-1} for Titanium White, 1725 cm^{-1} for Ultramarine Blue and Phthalocyanine Green); 1640 cm^{-1} (1636 cm^{-1} for Titanium White, 1646 cm^{-1} for Ultramarine Blue, 1632 cm^{-1} for Quinacridone Crimson and 1639 cm^{-1} for Phthalocyanine Green); 1560 cm^{-1} (1559 cm^{-1} for Titanium White and Phthalocyanine Green, 1552 cm^{-1} for Ultramarine Blue, 1566 cm^{-1} for Quinacridone Crimson); 1400 cm^{-1} (1402 cm^{-1} for Titanium White and Ultramarine Blue, 1399 cm^{-1} for Phthalocyanine Green).

With the exception of the absorptions around 1640 cm^{-1}, which may arise from residual water (as suggested even by absorptions centered at 3400 cm^{-1}), the other are possibly related to other paint additives such as a polyacid pigment dispersant (like Tamol^{TM}).

In spite of being characterized by the same diagnostic bands described above (with absorptions related to the APE surfactant: 2887cm^{-1}, 2741cm^{-1}, 2694cm^{-1}, 1362cm^{-1}, 1342cm^{-1} and 1106cm^{-1}), the spectrum collected for the Transparent Raw Sienna paint is

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[14] As after all pointed out in: Ormsby *et al.* 2009 (where the APE surfactant was tentatively identified with Triton-X405); Silva's PhD thesis 2011; Pintus, Wei and Schreiner, 2012.

dominated by two strong absorptions at 1556 cm^{-1} and 1402 cm^{-1}. These absorptions are supposed to arise from a Sodium polyacrylate dispersant. Even the

HEAVY BODY PAINTS (Liquitex®)					
Titanium White	Ultramarine Blue- Green Shade	Transparent Raw Sienna	Quinacridone Crimson	Phthalocyanine Green	Tentative Band Assignments
3360	3340	3240	-	3300	Water
2950	2947	-	2950	-	APE surf
	-	2927	-	-	APE surf
2881	**2881**	**2887**	**2881**	**2881**	**APE surf**
2861	2864	2861	2864	2864	APE surf
2741	**2741**	**2741**	**2741**	**2741**	**APE surf**
2694	**2691**	**2694**	**2694**	**2694**	**APE surf**
1715	1725	1728	-	1725	Org. Add.
1636	1646	1655sh	-	1639	Water
1559	1552	-	1566	1559	Org. Add.
-	-	1556	-	-	Pol.Disp
1512	**1516**	-	**1512**	**1516**	**APE surf**
1469	1466	1466	1466	1469	APE surf
1456	1452	1455	1456	1452	APE surf
-	-	1402	-	-	Pol.Disp
1402	1402	-	-	1399	Org. Add.
1362	**1362**	**1362**	**1359**	**1362**	**APE surf**
1343	**1343**	**1342**	**1342**	**1339**	**APE surf**
1279	1279	1279	1279	1279	APE surf
1243	1243	1243	1239	1243	APE surf
1186	1183		1189	1183	APE surf
1146	1143	1142	1146	1146	APE surf
1106	**1106**	**1106**	**1103**	**1106**	**APE surf**
1059	1059	1059	1059	1059	APE surf
-	-	-	1009	-	PV19
963	962	963	959	966	APE surf
-	-	892	-	-	PY42
842	843	842	842	843	APE surf

Table 3.1-5: FTIR absorption features (cm^{-1}) of the Heavy Body-Liquitex® paints’ water extracts, with tentative band assignment. In bold letters, the most diagnostic absorptions for the alkylphenol ethoxylate surfactant (APE surf.). The absorption bands that cannot be univocally referred to a compound, are generally assigned to Organic Additives (Org. Add). Pol. Disp=polyacrylate dispersant. sh= shoulder

THERMOGRAVIMETRIC ANALYSIS

In figure 3.1-14, the curves resulting from the themogravimetric analysis of the five Heavy Body-Liquitex® paints are shown.

As reported in literature, the thermal degradation process of waterborne acrylic paints containing different amounts of a *p*(MMA-BA) binder, was detected to occur in the 255÷410°C range (working in N_2 atmosphere). Higher temperatures were detected when considering the pure binder (264÷600°C).[15] The onset of p(MMA-EA) and p(MMA-BA) degradation in inert atmosphere, has been also reported to occur around 350-360°C.[16]

All curves display a main mass loss around 370 °C, related to the thermal degradation of the polymeric binder. Sometimes this degradation process continues to higher temperatures, where a slight weight loss is observed around 470°C (it is the case of Titanium White, Ultramarine Blue and one of the Raw Sienna samples).

Some samples (Titanium White and Ultramarine Blue) show an additional mass loss around 250°C, possibly related to the first degradation steps of vaious organic components.

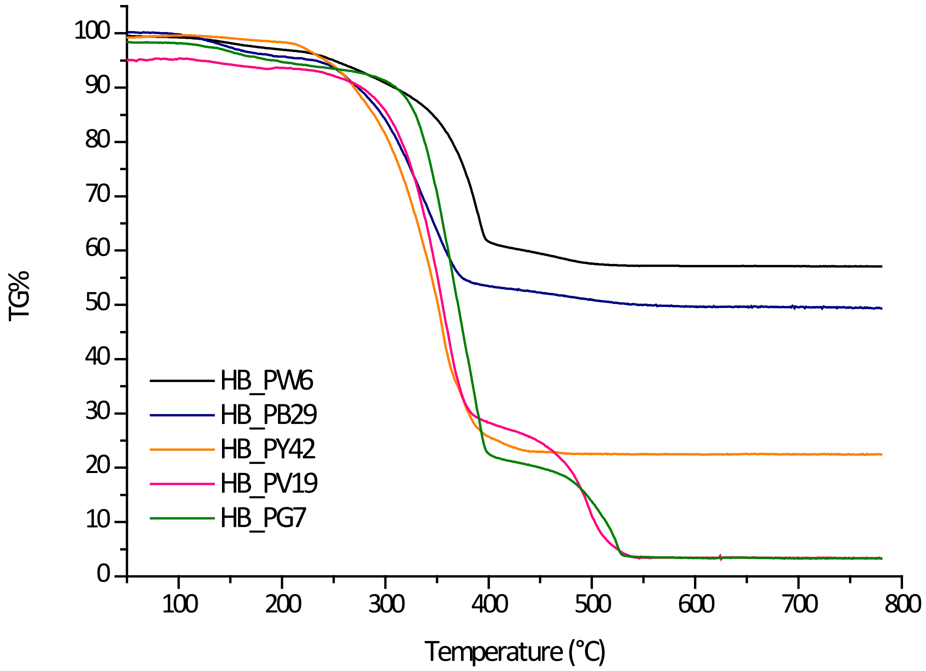

Fig. 3.1-14: TG curves of Heavy Body (HB) reference paints (Liquitex®).

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[15] Topçuoğlu, Altikaya and Balk Öse, 2006

[16] Argawal and Farris, 1999.

Sample	Low Temp. Weight Loss (%)	First step Weight Loss (%)	Second step Weight Loss (%)	Residual Weight %	Residues Identification
Titanium White(PW6)	6.89 (200÷300°C)	29.81 (300÷420°C)	3.32 (420÷520°C)	55.71	PW6
	6.15 (200÷300)	30.31 (300÷420)	3.21 (420÷520)	57.05	
Ultramarine Blue-Green Shade (PB29)	4.48 (210÷270°C)	36.88 (270÷420°C)	(1.47) (420÷520°C)	51.35	PB29-(SiO$_2$?)
	4.88 (210÷270°C)	37.65 (270÷420°C)	2.53 (420÷520°C)	49.32	
Transparent Raw Sienna (PY42)	8.80* (200÷290°C)	56.08 (290÷435°C)	9.82 (435÷520°C)	17.66	Fe$_2$O$_3$
	12.24* (200÷285°C)	63.16 (285÷450°C)	-	22.43	
Quinacridone Crimson (PV19)	-	64.71 (270÷450°C)	23.93* (450÷580°C)	3.26	SiO$_2$
	-	64.50 (260÷420°C)	23.62* (420÷550°C)	3.30	
Phthalocyanine Green (PG7)	-	72.84 (270÷450°C)	16.35* (450÷580°C)	2.83	SiO$_2$
	-	71.68 (270÷420°C)	17.71* (420÷550°C)	3.25	

Tab. 3.1-6: Together with the residual weights (%), the weight losses (%) ascribable to the thermal degradation of paints' main components are shown. Three degradation steps are considered: that occurring below 300°C (not always detected); the step related to binder degradation; a third step related to further binder degradation and/or degradation of some organic pigments. Together with the weight losses, the on*set* and end*set* temperatures of the degradation processes are shown. Residual thermally stable chars were analyzed through FTIR spectroscopy. * indicates values influenced by pigment thermal degradation processes.

For Titanium White and Ultramarine Blue paints, it is possible to evaluate the organic/inorganic components weight ratio. If considering all the weight losses occurring below 520°C, Titanium White paint turns out to contain a 40% by weight of organic materials, while Ultramarine Blue a 44%. If excluding the degradation steps occurring ant lower temperatures, White paint loses the 36% of its weight, while Ultramarine Blue the 39%.

As already seen for Flashe® paints, when interpreting the curves of Transparent Raw Sienna, Quinacridon Crimson and Phthalocyanine Green paints, the contribution due to pigments' degradation process has to be considered. Anyway, it could be noticed that the weight loss occurring in the 250-450°C range (mainly ascribable to binder decomposition) is significantly higher for Transparent Raw Sienna, Quinacridone Crimson and Phthalocyanine Green paints. This suggests a lower pigment volume concentration.

BRERA (Maimeri®)

FTIR SPECTROSCOPY: CHARACTERIZATION of PAINT FILMS

The infrared spectra collected for each Brera-Maimeri® paint layer are shown, together with a table presenting the main absorption features and tentative assignments (Tab. 3.1-7).

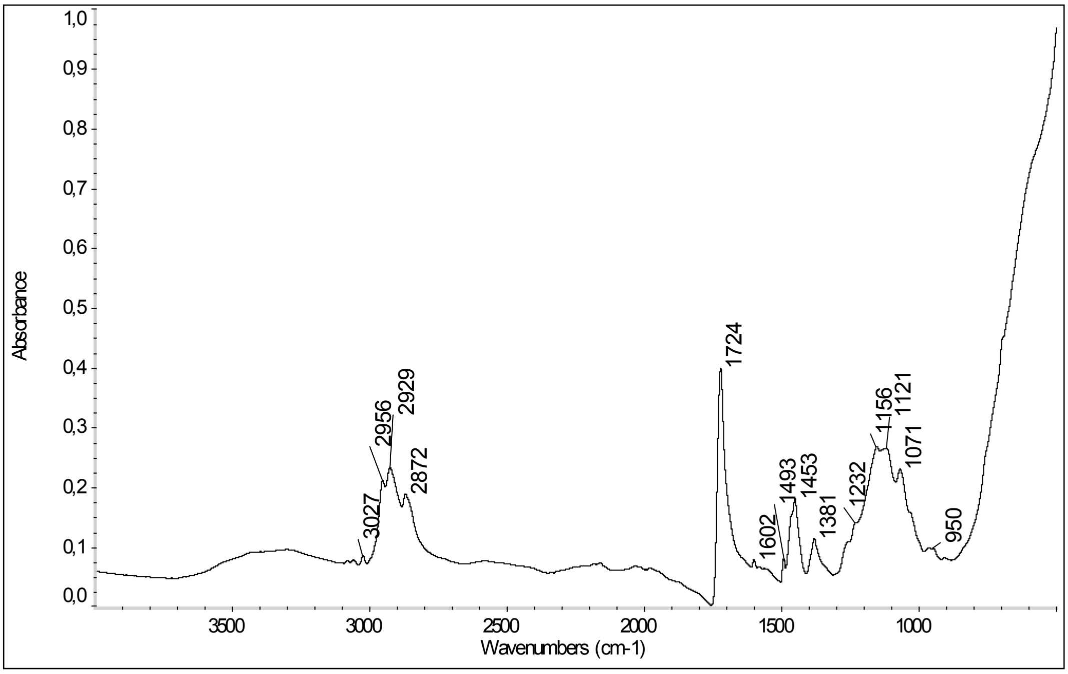

Fig. 3.1-15: FTIR-ATR spectrum from the Titanium White paint layer, Brera (Maimeri®)

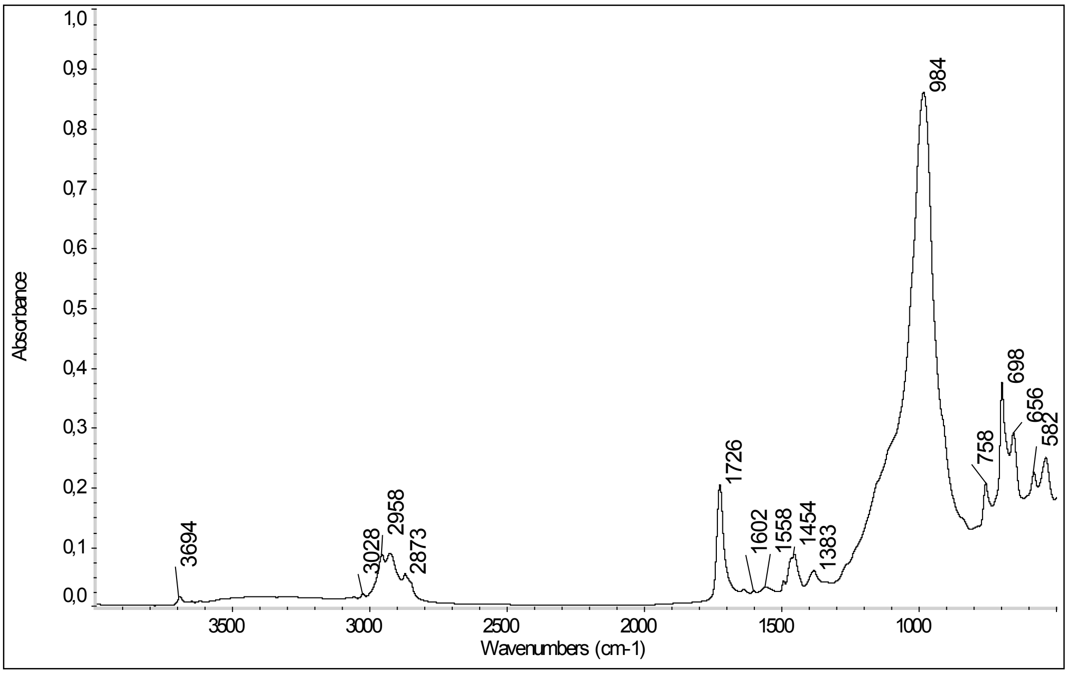

Fig. 3.1-16: FTIR-ATR spectrum from the Ultramarine paint layer, Brera (Maimeri®)

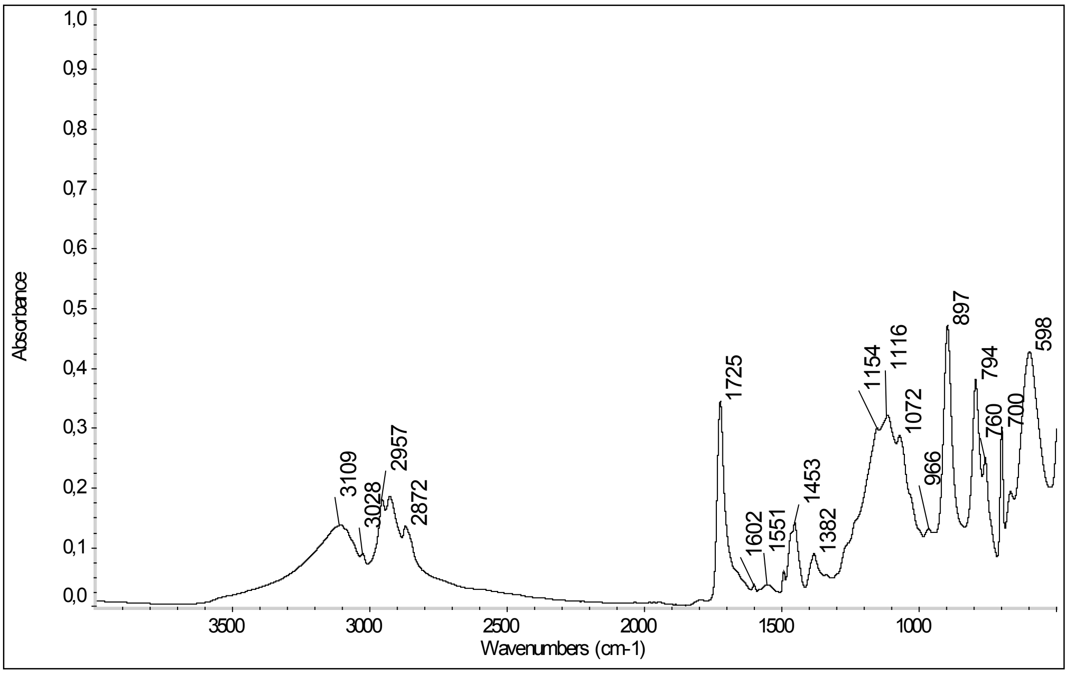

Fig. 3.1-17: FTIR-ATR spectrum from the Yellow Ochre paint layer, Brera (Maimeri®)

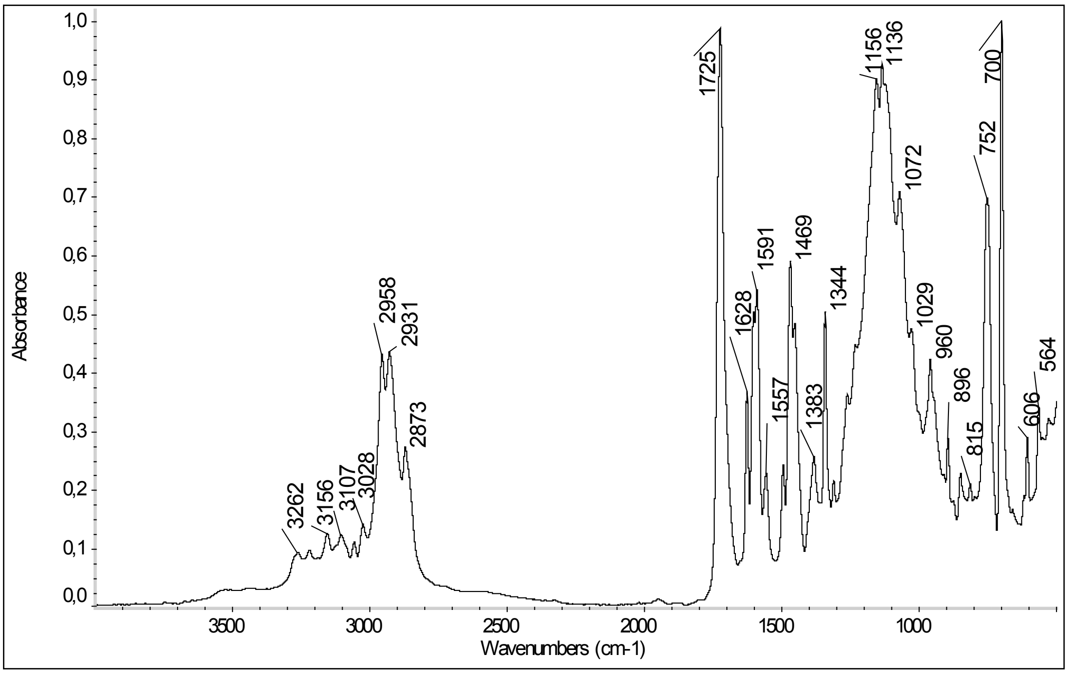

Fig. 3.1-18: FTIR-ATR spectrum from the Primary Red Magenta paint layer, Brera (Maimeri®)

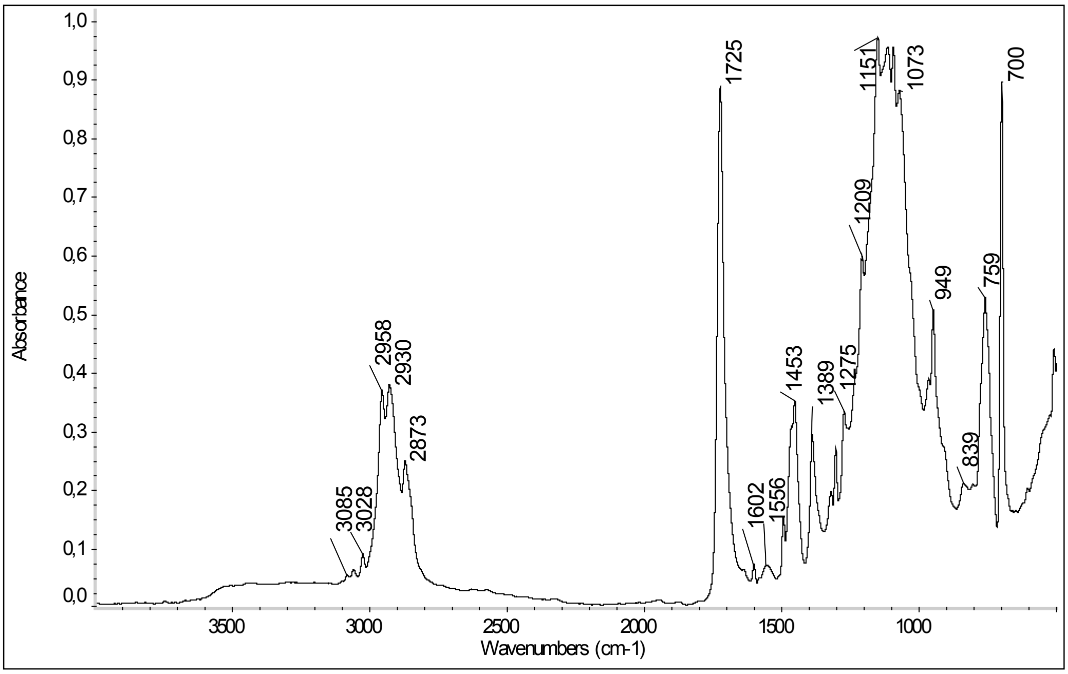

Fig. 3.1-19: FTIR-ATR spectrum from the Phthalo Green paint layer, Brera (Maimeri®)

As deducible from FTIR spectra, Brera paints consist of a styrene-acrylic binder. Even though the nature of the acrylic moiety cannot be precisely defined on the exclusive base of FTIR spectroscopy analysis, specialized literature suggests that the binder of Brera paints consists of a p(*n*BMA-2EHA-styrene) terpolymer.[17]

The main absorptions that can be related to the styrene-acrylic binder are:

- C-H aromatic stretching absorptions between 3100 and 3000 cm^{-1}, showing usually three peaks around: 3084 cm^{-1}, 3063 cm^{-1} and 3030 cm^{-1}
- C-H aliphatic stretching absorptions around: 2962 cm^{-1} (ν_{as} CH$_3$); 2926 cm^{-1}(ν_{as} CH$_2$); 2872 cm^{-1} (ν_{s} CH$_3$)
- C=O stretching band around 1725 cm^{-1}
- skeletal C-C aromatic stretching vibrations ("ring breathing"), displaying three sharps absorptions bands (around 1456 cm^{-1}, 1495 cm^{-1} and 1605 cm^{-1}) and a shoulder around 1580 cm^{-1}
- C-H bending absorptions of the acrylic moiety, around: 1452 cm^{-1} (CH$_3$ asym. bending/ CH$_2$ scissoring; partially overlaying with one of the "ring breathing" absorptions), 1387 cm^{-1} (CH$_3$ sym. bending)
- C-O stretching and C-C stretching absorptions of the acrylic moiety, around: 1160 cm^{1}, 1120cm^{-1}, 1070 cm^{-1}, 1030 cm^{-1}, 970 cm^{-1}, 950 cm^{-1}
- aromatic C-H out-of-plane bending around: 760 cm^{-1} and 700 cm^{-1} (indicative of a mono-substituted benzene ring).

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[17] Learner 2004: 85.

Even in this case, the features related to pigments' absorptions mainly coincide with those discussed for Flashe® paints.

BRERA PAINTS (Maimeri®)					
Titanium White	Ultramarine	Yellow Ochre	Primary Red Magenta	Phthalo Green	Tentative Band Assignments
-	3694	-	-	-	PB29
-	-	-	3262	-	PV19
-	-	-	3221	-	PV19
-	-	-	3156	-	PV19
-	-	3109	-	-	PY42
-	-	-	3107	-	PV19
3084	-	-	-	3085	Acr-styr. binder
3062	3061	-	3060	3062	Acr-styr. binder
3027	3028	3028	3028	3028	Acr-styr. binder
2956	2958	2957	2959	2958	Acr-styr. binder
2929	2930	2930	2931	2930	Acr-styr. binder
2872	2873	2872	2873	2873	Acr-styr. binder
1724	1726	1725	1725	1725	Acr-styr. binder
-	1638	-	-	-	PB29
-	-	-	1628	-	PV19
1602	1602	1602	1603	1602	Acr-styr. binder
-	-	-	1591	-	PV19
			1557	-	PV19
-	1558	1551	-	1556	Acr-styr. Binder/Add.
-	-	-	1496	-	Acr-styr. binder /PV19
1493	1493	1493	-	1494	Acr-styr. binder
-	-	-	1469	-	PV19
1453	1454	1453	1453	1453	Acr-styr. binder
1381	1383	1382	1383	1389	Acr-styr. binder
-	-	-	1344	-	PV19
-	-	-	-	1323	PG7
-	-	-	1313	-	PV19
-	-	-	-	1305	PG7
-	-	-	-	1275	PG7
-	-	-	1263	-	Acr-styr. Binder/PV19
1232	-	-	1234	-	Acr-styr. binder
-	-	-	-	1209	PG7
1156	-	1154	1156	-	Acr-styr. binder
-	-	-	-	1151	Acr-styr binder/PG7
-	-	-	1136	-	Acr-styr binder/PV19
1121	-	1116	1124	1116	Acr-styr. binder
-	-	-	-	1094	PG7
1071	-	1072	1072	1073	Acr-styr. binder
1034	-	-	1029	-	Acr-styr. binder

Table 3.1-7: FTIR-ATR absorption features (cm^{-1}) of Brera (Maimeri®) paint layers with tentative band assignments (table continuing in the following page).

BRERA PAINTS (Maimeri®)					
Titanium White	Ultramarine	Yellow Ochre	Primary Red Magenta	Phthalo Green	Tentative Band Assignments
-	984	-	-	-	PB29
966	-	966	-	966	Acr-styr. binder
-	-	-	960	-	Acr-styr. Binder/PV19
950	-	-	-	-	Acr-styr. binder
-	-	-	960	-	Acr-styr. binder/PV19
-	-	897	-	-	PY42
-	-	-	896	-	Acr-styr. binder
-	-	-	850	-	Acr-styr. binder
-	-	-	815	-	PV19
-	-	794	-	-	PY42
-	758	760	752	-	Acr-styr. binder
-	-	-	-	759	Acr-styr. binder/PG7
-	-	700	700	700	Acr-styr. binder
-	698	-	-	-	PB29
-	656	-	-	-	PB29
-	-	-	606	-	PV19
600	-	-	-	-	PW6
-	-	598	-	-	PY42
-	582	-	-	-	PB29
-	-	-	564	-	PV19
-	538	-	-	-	PB29

Table 3.1-7: FTIR-ATR absorption features (cm^{-1}) of Brera (Maimeri®) paint layers with tentative band assignement. Acr-styr. binder= p(*n*BMA-2EHA-styr); Add= additive; PW6= Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Red; PG7= Phathalocyanine Green

FTIR SPECTROSCOPY: CHARACTERIZATION of PAINTS' WATER EXTRACTS

The water soluble components of Brera- Maimeri® paints were investigated using the same analytical procedure described for Flashe® paints. The spectra of the paints' water extracts are presented in figure 3.1-20. The main absorption features with their tentative assignments are shown in table 3.1-8 .

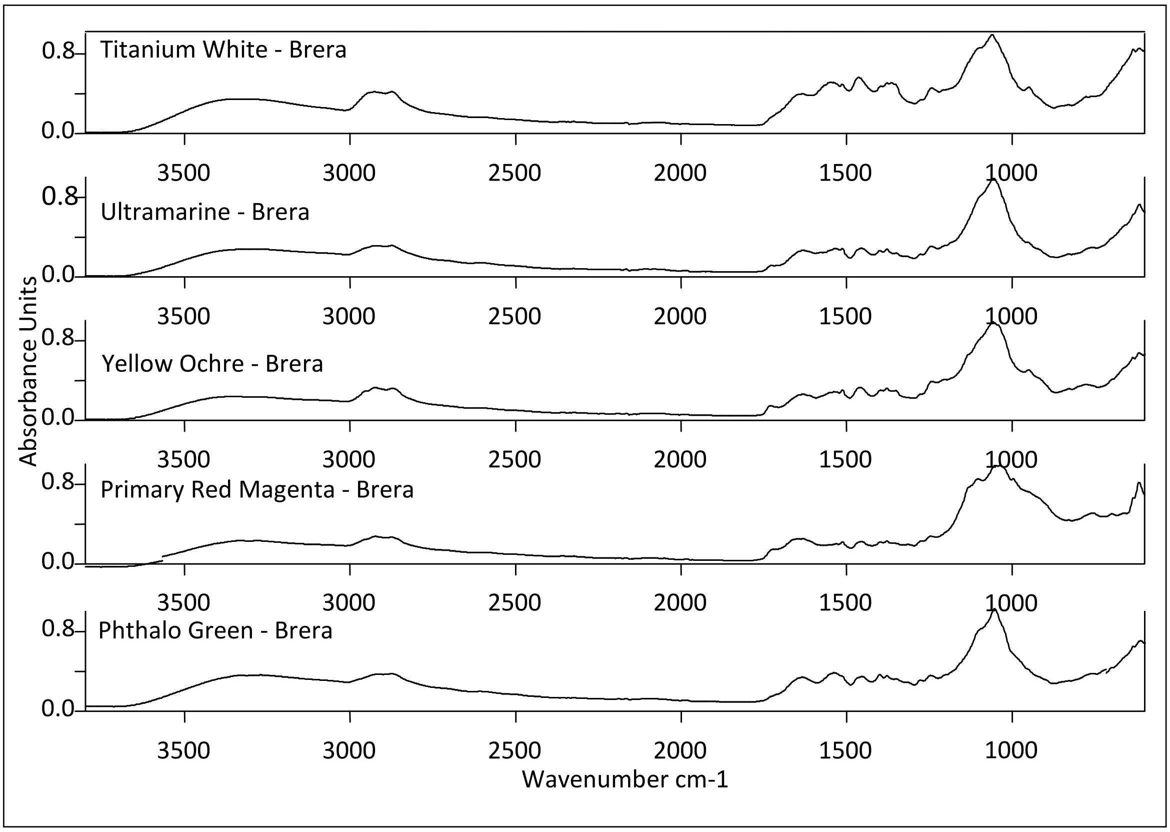

Fig. 3.1-20: FTIR spectra from Brera-Maimeri® paints' water extracts.

All the spectra collected for the water extracts of Brera- Maimeri® paints show a similar profile, with slight differences only in the intensity of the absorption bands.

Since, in this case, the quality of the spectra is worse than that of the spectra collected from the extracts of the other paints, the interpretation cannot be totally unambiguous. The absorption bands can be actually referred to a variety of water soluble additives which characterize the emulsion paint formulations (considering both, C-H stretching region and fingerprint region). Even if the diagnostic features of APE surfactant were not detected here, other features could be related to a other polyethoxylate-type surfactants.

A good match is gathered when comparing the collected spectra with reference spectra of ether-cellulose products (such as Hydroxy Propyl Cellulose, HPC). These products are often used in paint formulations as thickeners, and their spectra are characterized by a strong absorption around 1100 cm^{-1} (mainly ascribable to stretching vibrations of the C-O-C bonds).

BRERA PAINTS (Maimeri®)					
Titanium White	Ultramarine	Yellow Ochre	Primary Red Magenta	Phthalo Green	Tentative Band Assignments
3330	3268	3340	3320	3270	vOH- EC/water
-	2955	2951	2951	-	Org. Add.
2929	2926	2926	2929	2926	Org. Add.
2877	2874	2874	2874	2873	Org. Add.
-	1732	1732	1719	-	Org. Add.
1631	1632	1632	1641	1632	water
1548	1535	1538	1531	1541	Org. Add.
1515	1515	1512	1515	1515sh	Org. Add.
1463	1457	1457	1454	1454	Org. Add.
1396	1402	1399	1402	1402	EC
1379	1379	1379	1379	1379	EC
1363	-	-	-	-	Org. Add.
1352	1354	1354	1352(sh)	1350	EC
1276	1279	-	1273	1279	Org. Add.
1244	1244	1240	1247	1247	Org. Add.
-	-	1205	-	1205	Org. Add.
1101	1096sh	-	1104	1098sh	Org. Add.
1062	1059	1059	1053	1053	EC
-	-	-	1036	-	Org. Add.
-	-	-	998	-	Org. Add.
949	(956sh)	949	-	-	Org. Add.
826	829	829	829	832 (sh)	Org. Add.
774	-	781	-	-	Org. Add.
-	762	-	755	761	Org. Add.

Table 3.1-8: FTIR absorption features (cm^{-1}) of Brera-Maimeri® paints' water extracts, with tentative band assignment. Absorption bands that cannot be univocally referred to a compound, are generally assigned to Organic Additives (Org. Add.). vOH= hydroxyl group stretching. EC = Ether-Cellulose.
sh= shoulder

THERMOGRAVIMETRIC ANALYSIS

In figure 3.1-21, the curves resulting from the themogravimetric analysis of the five Brera-Maimeri® paints are shown.

The thermal degradation process of a styrene-methyl methacrylate copolymer, in inert atmosphere, has been reported to occur in the 360÷480°C range.[18] The oxidative thermal degradation of another styrene-acrylic copolymer (*p*(styrene-butylacrylate-acrylic acid) was observed around 403°C.[19]

All curves display a principle mass loss around 365°C, which could be due to the degradation process of the polymer binder, that sometimes finishes with a further degradation step occurring at higher temperatures (it is the case of Titanium White, Ultramarine and Yellow Ochre samples).
Titanium White paint show an additional mass loss around 280°C, possibly related to the first degradation steps of various organic materials.

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[18] Matusinović, Rogošić and Šipušić, 2009.

[19] Zhu *et.al.* 2008

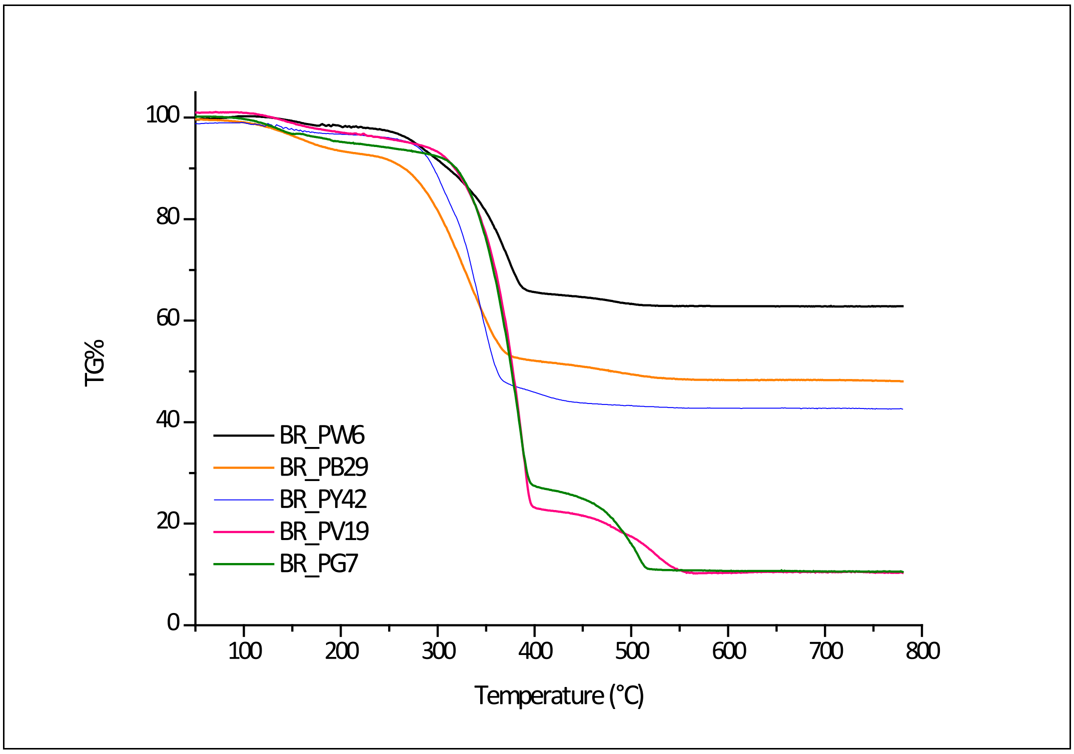


Fig. 3.1-21: TG curves of Brera (BR) reference paints (Maimeri®).

Sample	Low Temp. Weight Loss (%)	First step Weight Loss (%)	Second step Weight Loss (%)	Residual Weight %	Residues Identification
Titanium White(PW6)	9.29 (225÷300°C)	23.48 (300÷410°C)	2.62 (410÷550°C)	61.20	PW6 –SiO_2
	6.03 (240÷300)	26.34 (300÷410)	2.47 (410÷550)	62.80	
Ultramarine (PB29)	40.86 (225÷410°C)		3.39 (410÷550°C)	47.95	PB29-(SiO_2?)
	40.70 (225÷410°C)		3.18 (410÷550°C)	50.30	
Yellow Ochre (PY42)	11.45* (250÷320°C)	38.21* (320÷370°C)	3.69 (370÷500°C)	38.53	Fe_2O_3-SiO_2
	13.87* (250÷315°C)	35.09* (315÷380°C)	3.76 (380÷500°C)	42.58	
Primary Red Magenta (PV19)	-	68.75 (300÷410°C)	12.51* (420÷580°C)	6.02	SiO_2
	-	73.51 (270÷410°C)	12.20* (420÷580°C)	10.28	
Phthalo Green (PG7)	-	63.29 (300÷410°C)	15.46* (450÷550°C)	9.06	SiO_2
	-	65.42 (300÷410°C)	15.58* (420÷525°C)	10.48	

Tab. 3.1-9: Together with the residual weights (%), the weight losses (%) ascribable to the thermal degradation of paints' main components are shown. Three degradation steps are considered: that occurring below 300°C (not always detected); the step related to binder degradation; a third step related to further binder degradation and/or degradation of some organic pigments. Together with the weight losses, the on*set* and end*set* temperatures of the degradation processes are shown. Residual thermally stable chars were analyzed through FTIR spectroscopy. * indicates values influenced by pigment thermal degradation processes.

Even in this case, studying Titanium White and Ultramarine paints' thermograms, it is possible to evaluate the organic/inorganic components weight ratio. If considering all the weight losses occurring below 550°C, the Titanium White paint turns out to contain a 35% by weight of organic materials, while the Ultramarine a 44%.

Interpreting the curves of the Yellow Ochre, Primary Red Magenta and Phthalo Green paints instead, the contribution due to pigments' degradation process has to be considered. Anyway, it could be noticed that the weight loss occurring in the 300-410°C range (mainly ascribable to binder decomposition) is significantly higher for Primary Red Magenta and Phthalo Green paints, suggesting a lower pigment volume concentration.

3.1.1.2 Morphological and color characterization

In this section, the results gathered from the study of the paint layers' morphology are presented.

The morphology of a paint layer is supposed to play an important role for the conservation of a work of art, influencing its response to both ageing processes and conservation treatments.
The aim of this characterization was to point out if different commercial products lead to different paint layer morphologies.
Since the paint layer morphology is support dependant, the study was carried out on the samples cast on the mortar supports.

The surface of the samples was examined using Light Microscopy and Scanning Electron Microscopy, working at growing magnifications.
Moreover, a precise definition of the color of the surface in term of both, spectral distribution of the reflected light and colorimetric values in the CIEL*a*b* space, was assessed through measurements taken using a spectrophotometer.

The results gathered for the 5 vinyl paints (Flashe®-L&B), the 5 acrylic paints (Heavy Body-Liquitex®) and the 5 styrene-acrylic paints (Brera- Maimeri®) are dealt with separately.

FLASHE® PAINTS (Lefranc&Bourgeois)

LIGHT MICROSCOPY EXAMINATIONS [20]

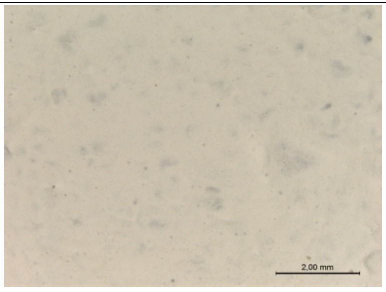
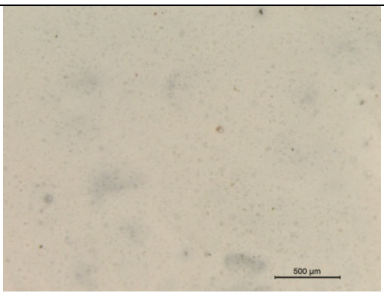
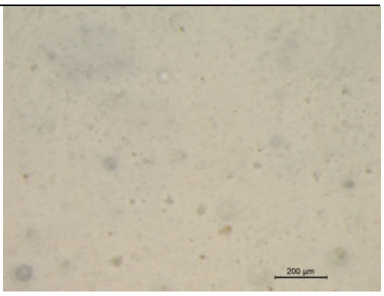
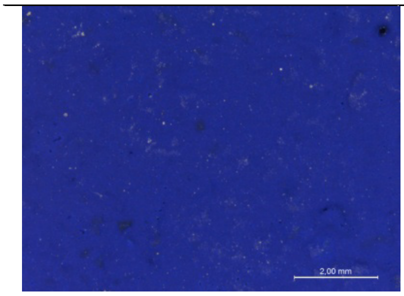
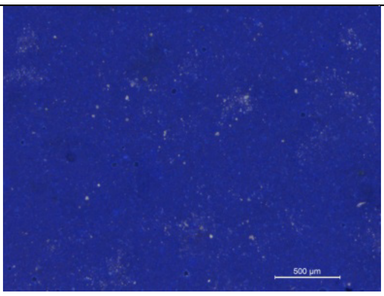
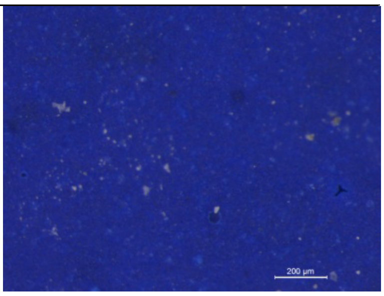
Table 3.1-10 shows the Light Microscopy pictures of Flashe® samples, taken at different magnifications (8X, 25X and 50X).

The paint layers look homogeneous and flat, and are characterized by an even distribution of a white extender (translucent areas in the White sample, lighter areas in the Ultramarine Blue, Ruby Red and Armor Green samples).

The Yellow Ochre and Ruby Red samples show small cracks.

All the paint layers are characterized by some pin-holes, especially in the case of Ruby Red and Armor Green samples. These defects do not present a perfectly rounded profile.

In most of the cases, the hiding properties of the paints are good. However, at high magnifications, some darker areas are sometimes detected (White, Ultramarine Blue and Ruby Red samples), usually in correspondence of areas where the paint layer is thinner, covering dark sand grains of relatively big size.

<table>
<tr><th colspan="3">FLASHE®- LeFranc&Bourgeois</th></tr>
<tr><td>WHITE (8X)</td><td>WHITE (25X)</td><td>WHITE (50X)</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
<tr><td>ULTRAMARINE BLUE (8X)</td><td>ULTRAMARINE BLUE (25X)</td><td>ULTRAMARINE BLUE (50X)</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
</table>

Tab.3.1-10: Light Microscopy examinations of the Flashe®-L&B samples. Pictures were taken at growing magnifications (8X,25X,50X). (the table continues in the following page).

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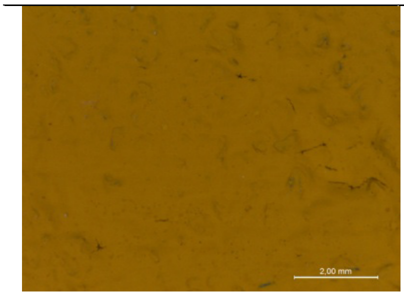
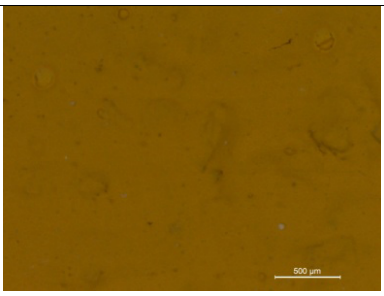
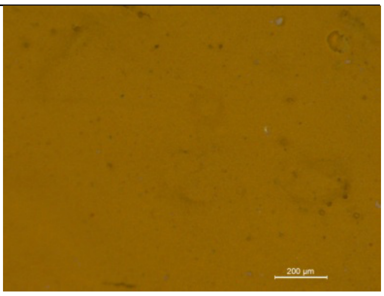
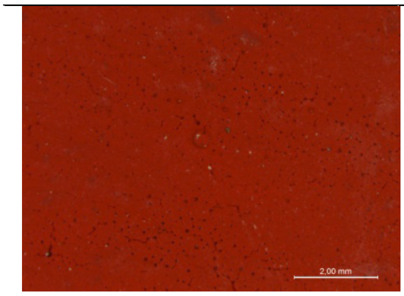
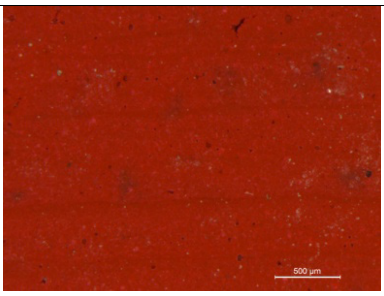
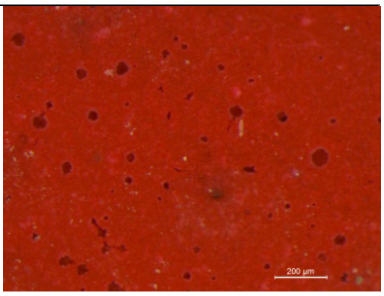
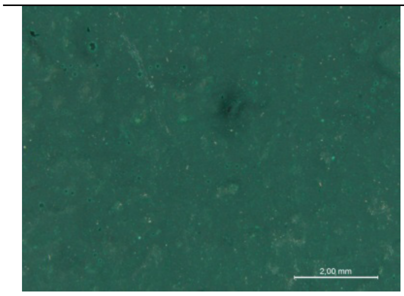
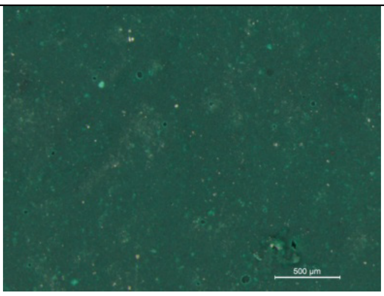
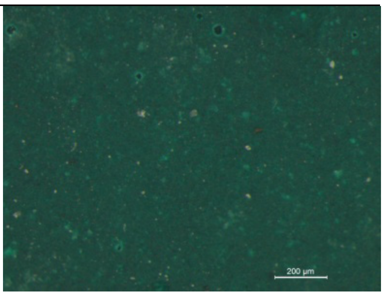
[20] The study of these samples, as well as of those presented as follows, was carried out using the Leica DMR microscope.

FLASHE®- LeFranc&Bourgeois		
YELLOW OCHRE (8X)	YELLOW OCHRE (25X)	YELLOW OCHRE (50X)
		
RUBY RED (8X)	RUBY RED (25X)	RUBY RED (50X)
		
ARMOR GREEN (8X)	ARMOR GREEN (25X)	ARMOR GREEN (50X)
		

Tab.3.1-10: Light Microscopy examinations of the Flashe®-L&B samples. Pictures were taken at growing magnifications (8X,25X,50X).

SCANNING ELECTRON MICROSCOPY EXAMINATIONS [21]

The following 5 tables (from 3.1-11 to 3.1-15) present the results of the Scanning Electron Microscopy examinations of the Flashe® samples.

Each table refers to one of the samples and includes pictures taken at different magnifications (100X, 500X, 1000X and 5000X), using Secondary Electrons (SE). The same pictures, taken using Back Scattered Electrons (BSE), are not shown here but they were considered when discussing results.

Even if the Energy Dispersive X-ray (EDX) analysis can be grouped with the analytical techniques which aid to the chemical characterization of the paints, the EDX spectra acquired working on areas at 500X, are displayed at the end of each table.

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[21] The study of this samples, as well as of those presented as follows, was carried out using the Jeol JSM 6300 Scanning Electron Microscope.

Being characterized by high amounts of inorganic components, the Flashe® paint layers look quite rough and discontinuous.

All the paint layers are characterized by pin-holes, which do not always have a perfectly rounded profile. Some samples show small cracks (White, Ultramarine Blue). Bigger cracks, detectable when studying the sample at low magnifications (100X) are due to the sampling.

With the exception of the Yellow Ochre sample which shows a peculiar acicular pigment morphology, the other inorganic components present homogeneous shape and dimensional distribution. Since this is true even for the paints consisting of organic pigments, all the paint layers are supposed to contain considerable amounts of an inorganic extender.

A better discrimination between the inorganic components was sometimes achieved working with BSE, thanks to the atomic number contrast (this was particularly true for the White sample).

Basing on BSE images, EDX spectra were collected considering both, areas and local points. By doing so, most of the inorganic components have been identified with a calcium carbonate extender, with variable particle size. It was confirmed that all the paints are characterized by this extender.

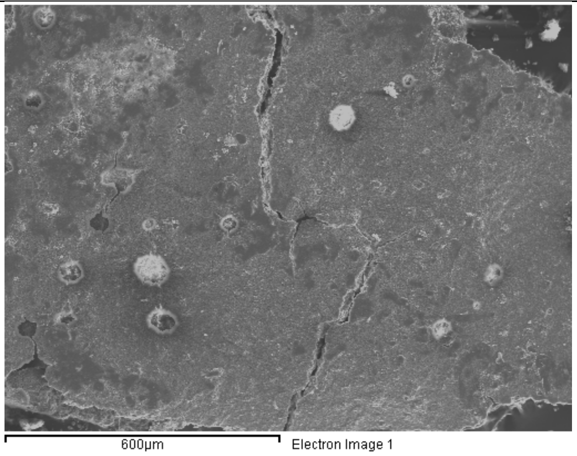
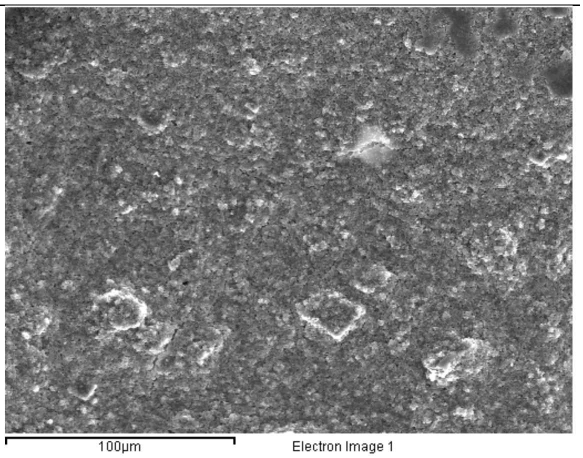
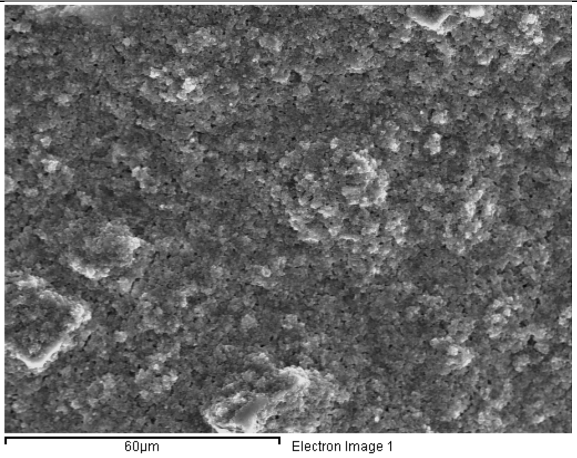
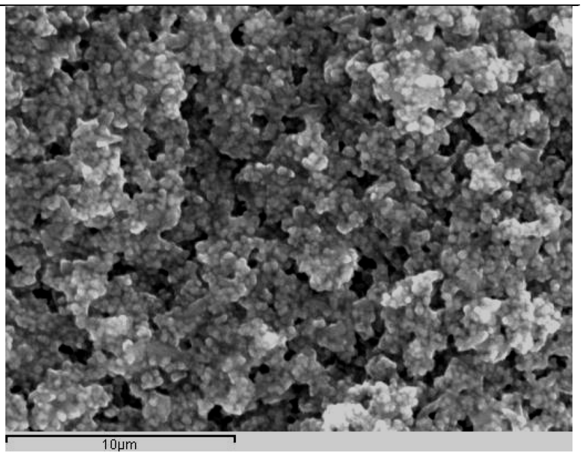
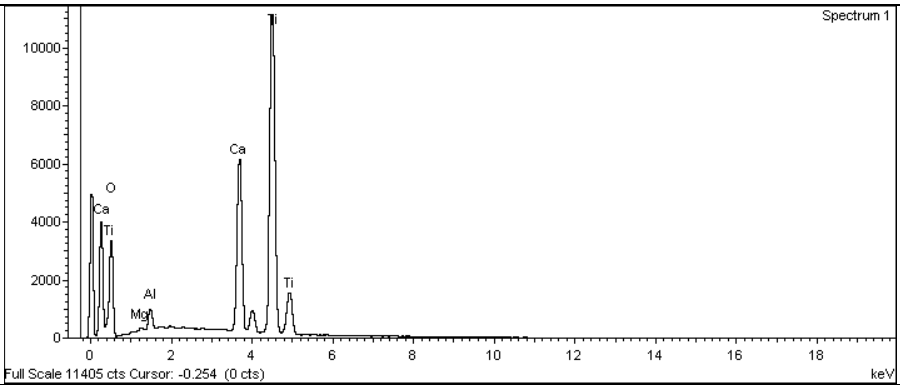
Moreover, EDX analysis confirmed that:

- the White paint consists of a Titanium based pigment. Even though the paint is supposed to contain both, PW6 (Titanium White) and PW5 (Lithopone) pigments, no elements ascribable to ZnS-$BaSO_4$ were detected.
- the Ultramarine Blue paint contains a pigment characterized by Sodium, Aluminuim, Silicon and Sulphur
- the Yellow Ochre paint contains an Iron based pigment
- the Armor Green paint contains a pigment characterized by Chlorine and Copper.

No element ascribable to an inorganic pigment were detected for the Ruby Red paint.

Element such as Aluminium, Magnesium, Silicon and Potassium were sometimes assigned to the presence of surface dust.

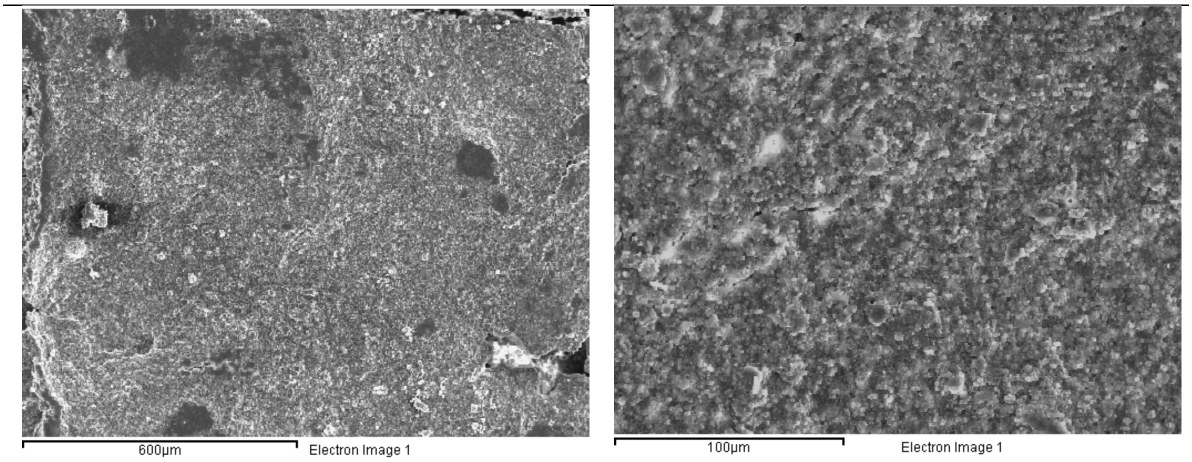
A more detailed interpretation of the EDX spectra is given in the captions of the tables.

FLASHE ® PAINTS (LeFranc and Bourgeois) - WHITE SAMPLE -	
Secondary Electrons Image (100X)	Secondary Electrons Image (500X)
	
Secondary Electrons Image (1000X)	Secondary Electrons Image (5000X)
	
EDX Spectrum -500X -area of about 200µm x 150µm-	
	

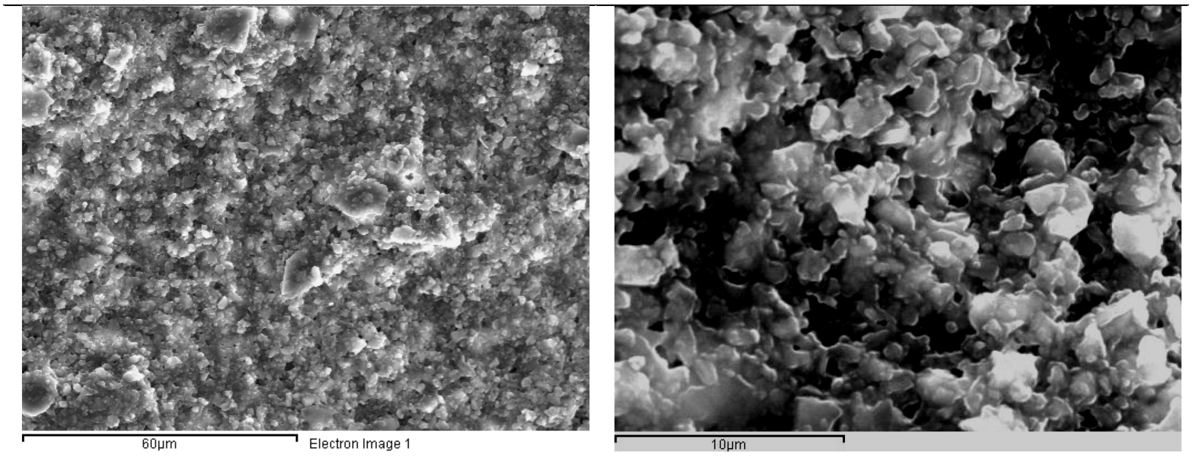
Tab. 3.1-11: The table shows the main results collected from the Flashe® White sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X), are presented together with an EDX spectrum collected for an area.

EDX analysis confirmed the presence of: Titanium (Ti), Calcium (Ca), Aluminium (Al) and Magnesium (Mg). While the latter two elements are supposed to derive from surface dust, Titanium and Calcium respectively suggest the presence of Titanium White pigment (TiO_2) and calcium carbonate extender ($CaCO_3$). Local spectra collected at 5000X, suggested that the Titanium pigment corresponds to the small bright rounded particle, while the extender corresponds to the bigger sized, grey particles.

FLASHE ® PAINTS (LeFranc and Bourgeois) – ULTRAMARINE BLUE SAMPLE -

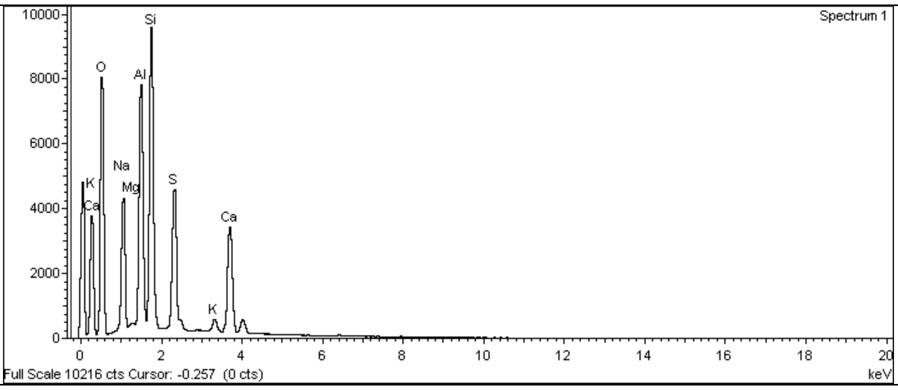


Secondary Electrons Image (100X) | Secondary Electrons Image (500X)



Secondary Electrons Image (1000X) | Secondary Electrons Image (5000X)

EDX Spectrum - 500X - area of about 200µm x 150µm-



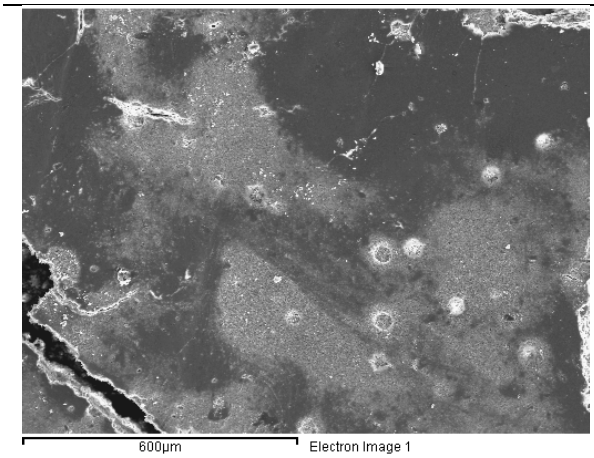
Tab. 3.1-12: The table shows the main results collected from the Flashe® Ultramarine Blue sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X), are presented together with an EDX spectrum collected for an area.

EDX analysis confirmed the presence of: Sodium (Na), Aluminium (Al), Silicon (Si), Sulphur (S), Calcium (Ca) and of negligible amounts of Magnesium (Mg) and Potassium (K).

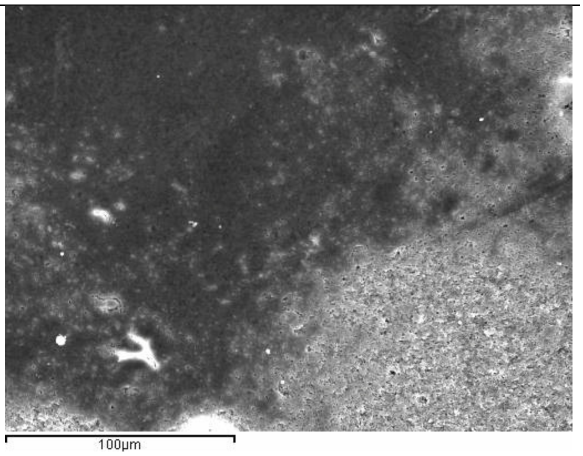
While Sodium, Aluminium, Silicon and Sulphur are mainly ascribible to the Ultramarine Blue pigment ($2Na_2Al_2Si_2O_6 \cdot NaS_2$), Calcium is related to the calcium carbonate extender ($CaCO_3$).

FLASHE ® PAINTS (LeFranc and Bourgeois) – YELLOW OCHRE SAMPLE -

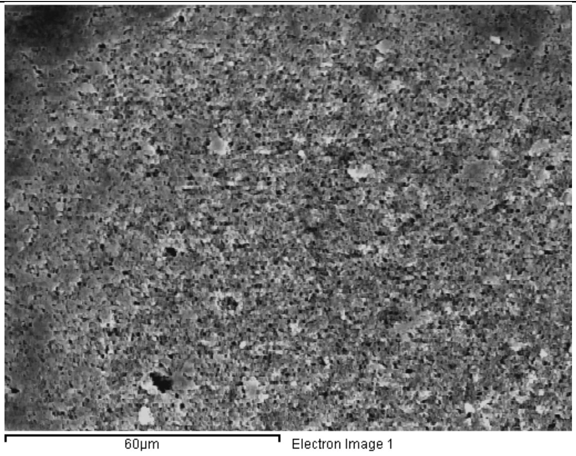
Secondary Electrons Image (100X)



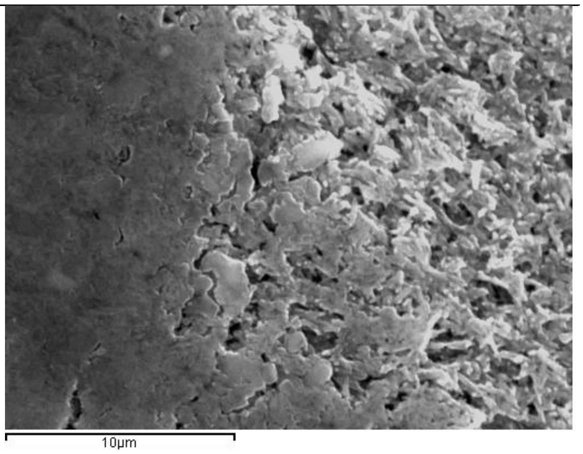
Secondary Electrons Image (500X)



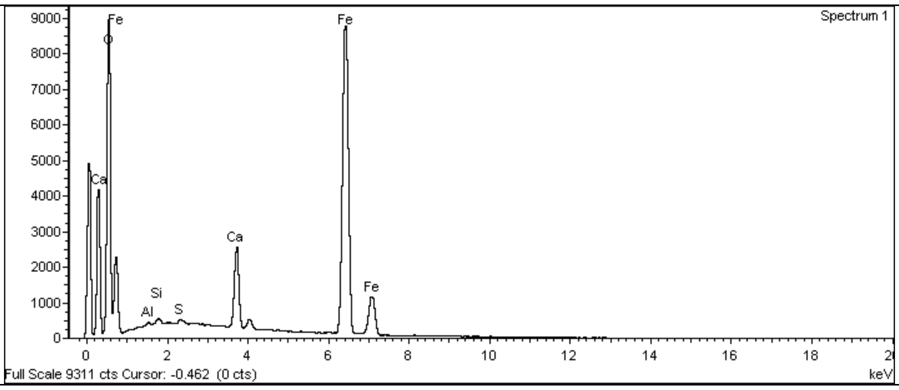
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



EDX Spectrum -500X -area of about 100µm x 70µm-

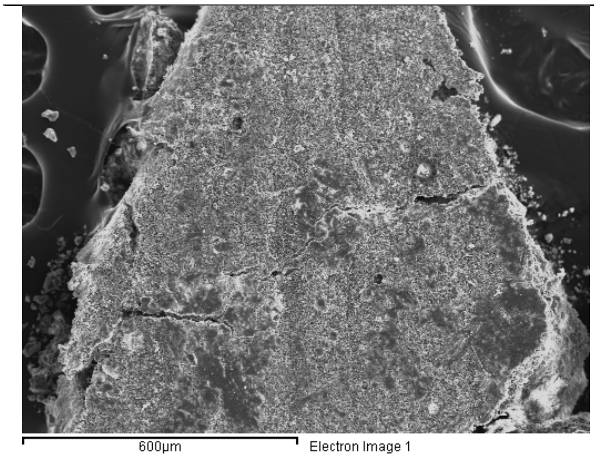
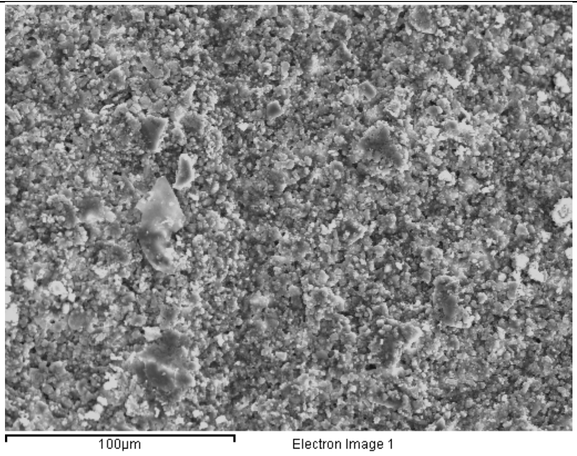
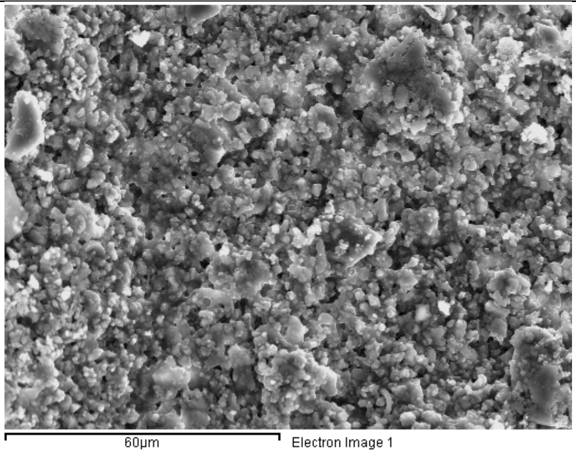
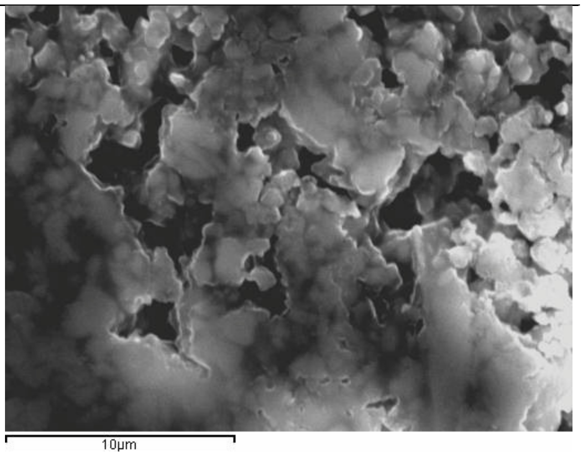


Tab. 3.1-13: The table shows the main results collected for the Flashe® Yellow Ochre sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X), are presented together with an EDX spectrum collected for one of the rough areas.

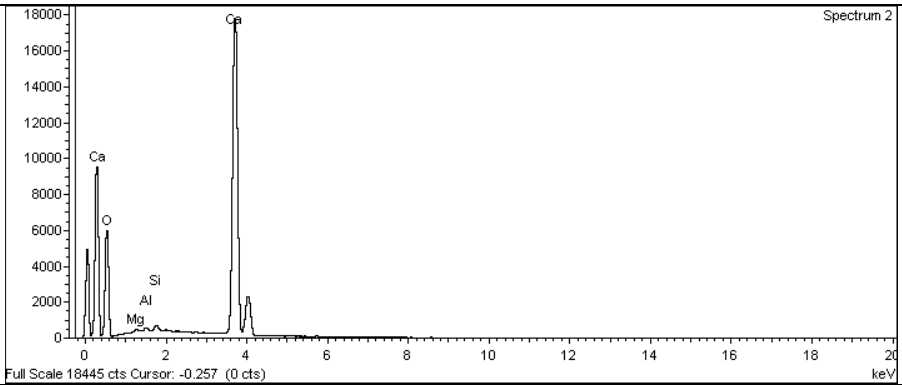
The images taken at 100X, 500X and 5000X evidenced both, darker smooth areas and brighter rough areas (at 1000X the picture was taken in one of the rough areas). As confirmed by the EDX analysis this difference is only due to a patchy distribution of the binder, that concentrates in the smooth areas.

EDX analys, collected in both areas, confirmed the presence of: slight amounts of Aluminium (Al), Silicon (Si) and Sulphur (S), higher amounts of Calcium (Ca) and Iron (Fe). Al, Si and S are supposed to derive from surface dust, Fe is ascribable to an Iron based yellow pigment (maybe $FeO(OH)\cdot H_2O$), while Ca is related to the calcium carbonate extender ($CaCO_3$).

FLASHE ® PAINTS (LeFranc and Bourgeois) - RUBY RED SAMPLE -

Secondary Electrons Image (100X)	Secondary Electrons Image (500X)
	
Secondary Electrons Image (1000X)	Secondary Electrons Image (5000X)
	

EDX Spectrum- 500X -area of about 100µm x 150µm-



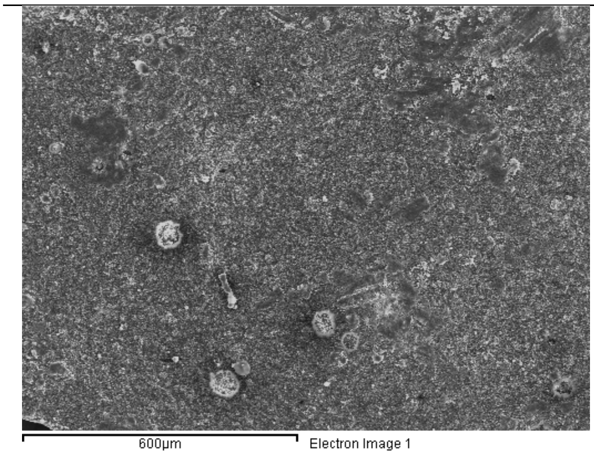
Tab. 3.1-14: The table shows the main results collected from the Flashe® Ruby Red sample Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X), are presented together with an EDX spectrum collected for an area.

Even though the paint is based on an organic pigment (PV19), the paint layers is characterized by the homogeneous distribution of an inorganic component.

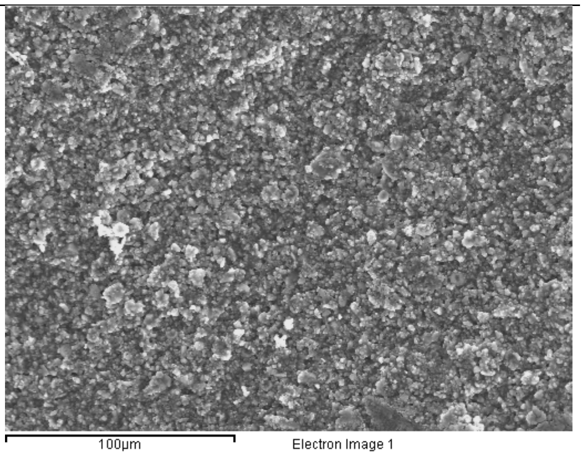
EDX analysis confirm the presence of: negligible amounts of Magnesium (Mg), Aluminium (Al) and Silicon (Si), high amounts of Calcium (Ca). This suggests the predominance of a calcium carbonate extender ($CaCO_3$).

FLASHE ® PAINTS (LeFranc and Bourgeois) – ARMOR GREEN SAMPLE -

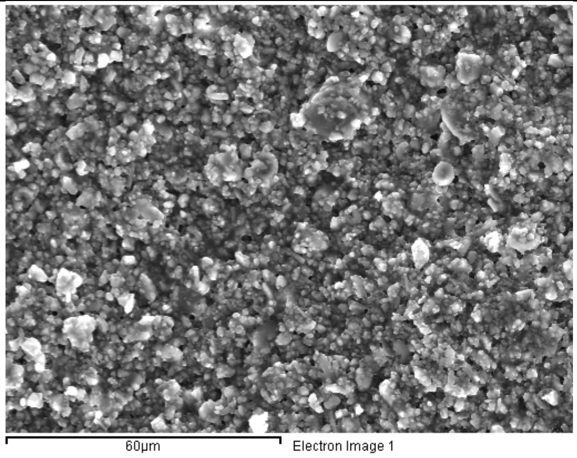
Secondary Electrons Image (100X)



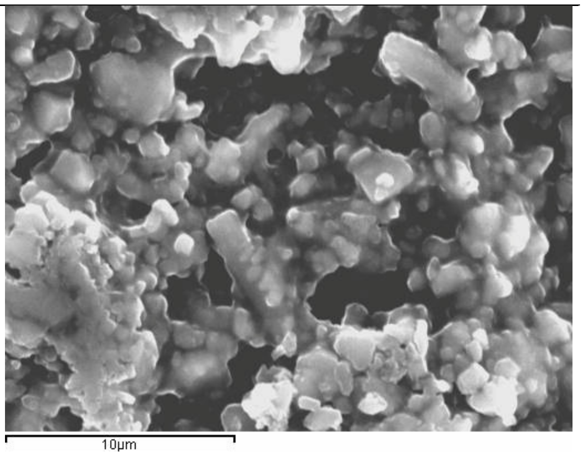
Secondary Electrons Image (500X)



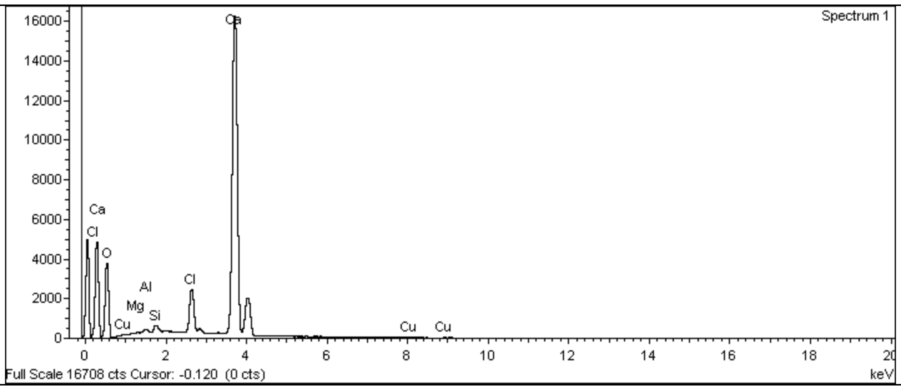
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



EDX Spectrum-500X -area of about 200µm x 150µm-



Tab. 3.1-15: The table shows the main results collected from the Flashe® Armor Green sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X), are presented together with an EDX spectrum collected for an area.

Even in this case, the paint is based on an organic pigment (PG7), but the paint layers is characterized by the homogeneous distribution of an inorganic component.

EDX analysis confirm the presence of: slight amounts of Magnesium (Mg), Aluminium (Al), Silicon (Si), and Copper (Cu); higher amount of Clorine (Cl) and a predominance of Calcium (Ca). Mg, Al and Si are supposed to derive from surface dust, Cu and Cl are ascribable to the Phthtalocyanine green pigment, while the high amount of Ca suggests the predominance of a calcium carbonate extender ($CaCO_3$).

COLORIMETRIC MEASUREMENTS

The colorimetric values in the CIEL*a*b*76 color space, reported in the Table 3.1-16, were evaluated from the reflectance spectra collected from the Flashe® samples.

The measurements were taken in 3 different areas of each sample. A set of 3 spectra was acquired for each point, with final colorimetric values coming from an average of 9 acquisitions (errors correspond to standard deviations).

In figure 3.1-22, the reflectance spectra are displayed. Considering the negligible variation between data acquired including or not the specular reflectance of light, only SCE spectra are shown. In SCE mode only the diffuse reflectance is measured, producing a color evaluation which correlates to the way the observer see the color of the object.

SAMPLE NAME	SCI			SCE		
	a*	b*	L*	a*	b*	L*
White (PW6-PW5)	-1.03±0.03	1.26±0.24	95.49±0.84	-0.95±0.03	1.31±0.24	95.44±0.85
Ultramarine Blue (PB29)	40.69±0.59	-62.17±0.35	12.80±0.10	39.65±0.63	-62.07±0.36	13.35±0.11
Yellow Ochre (PY42)	16.62±0.12	56.80±0.52	60.40±0.21	16.47±0.12	55.68±0.50	60.75±0.22
Ruby Red (PV19)	61.97±0.36	29.49±0.60	33.37±0.24	61.96±0.35	28.18±0.60	33.76±0.24
Armor Green (PG7)	-57.93±0.49	4.88±0.46	20.80±0.27	-57.00±0.60	4.51±0.50	21.69±0.28

Tab. 3.1-16: Colorimetric values in the CIEL*a*b*76 color space, evaluated from the reflectance spectra of Flashe® samples. L* indicates lightness, a* and b* are the chromaticity coordinates (in the chromaticity diagram +a*, -a* +b* and -b* respectively indicate the red, green, yellow and blue directions). Data acquired with two methods, that including and that excluding the specular reflectance (respectively SCI and SCE), are shown.

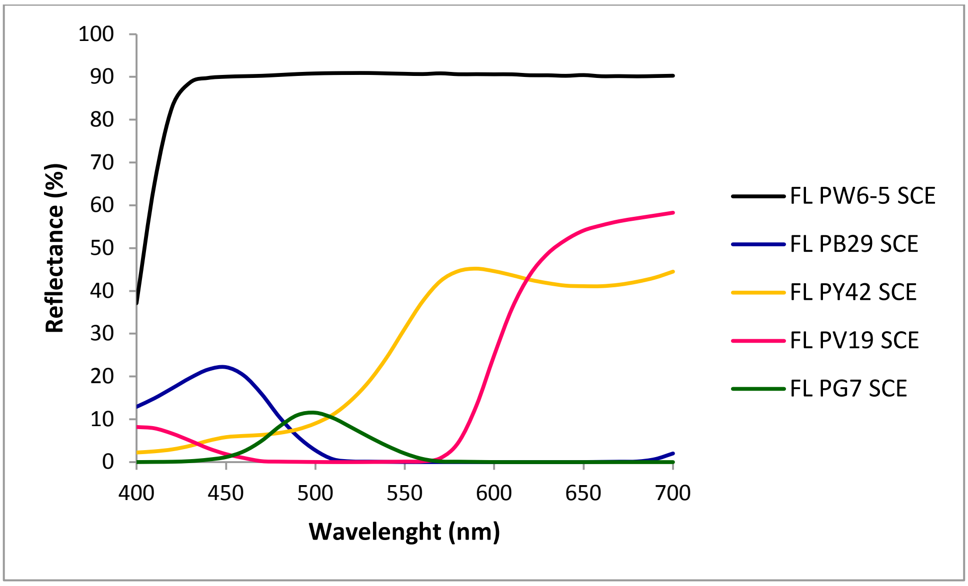


Fig.3.1-22: Reflectance spectra acquired for Flashe® samples according to the SCE method.

HEAVY BODY PAINTS (Liquitex®)

LIGHT MICROSCOPY EXAMINATIONS

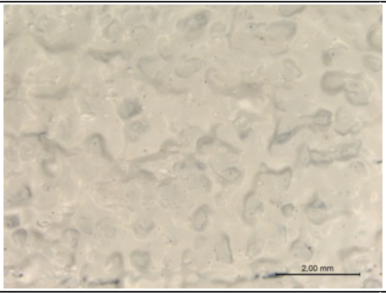
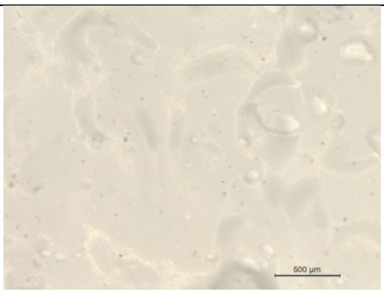
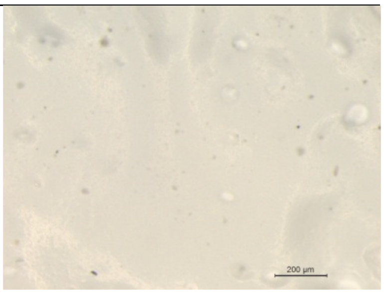
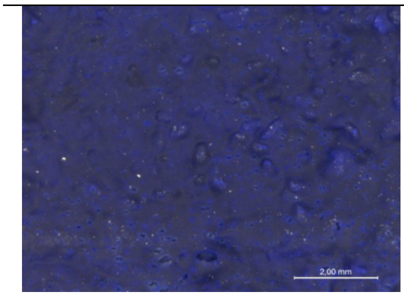
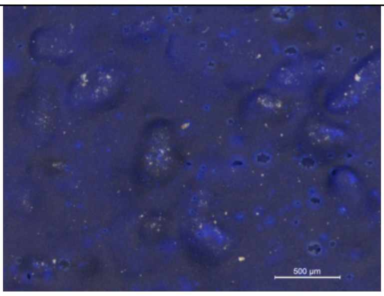
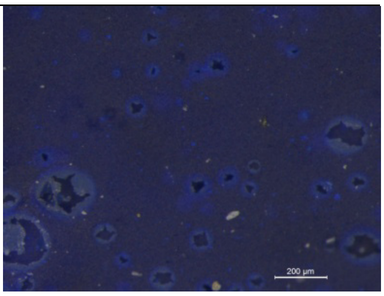
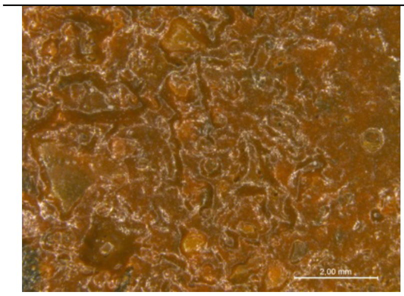
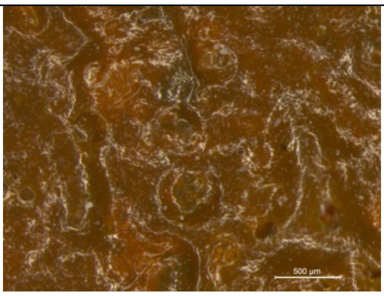
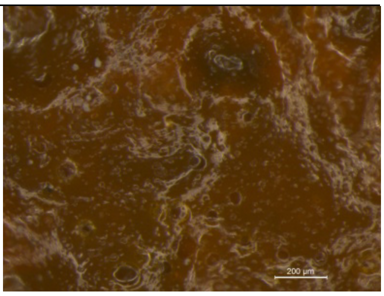
Table 3.1-17 shows the Light Microscopy pictures of Heavy Body- Liquitex® samples, taken at different magnifications (8X, 25X and 50X).

The paints result in homogeneous layers, whose morphology reflects the morphology of the underlying mortar support (with sand grains differing in shape and size).

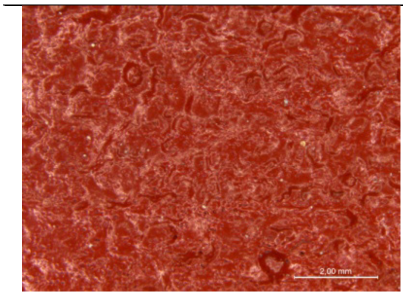
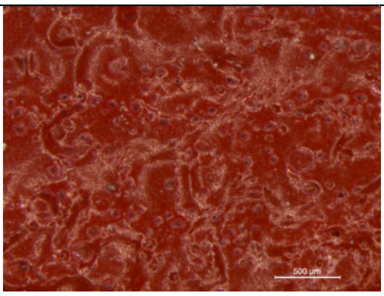
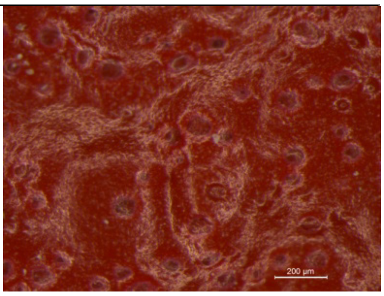
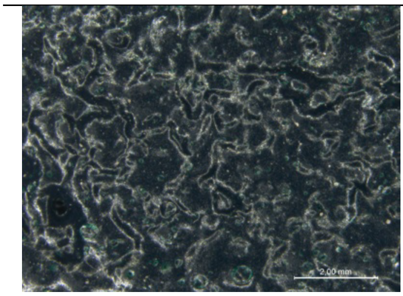
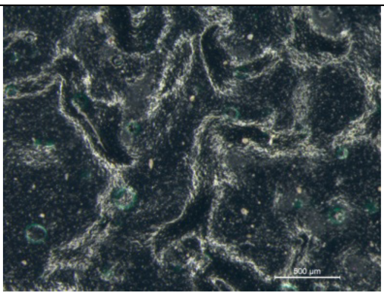
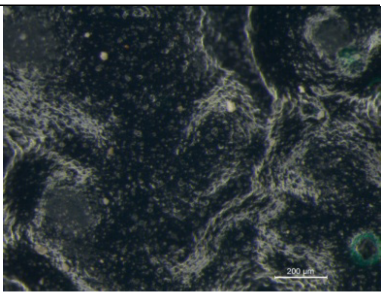
With the exception of the Transparent Raw Sienna, the hiding properties of the paints are good. The Titanium White sample presents a semi-gloss surface, the Ultramarine Blue a flat surface, while the other samples a quite gloss surface.

All the paint layers are characterized by some pin-holes. This is particularly evident for Transparent Raw Sienna, Quinacridone Crimson and Phthalocyanine Green samples which are characterized by an even distribution of pin-holes, differing in size (with the smallest showing diameters about 10 µm).

The pin-holes of Ultramarine Blue sample do not present a perfectly rounded profile.

HEAVY BODY (Liquitex®)		
TITANIUM WHITE (8X)	TITANIUM WHITE (25X)	TITANIUM WHITE (50X)
		
ULTRAMARINE BLUE (8X)	ULTRAMARINE BLUE (25X)	ULTRAMARINE BLUE (50X)
		
TRANSPARENT RAW SIENNA (8X)	TRANSPARENT RAW SIENNA(25X)	TRANSPARENT RAW SIENNA(50X)
		

Tab.3.1-17: Light Microscopy examinations of Heavy Body-Liquitex® samples. Pictures were taken at growing magnifications (8X,25X,50X). (the table continues in the following page).

HEAVY BODY (Liquitex®)		
QUINACRIDONE CRIMSON (8X)	QUINACRIDONE CRIMSON (25X)	QUINACRIDONE CRIMSON (50X)
		
PHTHALOCYANINE GREEN (8X)	PHTHALOCYANINE GREEN (25X)	PHTHALOCYANINE GREEN (50X)
		

Tab.3.1-17: Light Microscopy examinations of Heavy Body-Liquitex® samples. Pictures were taken at growing magnifications (8X,25X,50X). (the table continues in the next page).

SCANNING ELECTRON MICROSCOPY EXAMINATIONS

The following 5 tables (from 3.1-18 to 3.1-22) present the Scanning Electron Microscopy examinations of Heavy Body-Liquitex® samples. Data are displayed in the same order described for Flashe® samples.

If compared to Flashe® samples, the Heavy Body-Liquitex® ones show a higher amounts of binder, with paint layers that generally look smooth and homogeneous. This is especially true for Transparent Raw Sienna, Quincridone Crimson and Phthalocyanine Green samples where it is almost impossible to distinguish the pigments.

The Titanium White sample is characterized by a slightly higher amount of inorganic components (the Titanium based pigment), while the Ultramarine Blue sample is the only one showing a little roughness of the surface. This is supposed to be due to the size of the pigment particles, which is larger than that seen for the Titanium White sample. The amount of pigment, instead, seems to be more or less the same.

Moreover, both samples show a homogeneous distribution of the pigments, which are completely embedded in the polymeric binder matrix.

All the sample, but especially the Transparent Raw Sienna, the Quinacridone Crimson and the Phthalocyanine Green, are characterized by pin-holes. The pin-holes of the Ultramarine Blue sample do not have a perfectly rounded profile. Studying the paint layers at higher magnifications, small cracks are detected for the Ultramarine Blue and Phthalocyanine Green samples.

Basing on BSE images, EDX spectra were collected considering both, areas and local points. By doing so, it was confirmed that:

- the Titanium White paint consists of a Titanium based pigment.
- the Ultramarine Blue paint contains a pigment characterized by Sodium, Aluminium, Silicon and Sulphur
- the Transparent Raw Sienna paint contains an Iron based pigment
- the Phthalocyanine Green paint contains a pigment characterized by Chlorine and Copper.

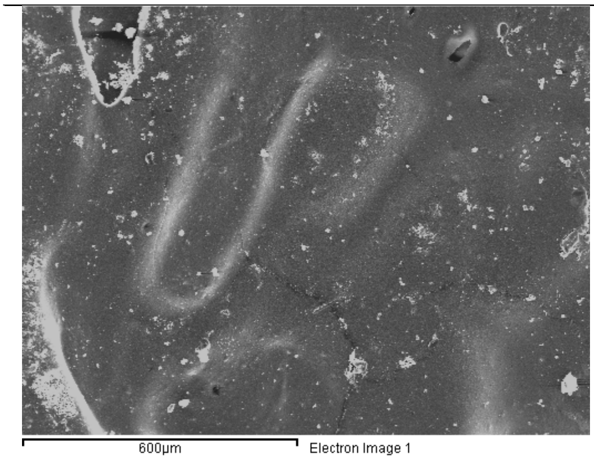
No element ascribable to an inorganic pigment were detected for the Quinacridone Crimson paint. The detection of Silicon in the Quinacridone Crimson and Phthalocyanine Green paints suggested the presence of an extender such as silica (SiO_2).

Element such as Sodium, Aluminium, Magnesium, Sulphur, Silicon, Potassium, Calcium and Manganese were sometimes assigned to the presence of surface dust.

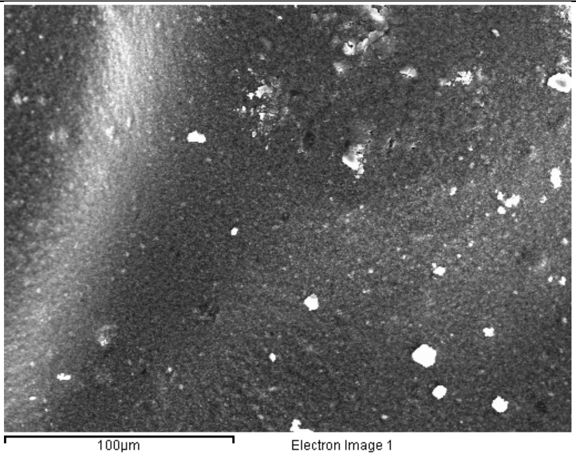
A more detailed interpretation of the EDX spectra is given in the captions of the tables.

HEAVY BODY PAINTS (Liquitex®) - TITANIUM WHITE SAMPLE -

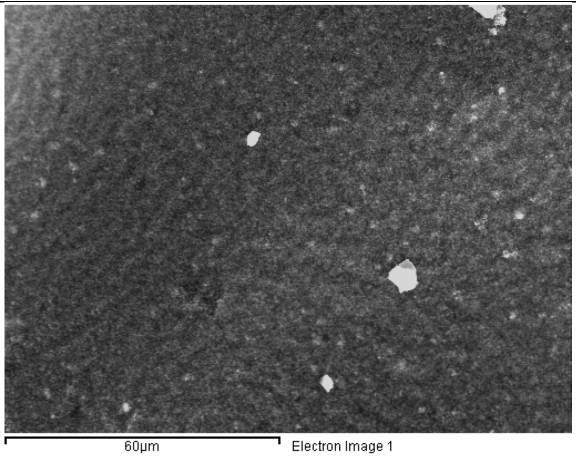
Secondary Electrons Image (100X)



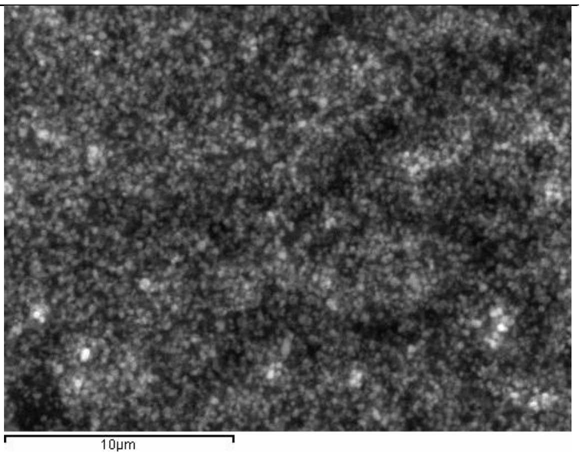
Secondary Electrons Image (500X)



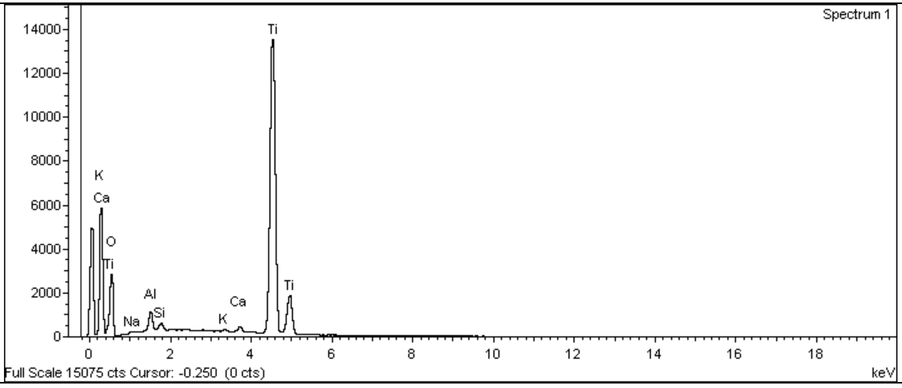
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



EDX Spectrum-500X -area of about 200µm x 150µm-



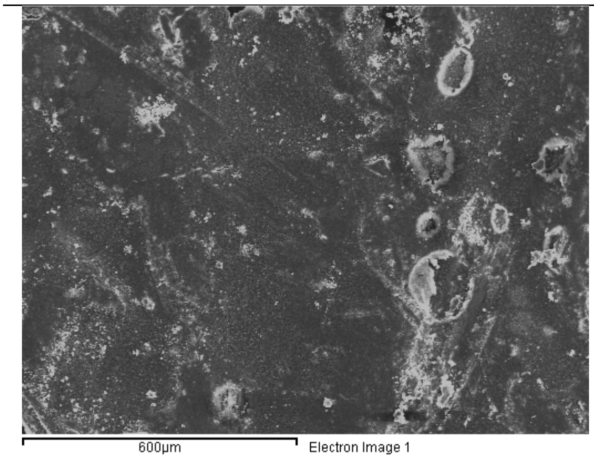
Tab. 3.1-18: The table shows the main results collected from the Heavy Body Titanium White sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area.

EDX analysis confirmed the presence of: negligible amounts of Sodium (Na), Silicon (Si), Potassium (K) and Calcium (Ca); slightly higer amounts of Aluminium (Al); high amounts of Titanium (Ti).

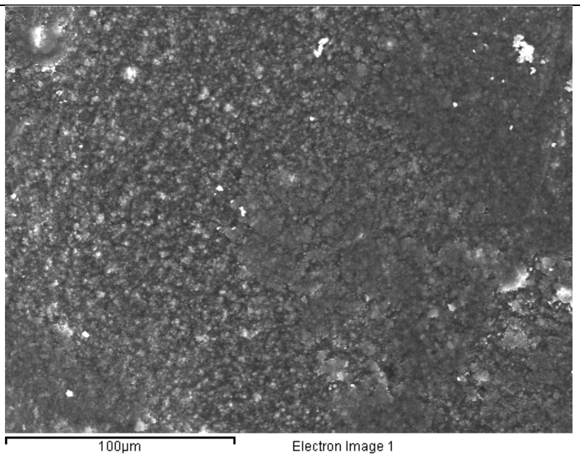
The pigment is so cofirmed to be a Titatium based one (TiO_2).

HEAVY BODY PAINTS (Liquitex®) - ULTRAMARINE BLUE SAMPLE -

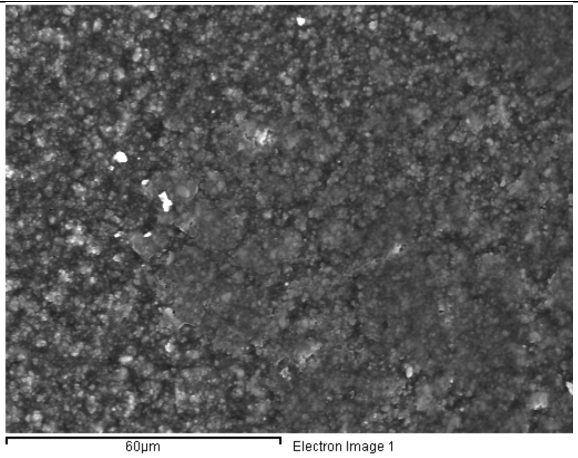
Secondary Electrons Image (100X)



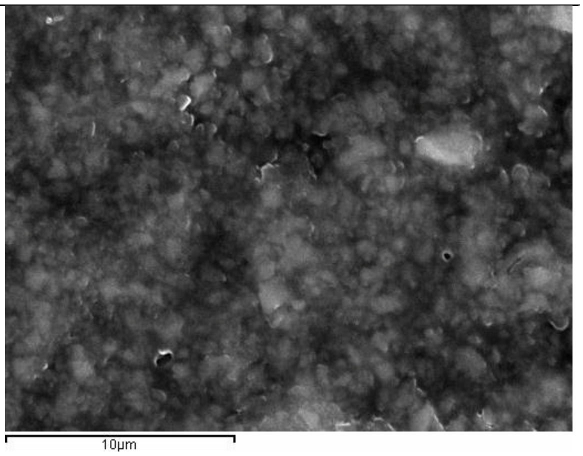
Secondary Electrons Image (500X)



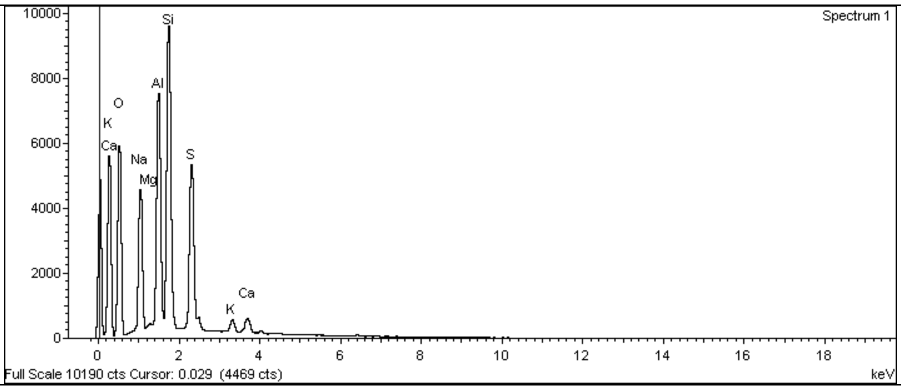
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



EDX Spectrum - 500X -area of about 200μm x 150μm-

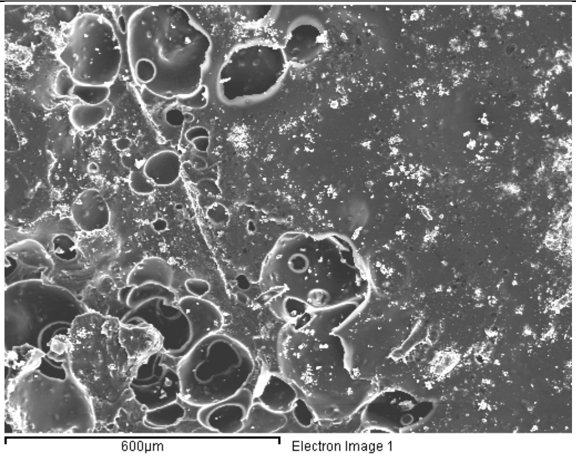


Tab. 3.1-19: The table shows the main results collected from the Heavy Body Ultramarine Blue sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area.

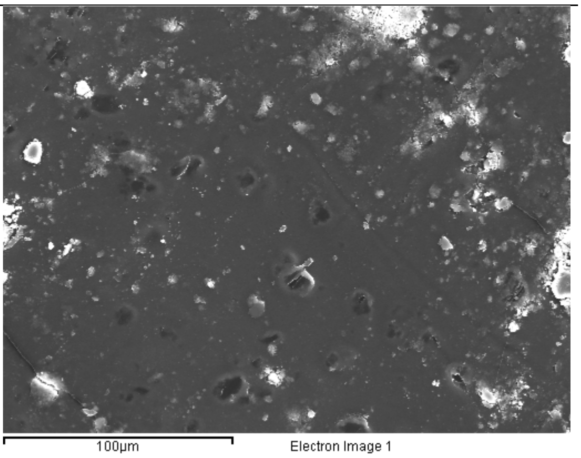
EDX analysis confirmed the presence of: negligible amounts of Magnesium (Mg), Potassium (K) and Calcium (Ca); higher amounts Sodium (Na), Aluminium (Al), Silicon (Si), Sulphur (S). These elements are mainly ascribible to the Ultramarine Blue pigment ($2Na_2Al_2Si_2O_6 \cdot NaS_2$)

HEAVY BODY PAINTS (Liquitex®) – TRANSPARENT RAW SIENNA SAMPLE -

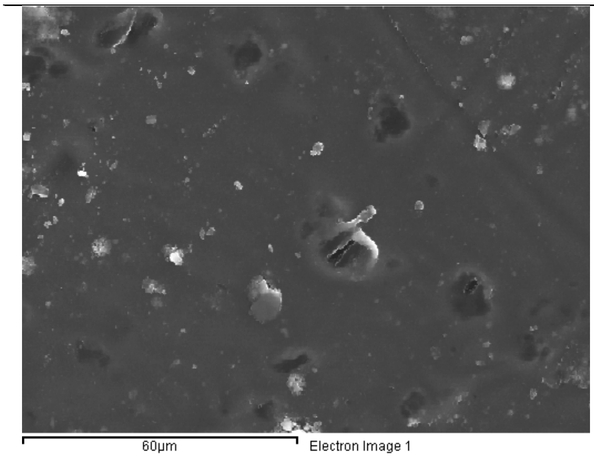
Secondary Electrons Image (100X)



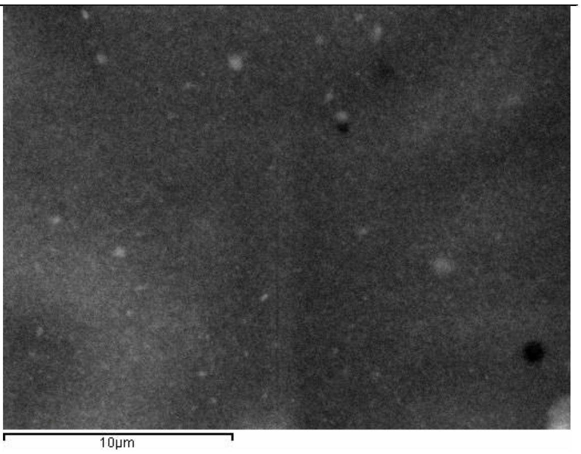
Secondary Electrons Image (500X)



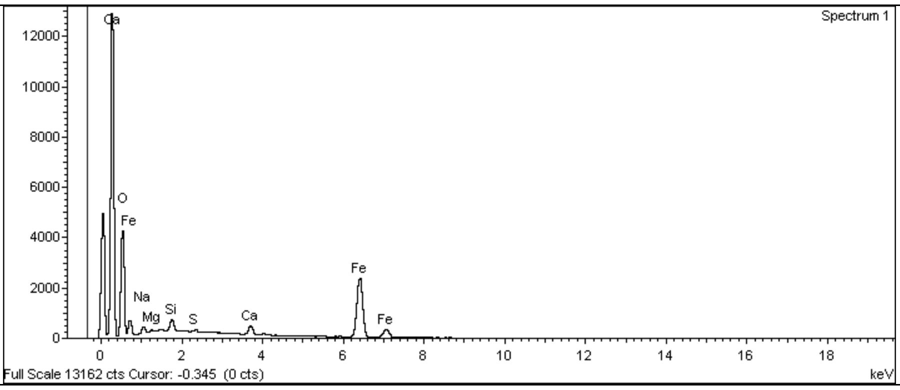
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



EDX Spectrum - 500X -area of about 100µm x 100µm-

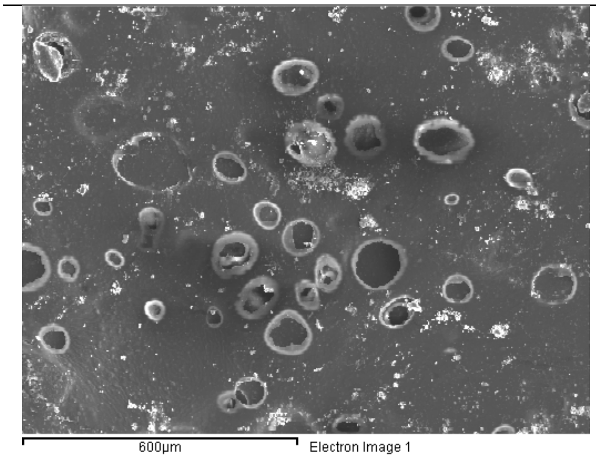


Tab. 3.1-20: The table shows the main results collected from the Heavy Body Transparent Raw Sienna sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area.

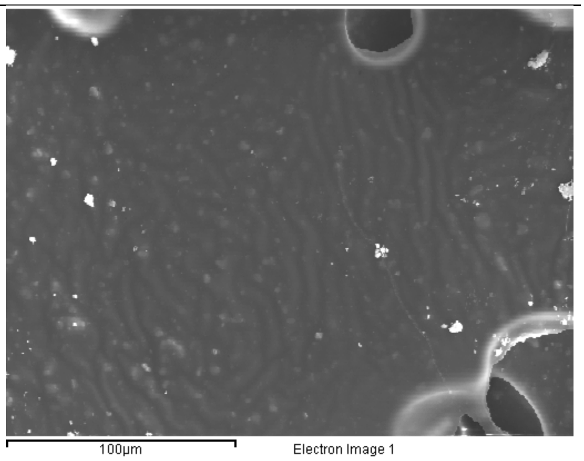
EDX analys confirmed the presence of: Sodium (Na), Magnesium (Mg), Silicon (Si), Sulphur (S), Calcium (Ca) and Iron (Fe). While the majority of these elements is probably related to surface dust and deposites, Fe is ascribable to an Iron based yellow pigment (likely $FeO(OH)\cdot H_2O$).

HEAVY BODY PAINTS (Liquitex®) – QUINACRIDONE CRIMSON SAMPLE -

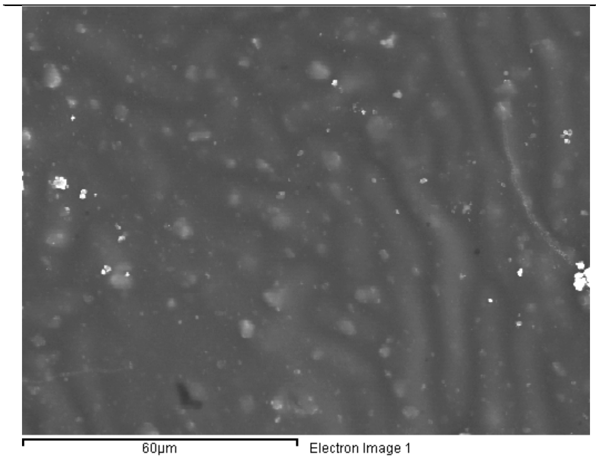
Secondary Electrons Image (100X)



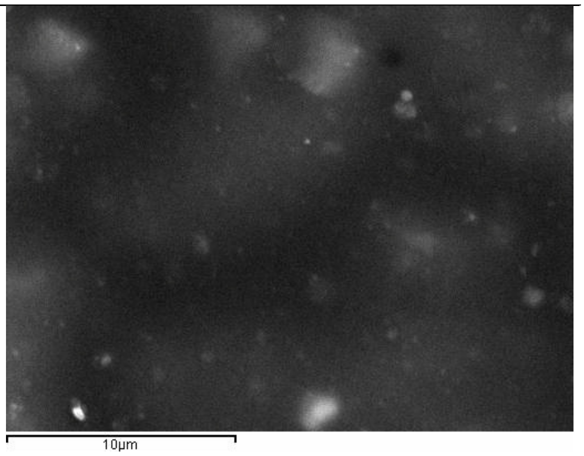
Secondary Electrons Image (500X)



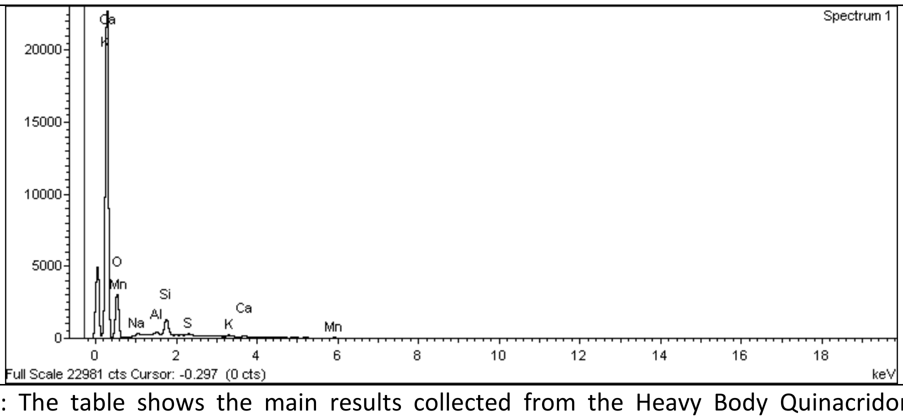
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



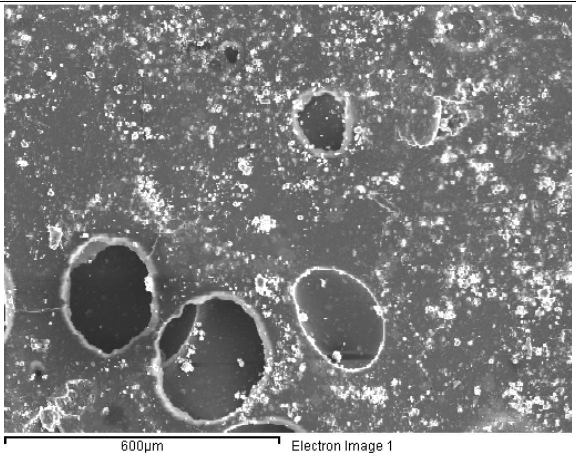
EDX Spectrum- 500X -area of about 100µm x 150µm-



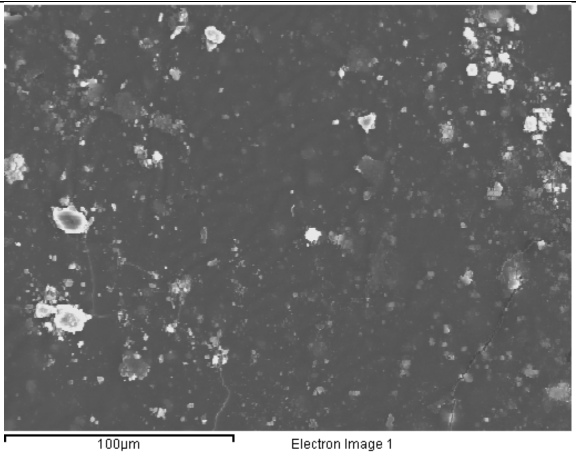
Tab. 3.1-21: The table shows the main results collected from the Heavy Body Quinacridone Crimson sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area. At higher magnifications, some wrinkles are detected. EDX analysis confirmed the presence of: Sodium (Na), Aluminium (Al), Sulphur (S), Potassium (K), Calcium (Ca), Manganese (Mn), and higher amounts of Silicon (Si). Since the Quinacridone Crimson paint is supposed to consist of an organic pigment (PV19), the majority of these elements is probably related to surface dust and deposits. Silicon could be however due to an extender (likely SiO_2).

HEAVY BODY PAINTS (Liquitex®) – PHTHALOCYANINE GREEN SAMPLE -

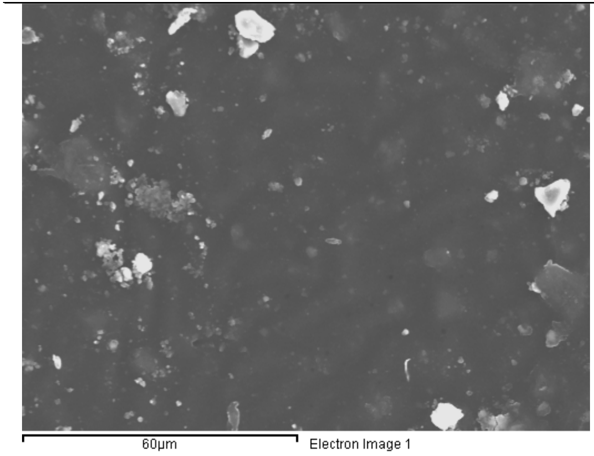
Secondary Electrons Image (100X)



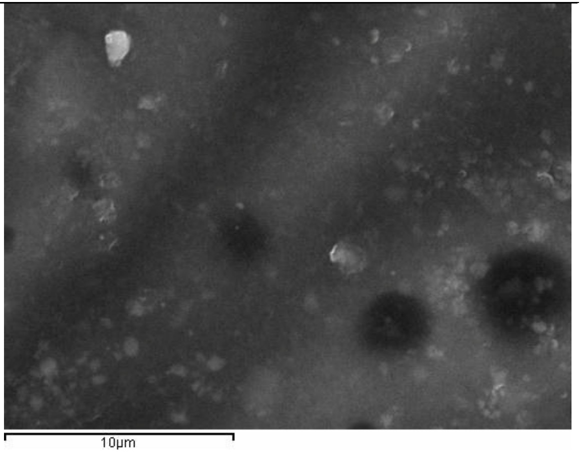
Secondary Electrons Image (500X)



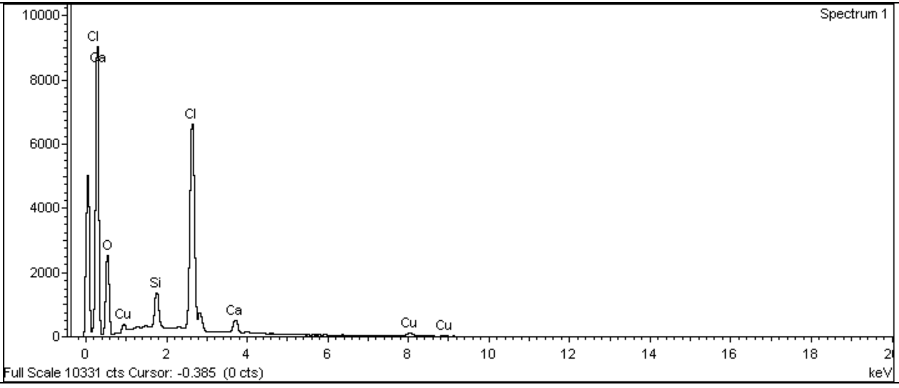
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



EDX Spectrum -500X -area of about 100µm x 150µm-



Tab. 3.1-22: The table shows the main results collected from the Heavy Body Phthlocyanine Green sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area.

EDX analysis confirmed the presence of: Silicon (Si), Clorine (Cl), Calcium (Ca) and Copper (Cu). While Copper and Clorine are ascribable to the Phthtalocyanine Green pigment, Calcium and Silicon could be related to some deposites. The Silicon could be also due to an extender (likely SiO_2).

COLORIMETRIC MEASUREMENTS

The colorimetric values in the CIEL*a*b*76 color space, reported in the table 3.1-23, were evaluated from the reflectance spectra collected from the Heavy Body-Liquitex® samples.

The measurements were taken according to the same method described for the Flashe® samples.

In figure 3.1-23, the SCE reflectance spectra are displayed.

SAMPLE NAME	SCI			SCE		
	a*	b*	L*	a*	b*	L*
Titanium White (PW6)	-1.07±0.02	1.50±0.20	96.21±0.39	-1.01±0.03	1.55±0.20	95.83±0.40
Ultramarine Blue (PB29)	24.55±1.71	-37.56±1.41	2.17±0.17	25.58±1.65	-38.66±1.34	2.45±0.17
Transparent Raw Sienna (PY42)	17.66±0.37	35.98±0.54	35.61±0.53	17.50±0.30	35.76±0.67	35.90±0.64
Quinacridon Red (PV19)	53.20±0.52	29.35±0.71	25.71±0.36	52.84±0.54	28.35±0.51	26.09±0.27
Phthalocyanine Green (PG7)	-22.97±1.05	-6.14±0.97	8.03±0.90	-23.64±0.52	-6.17±0.51	8.39±0.63

Tab. 3.1-23: Colorimetric values in the CIEL*a*b*76 color space, evaluated from the reflectance spectra of the Heavy Body samples. L* indicates lightness, a* and b* are the chromaticity coordinates (in the chromaticity diagram +a*, -a* +b* and -b* respectively indicate the red, green, yellow and blue directions). Data collected including and excluding the specular reflectance (respectively SCI and SCE), are shown.

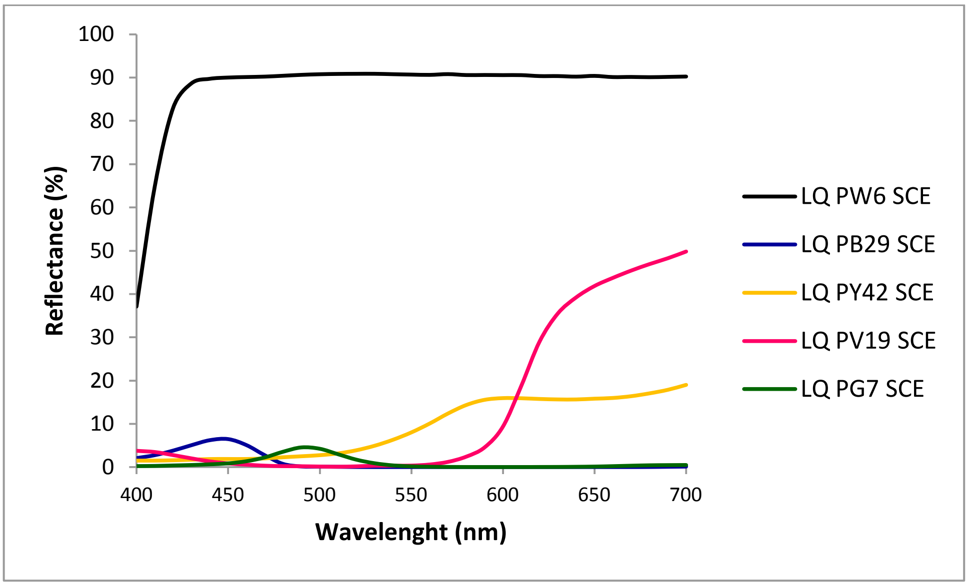


Fig.3.1-23: Reflectance spectra acquired for Heavy Body samples according to the SCE method.

BRERA PAINTS (Maimeri®)

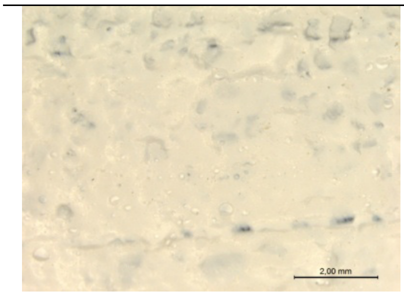
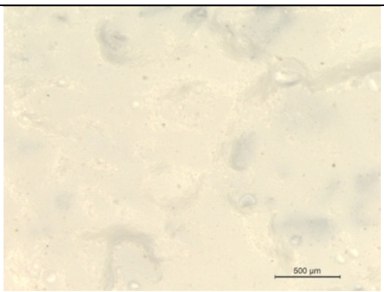
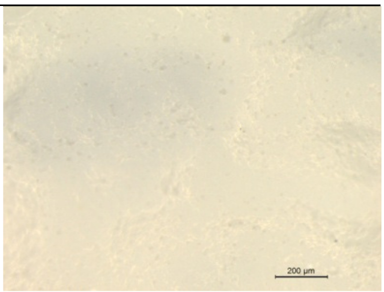
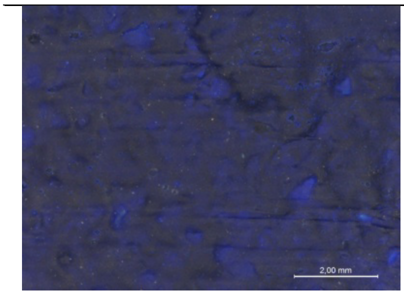
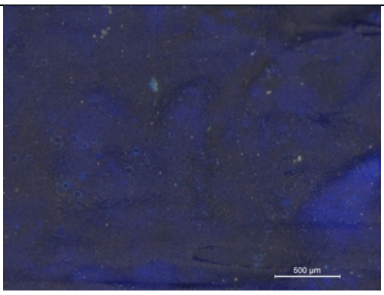
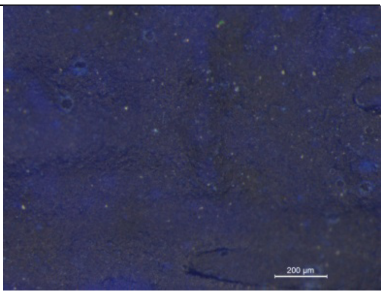
LIGHT MICROSCOPY EXAMINATIONS

Table 3.1-24 shows the Light Microscopy pictures of Brera-Maimeri® samples, taken at different magnifications (8X, 25X and 50X).

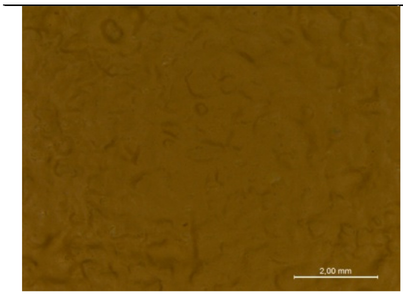
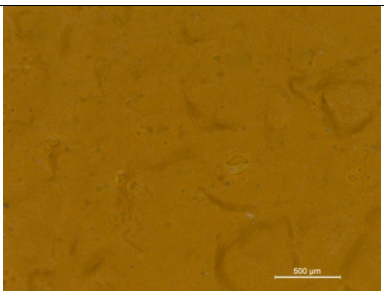
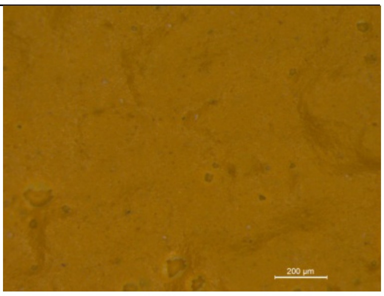
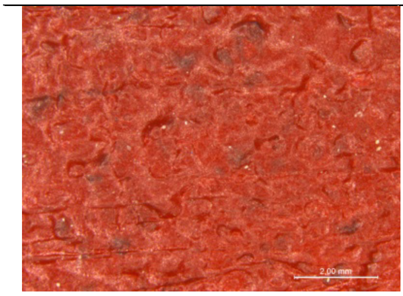
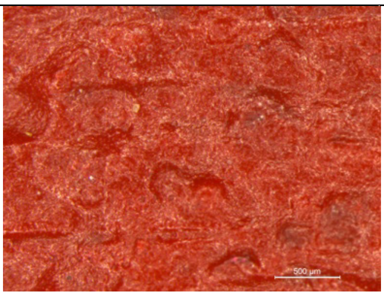
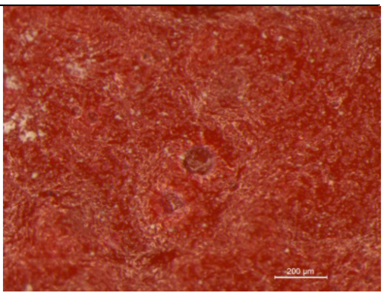
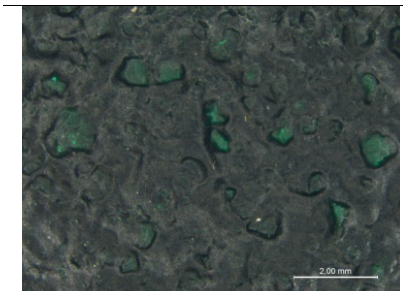
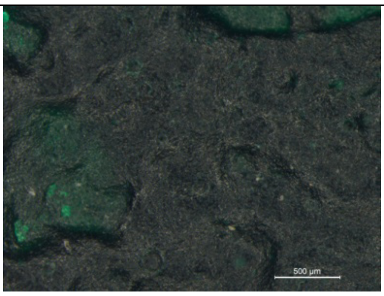
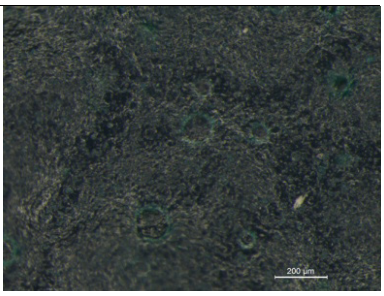
The paints result in homogeneous layers, whose morphology reflects the morphology of the underlying mortar support (with sand grains differing in shape and size).

The hiding properties of the paints are generally good. However, where the paint layers are thinner, they look lighter (Ultramarine and Phthalo Green samples) or they are not able to perfectly hide the support and, in correspondence of dark sand grains, the paint layers look darker (Titanium White and Primary Red Magenta samples).
The Titanium White, Ultramarine and Yellow Ochre samples present a semi-gloss surface, while the other samples present a quite gloss surface.

All the paint layers are characterized by some pin-holes. This is evident especially for Primary Red Magenta and Phthalo Green samples that are characterized by an even distribution of pin-holes, differing in size (with the smallest showing diameters about 10 µm). The pin-holes of the Ultramarine Blue and Yellow Ochre samples do not present a perfectly rounded profile.

BRERA (Maimeri®)		
TITANIUM WHITE (8X)	TITANIUM WHITE (25X)	TITANIUM WHITE (50X)
		
ULTRAMARINE (8X)	ULTRAMARINE (25X)	ULTRAMARINE (50X)
		

Tab.3.1-24: Light Microscopy examinations of Brera-Maimeri® samples. Pictures were taken at growing magnifications (8X,25X,50X). (the table continues in the following page).

BRERA (Maimeri®)		
YELLOW OCHRE (8X)	YELLOW OCHRE (25X)	YELLOW OCHRE (50X)
		
PRIMARY RED MAGENTA (8X)	PRIMARY RED MAGENTA (25X)	PRIMARY RED MAGENTA (50X)
		
PHTHALO GREEN (8X)	PHTHALO GREEN (25X)	PHTHALO GREEN (50X)
		

Tab.3.1-24: Light Microscopy examinations of Brera-Maimeri® samples. Pictures were taken at growing magnifications (8X,25X,50X).

SCANNING ELECTRON MICROSCOPY EXAMINATIONS

The following 5 tables (from 3.1-25 to 3.1-29) present the Scanning Electron Microscopy examinations of Brera samples. Data are displayed in the same order described for Flashe® samples.

Brera samples seem to be characterized by variable amounts of binder. The Primary Red Magenta and Phthalo Green samples, show the highest amount of binder and look perfectly smooth and homogeneous. The titanium White and Yellow Ochre samples are characterized by higher amount of inorganic components (mainly, a Titanium based pigment for the former, and an Iron based acicular pigment for the latter).

The Ultramarine Blue sample is the only one characterized by a certain roughness of the surface, which is ascribable to the pigment particle size, which is much larger than that seen for the other samples. In spite of the different particle size, all the paint layers show a homogeneous distribution of the pigments, which are completely embedded in the polymeric binder matrix. All the sample are characterized by some pin-holes.

Basing on BSE images, EDX spectra were collected considering both, areas and local points. By doing so, some of the inorganic components have been identified with a Silicon based extender (likely SiO_2), whose presence is above all appreciable for those samples containing the organic pigments (PV19 and PG7).

Moreover, EDX analysis confirmed that:

- the Titanium White paint consists of a Titanium based pigment
- the Ultramarine paint contains a pigment characterized by Sodium, Aluminium, Silicon and Sulphur
- the Yellow Ochre paint contains an Iron based pigment
- the Phthalo Green paint contains a pigment characterized by Chlorine and Copper.

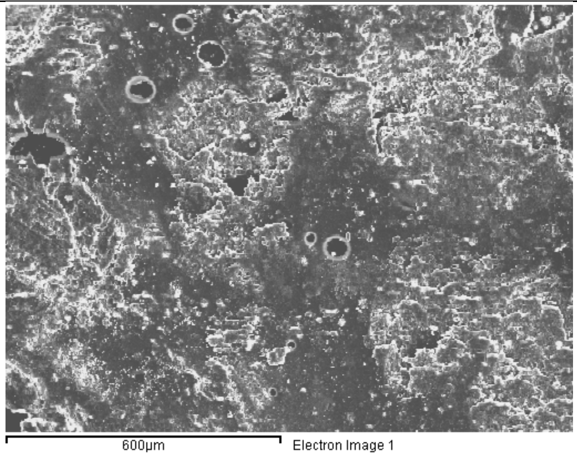
No elements ascribable to an inorganic pigment were detected for the Primary Red Magenta paint.

Elements such as Sodium, Aluminium, Sulphur, Chlorine, Potassium and Calcium were sometimes assigned to the presence of surface dust.

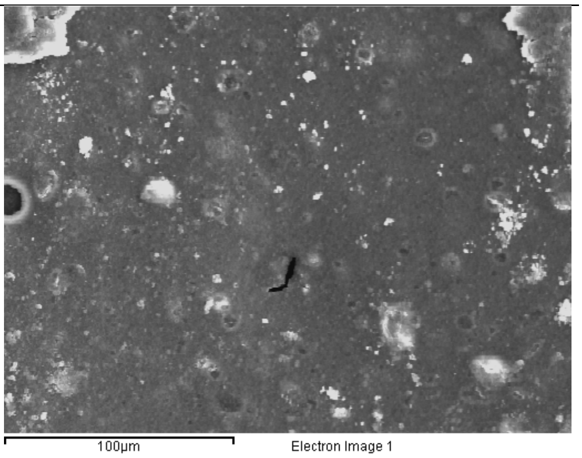
A more detailed interpretation of the EDX spectra is given in the captions of the tables.

BRERA PAINTS (Maimeri®) - TITANIUM WHITE SAMPLE -

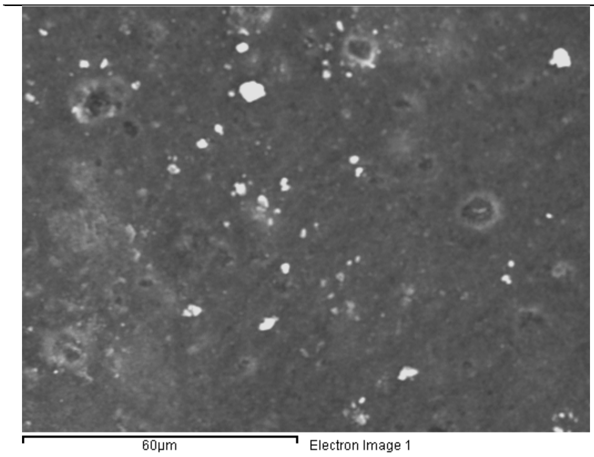
Secondary Electrons Image (100X)



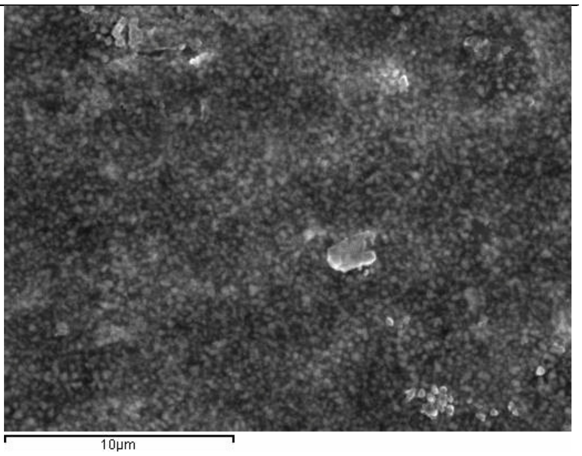
Secondary Electrons Image (500X)



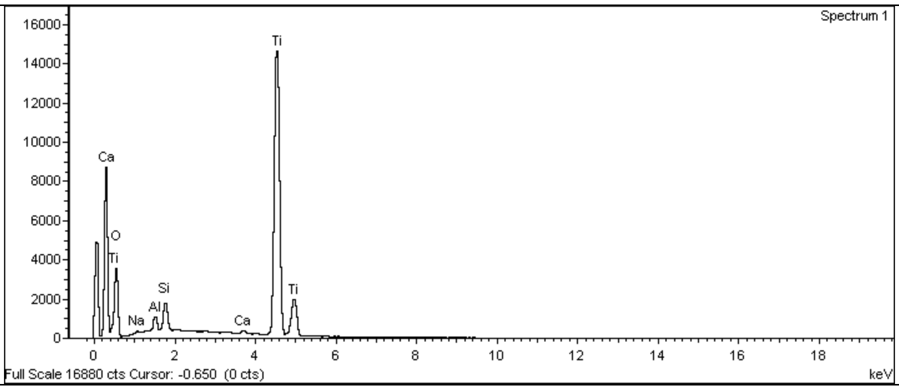
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



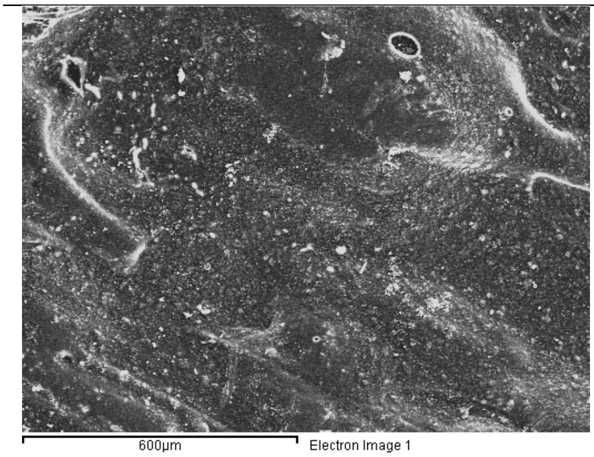
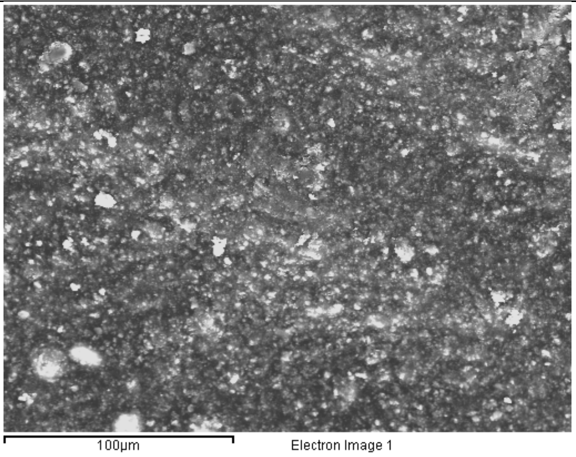
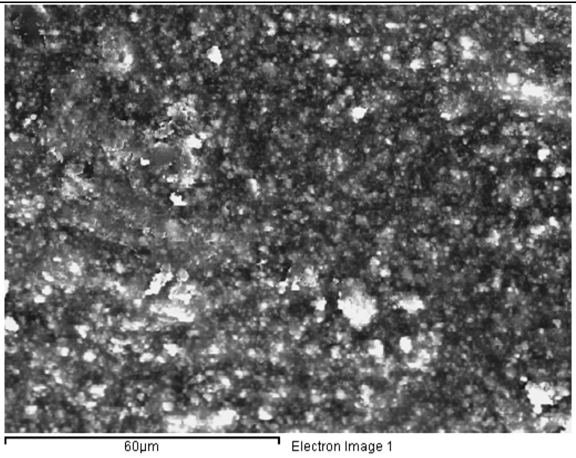
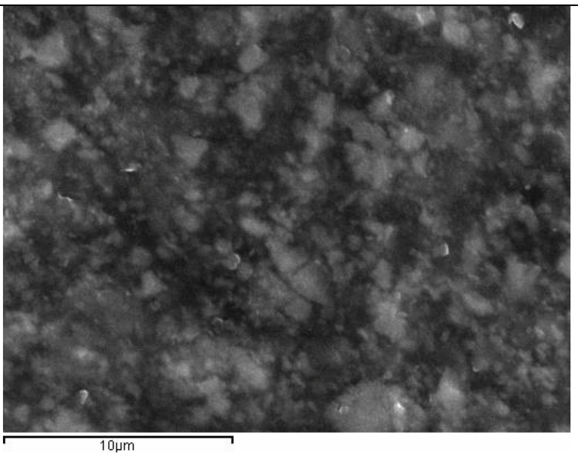
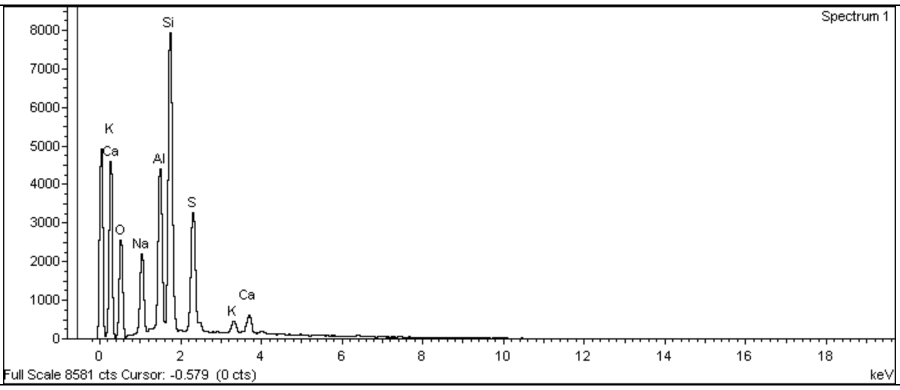
EDX Spectrum -500X -area of about 200µm x 150µm-



Tab. 3.1-25: The table shows the main results collected from the Brera Titanium White sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area.

The discontinuous surface morphology detected at low magnifications (100X) is probably due to the sampling. At higher magnification indeed, the paint layer is more homogeneous.

EDX analysis confirmed the presence of: negligible amounts of Sodium (Na), and Calcium (Ca); slightly higer amounts of Aluminium (Al) and Silicon (Si); high amounts of Titanium (Ti). The white pigment is cofirmed to be Titatium based (TiO_2). The other elements could be due to surface deposits. Silicone is possibly related to an extender (SiO_2).

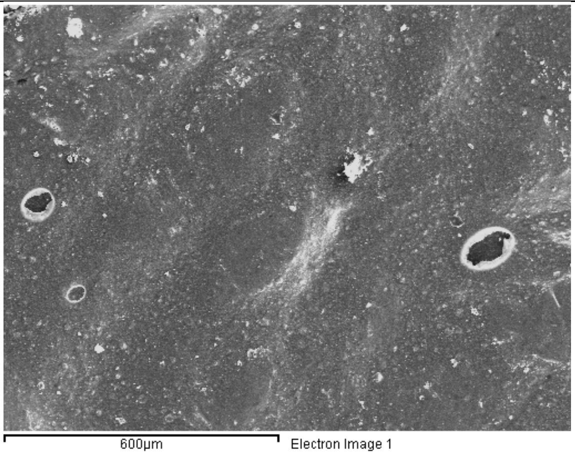
BRERA PAINTS (Maimeri®) –ULTRAMARINE SAMPLE -	
Secondary Electrons Image (100X)	Secondary Electrons Image (500X)
	
Secondary Electrons Image (1000X)	Secondary Electrons Image (5000X)
	
EDX Spectrum -500X -area of about 200µm x 150µm-	
	

Tab. 3.1-26: The table shows the main results collected from the Ultramarine Brera sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area.

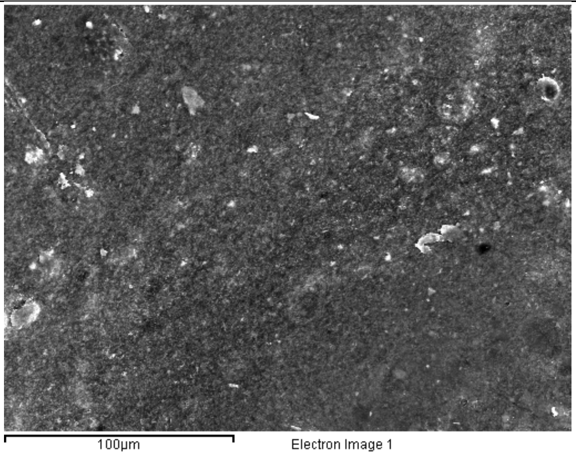
EDX analysis confirmed the presence of: negligible aounts of Potassium (K) and Calcium (Ca); higher amounts of Sodium (Na), Aluminium (Al), Silicon (Si) and Sulphur (S). These elements are mainly ascribible to the Ultramarine Blue pigment ($2Na_2Al_2Si_2O_6 \cdot NaS_2$).

BRERA PAINTS (Maimeri®) – YELLOW OCHRE SAMPLE -

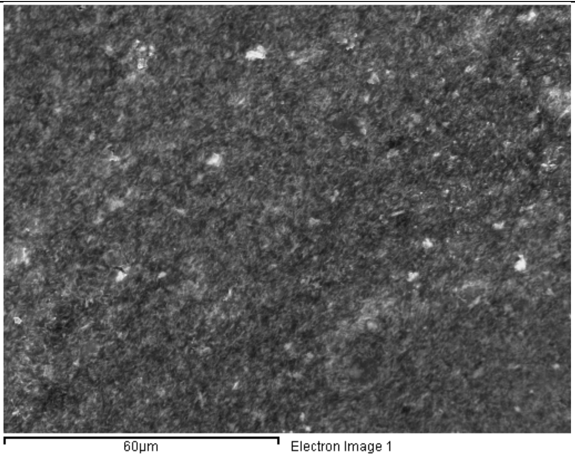
Secondary Electrons Image (100X)



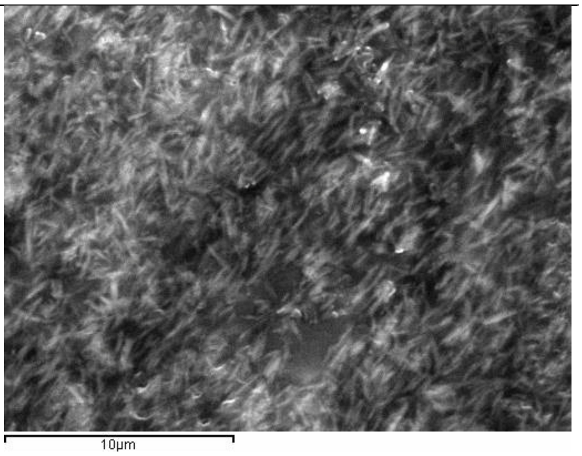
Secondary Electrons Image (500X)



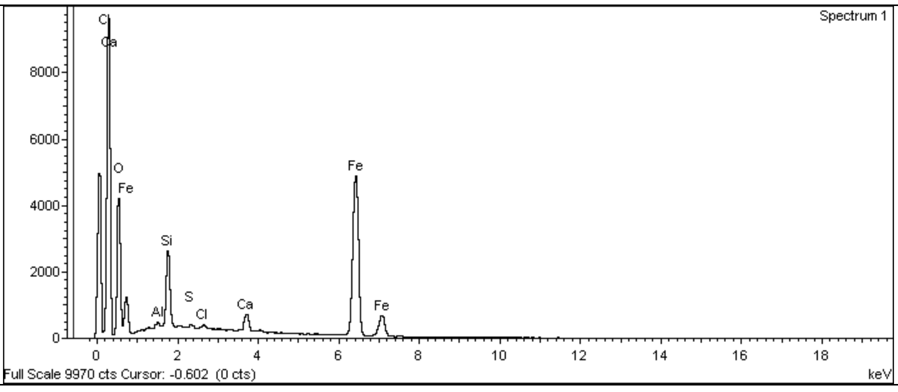
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)



EDX Spectrum- 500X -area of about 200µm x 150µm-

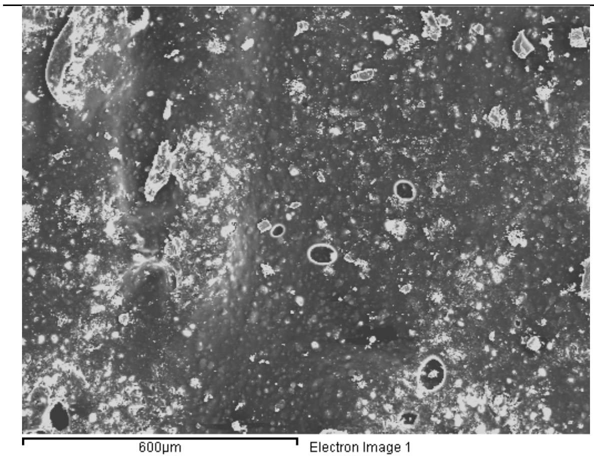


Tab. 3.1-27: The table shows the main results collected from the Yellow Ochre Brera sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for one of the rough areas.

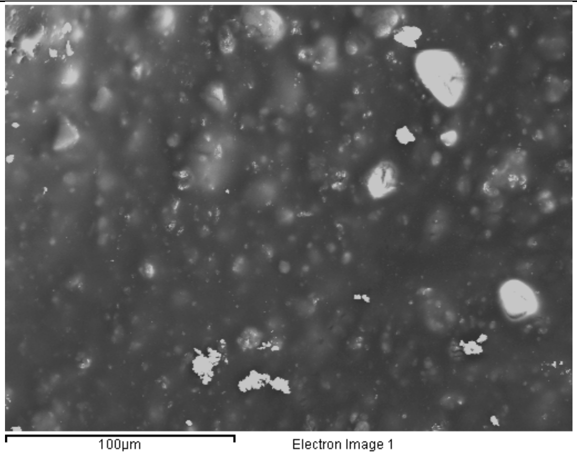
EDX analys confirmed the presence of: negligible amounts of Aluminium (Al), Sulphur (S), Chlorine (Cl) and Calcium (Ca); higher amounts of Silicon (Si) and Iron (Fe). While the majority of the elements is probably due to surface dust and deposites, Si could be ascribed to an extender (likely SiO_2) and Fe to Iron based yellow pigment (likey $FeO(OH)\cdot H_2O$).

BRERA PAINTS (Maimeri®) - PRIMARY RED MAGENTA SAMPLE -

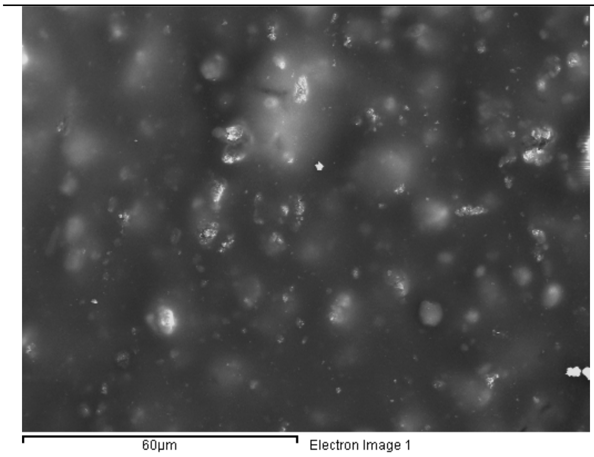
Secondary Electrons Image (100X)



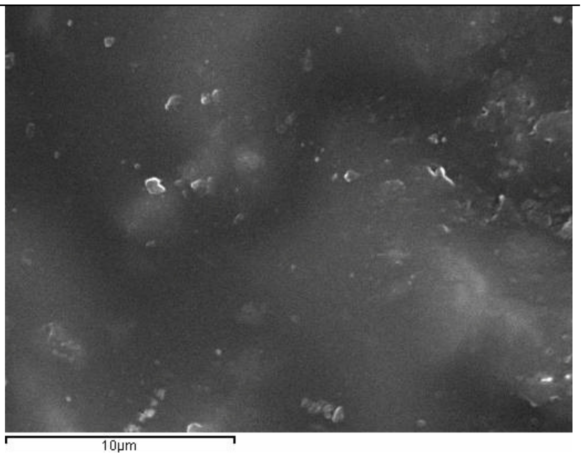
Secondary Electrons Image (500X)



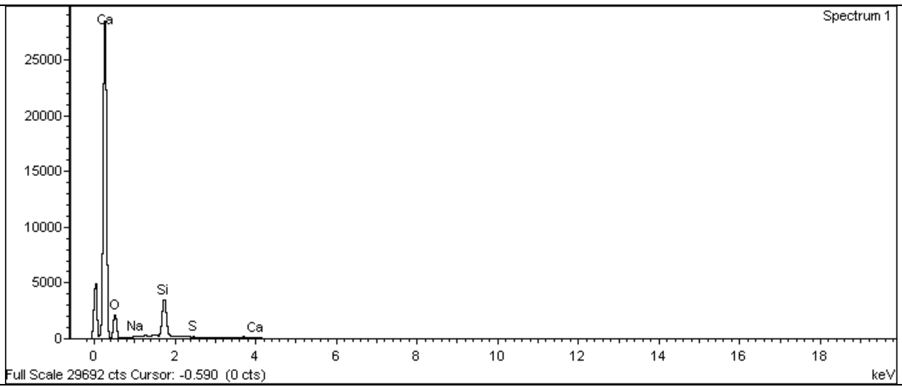
Secondary Electrons Image (1000X)



Secondary Electrons Image (5000X)

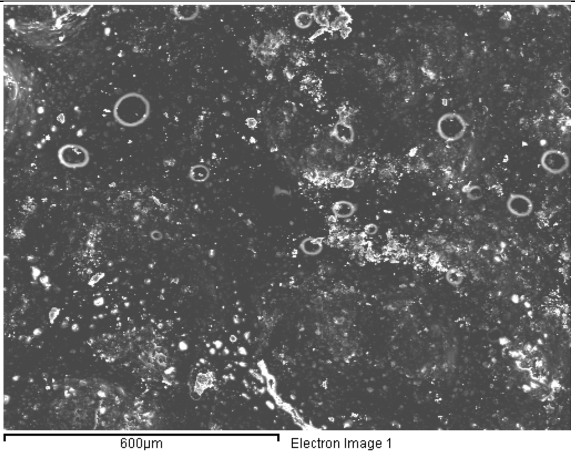
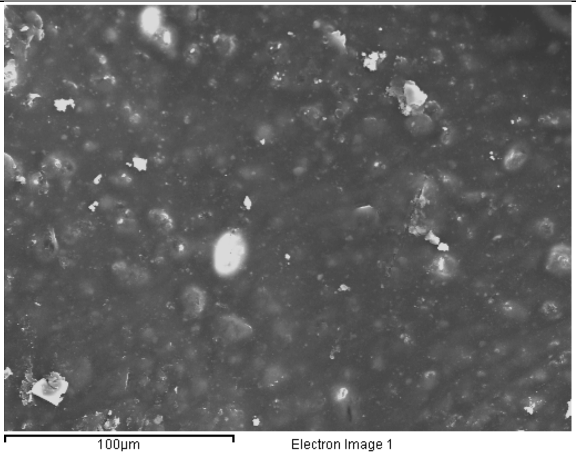
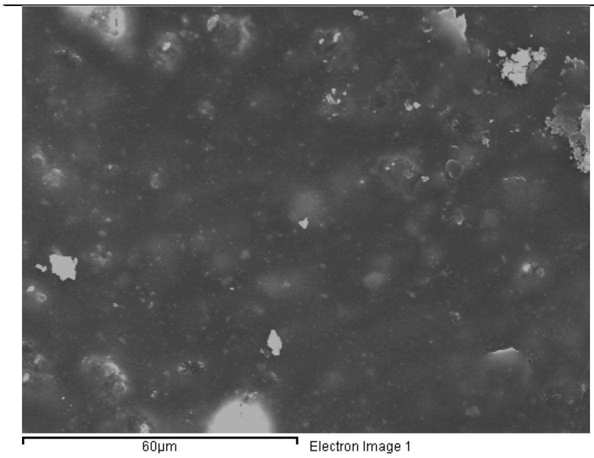
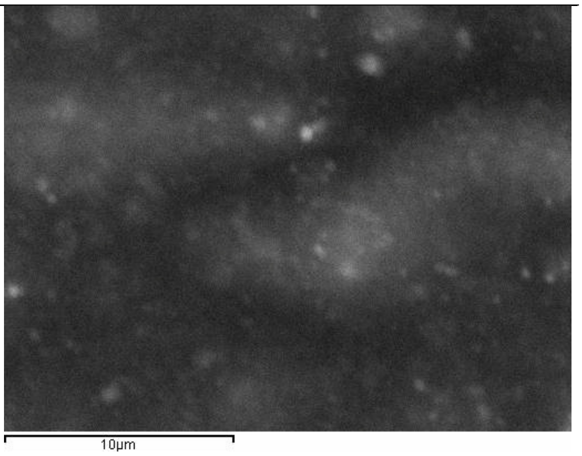
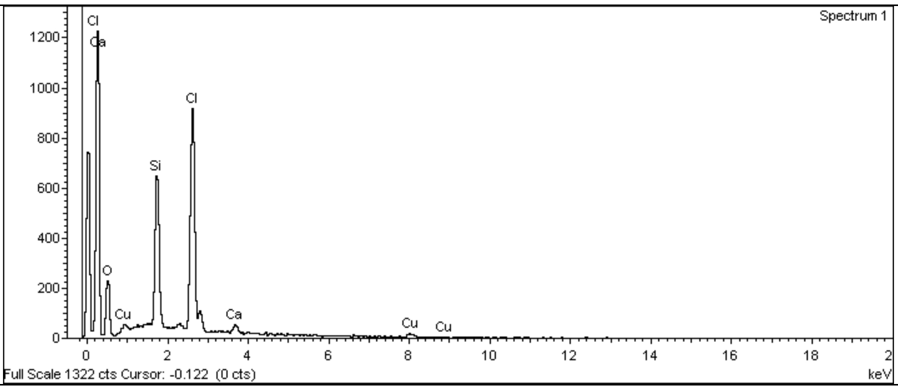


EDX Spectrum- 500X -area of about 100µm x 150µm-



Tab. 3.1-28: The table shows the main results collected from the Primary Red Magenta Brera sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area.

EDX analysis confirmed the presence of: negligible amounts of Sodium (Na), Sulphur (S), and Calcium (Ca); higher amounts of Silicon (Si). This latter element is possibly related to a Silicon based extender (likely SiO_2).

BRERA PAINTS (Maimeri®) - PHTHALO GREEN SAMPLE -	
Secondary Electrons Image (100X)	Secondary Electrons Image (500X)
	
Secondary Electrons Image (1000X)	Secondary Electrons Image (5000X)
	
EDX Spectrum- 500X -area of about 100µm x 150µm-	
	

Tab. 3.1-29: The table shows the main results collected from the Phthalo Green Brera sample. Four images, taken using SE at growing magnifications (100X, 500X, 1000X and 5000X) are presented, together with an EDX spectrum collected for an area.

EDX analysis confirmed the presence of: Calcium (Ca); Copper (Cu); Silicon (Si) and Chlorine (Cl). While Copper and Chlorine are ascribable to the Phthalo Green pigment, the Silicon is possilby related to an extender (likely SiO_2). Calcium is possibly due to surface deposits.

COLORIMETRIC MEASUREMENTS

The colorimetric values in the CIEL*a*b*76 color space of Table 3.1-30 were evaluated from the reflectance spectra acquired from the Brera-Maimeri® samples.

The measurements were taken according to the same method described for the Flashe® samples. In figure 3.1-24, the SCE reflectance spectra are displayed.

SAMPLE NAME	SCI			SCE		
	a*	b*	L*	a*	b*	L*
Titanium White (PW6)	-1.02±0.04	1.42±0.15	95.98±0.39	-0.93±0.04	1.46±0.15	95.83±0.40
Ultramarine (PB29)	28.96±0.31	-42.57±0.36	3.52±0.21	29.23±0.39	-43.26±0.30	3.93±0.26
Yellow Ochr e (PY42)	17.46±0.08	54.80±0.63	54.74±0.09	17.31±0.08	53.70±0.63	55.09±0.08
Primary Red Magenta (PV19)	50.76±0.42	21.06±0.32	29.39±0.30	50.20±0.72	20.78±0.50	29.76±0.37
Phthalo Green (PG7)	-18.85±1.50	-6.85±1.26	6.68±0.17	-20.35±1.70	-7.58±1.31	7.62±0.17

Tab. 3.1-30: Colorimetric values in the CIEL*a*b*76 color space, evaluated from the reflectance spectra of the Brera-Maimeri® samples. L* indicates lightness, a* and b* are the chromaticity coordinates (in the chromaticity diagram +a*, -a* +b* and -b* respectively indicate the red, green, yellow and blue directions). Data acquired with the methods including and excluding the specular reflectance (respectively SCI and SCE) are shown.

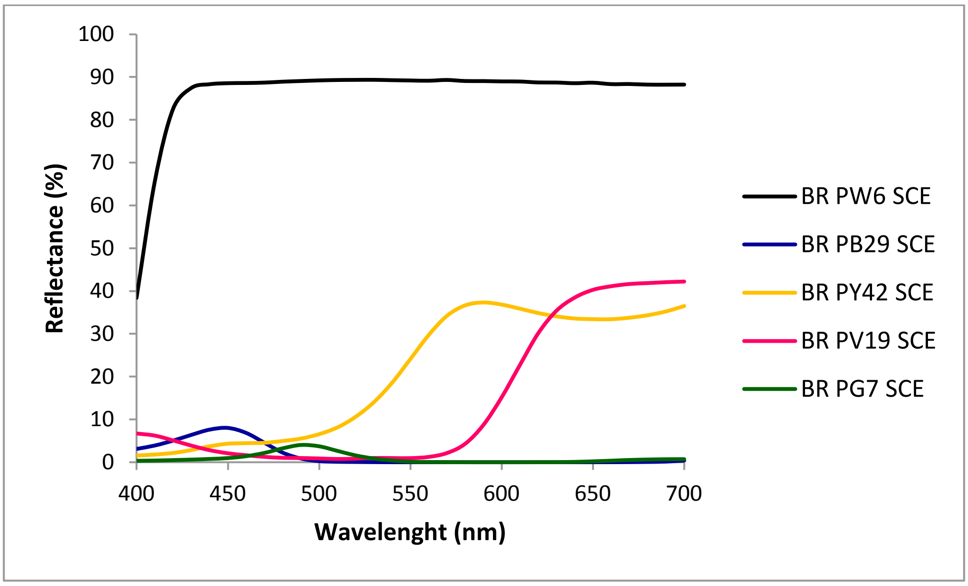


Fig.3.1-24: Reflectance spectra acquired for Brera samples according to the SCE method.

3.1.1.3 Discussing results

The chemical characterization of the paint films mainly confirmed what already known from technical data sheets and existing literature.

As deducible from the FTIR spectra, Flashe® paints (LeFranc&Bourgeois) consist of a vinyl binder (p(VAc-VeoVa) copolymer), the Heavy Body (Liquitex®) paints of an acrylic binder (p(*n*BA-MMA) copolymer) while the Brera (Maimeri®) ones of a styrene-acrylic binder (p(*n*BMA-2EHA-styrene) terpolymer).

The results of FTIR spectroscopy analysis and energy dispersive X-ray microanalysis, also confirmed that the composition of the pigments mainly correspond to paints manufacturers' declarations. White paints consist of a Titanium Dioxide pigment (TiO_2, PW6),[22] an artificial Ultramarine Blue pigment ($2Na_2Al_2Si_2O_6 \cdot NaS_2$, PB29) was detected in the Blue paints, a Mars Yellow pigment ($FeO(OH) \cdot H_2O$, PY42)[23] in the Yellow paints, a Phthalocyanine Green (a chlorinated copper phthalocyanine with chemical formula ranging from $C_{32}H_3Cl_{13}CuN_8$ to $C_{32}HCl_{15}CuN_8$, PG7) in the Green paints and a Quinacridone pigment ($C_{20}H_{12}N_2O_2$, PV19) in the Red paints. All the blue pigments turned out to contain slight amounts of Kaolinite ($Al_2Si_2H_4O_9$).[24]

Flashe® and Brera-Maimeri® paints are respectively characterized by a calcium carbonate extender ($CaCO_3$) and a Silicon based extender (presumably SiO_2).

No extenders were instead detected for the majority of the Heavy Body-Liquitex® paints, with only the Quinacridone Crimson and the Phtalocyanine Green which possibly contain slight amounts of silica (SiO_2). This result was suggested both by the SEM-EDX analysis of the paint layers and the FTIR spectroscopy characterization of the white chars, coming from the Thermogravimetric Analysis.

The paints' organic additives were partially identified through FTIR analysis of the paints' water extracts. The Brera-Maimeri® paints are supposed to contain an ether-cellulose thickener (characterized by a strong absorption at about 1060 cm^{-1}).

The diagnostic features of an alkylphenol ethoxylate surfactant (a small band around 1511 cm^{-1}, a doublet around 1360 cm^{-1} and 1342 cm^{-1}, and a strong sharp absorption at

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[22] It is to remember that the Flashe® White paint contain both, Titanium Dioxide (TiO_2, PW6) and Lithopone (ZnS-$BaSO_4$, PW5) pigments. Even though no elements ascribable to this latter pigment were detected through SEM-EDX analysis, some features ascibable to Lithopone were seen in the FTIR spectrum of the paint.

[23] The Mars Yellow pigment was indentified not only because of the diagnostic features seen in the FTIR spectrum and the detection of Iron (Fe) through SEM-EDX analysis, but also because of the acicular morphology shown by its particles. According to *The Pigment Compendium CD-ROM* Elsevier (2004) indeed: the particles of iron oxide hydroxide (the synthetic equivalent of the mineral goethite), generally appear as finely fibrous, round or bacterial in shape. The principal habit for this compound is acicular and it is promoted by rapid growth conditions during manufacture (reported particle size are from a few tens of nm to several micrometers or more).

[24] This result is consistent with pigment manufacture procedure (Plesters, 1993). Similar results have been moreover reported for other Ultramarine Blue artists' grade acrylic paints (Pintus, Wei, Schreiner, 2012)

1110 cm^{-1}) were instead detected for the Flashe® and Heavy Body-Liquitex® paints. The spectra of Flashe® White, Flashe® Armor Green and Heavy Body-Liquitex® Transparent Raw Sienna paints presented two additional strong absorptions around 1550 cm^{-1} and 1405 cm^{-1}, tentatively assigned to the stretching vibrations of the carboxylate ion of an anionic pigment dispersant (such as sodium polyacrylate).

It was not possible to interpret the other spectral bands in a certain way. Most of the spectra actually showed some absorptions in the C-H stretching region and in the fingerprint region which could be referred to a variety of water soluble additives, possibly included in the emulsion paints manufacturing (such as: polyacid pigment dispersants like Tamol^{TM}; methenamine derivative preservative like Dowicil^{TM}75; phosphates; fatty acids monoethanolamiamide ethoxylates etc…).

A full identification of these additives went beyond the purpose of this preliminary characterization, which was carried out in the attempt of detecting some diagnostic features to monitor while studying the phase-separation process of the main water-soluble components of the paints.

The thermogravimetric analysis pointed out that, in Flashe® paints films, only the 25-30% by weight could be referred to the binder, while a variable percentage of the inorganic content can be ascribed to the calcium carbonate extender (from a minimum of 4% for Yellow Ochre to a maximum of 30% for Ruby Red).

Heavy Body-Liquitex® and Brera-Maimeri® paints are characterized by higher amounts of binder (40-45% for the former, 35-45% for the latter). Even though an exact evaluation of the binder content is possible only for those paints characterized by pigments that are thermally stable in the scanned temperature range (Titanium White and Ultramarine Blue), data collected for both Heavy Body and Brera paints suggest that, when organic with high tinting strength are used, lower pigment amounts are required (it is the case of paints containing organic pigments as Quinacridone Red and Phthalocyanine Green).

The information coming from the paints' chemical characterization, is consistent with data detected as far as the morphology and physical properties the of the paint layers.

The Flashe® paints, characterized by lower binder amounts, result in paint layers that look rough and discontinuous, and that are sometimes affected by cracks.[25] The inclusion of the calcium carbonate extender in these formulations also influences the color of the paint layers, which look flat and light.

The L* values detected when measuring the color of Flashe® paints are actually quite high, with the lowest one detected for the Ultramarine Blue paint (about 13). This value is much higher than those detected for the Heavy Body-Liquitex® Ultramarine Blue paint (about 2) and the Brera-Maimeri® Ultramarine paint (about 4).

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[25] The brittle character of Flashe® paint films was also detected by Silva (PhD tehesis, 2011).

The Heavy Body-Liquitex® paints are characterized by higher amounts of binder, and have smooth and homogeneous paint layers. This is especially true for the Transparent Raw Sienna, the Quinacridone Crimson and the Phthalocyanine Green samples that present quite gloss surfaces. The Ultramarine Blue sample looks flatter than the Titanium White sample because of pigment particle size reasons (as confirmed by TGA, the amount of pigment is instead more or less the same in both paints).
Analogous considerations can be drawn for Brera-Maimeri® paints.

Pin-holes, or craters defects were detected for most of the paint layers and could be related to the surfactants included in the paints' formulations. It has been already pointed out that this kind of defect is often produced in emulsion paints, as a result of the foam created during both manufacturing and application.[26] Results suggest that: the higher the amount of dispersing agents required for stabilizing the formulation, the higher is the amount of detected pin-holes (as in the case of the paints consisting of organic pigments). It could be also noticed that the pin-holes do not look perfectly rounded in those paints where the binder content is lower (e.g. in Flashe® paints).

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[26] Jablowsky *et al.* 2003

3.1.2 Artificial ageing

3.1.2.1 Rising damp cycles

In this section the results coming from the rising damp ageing are presented, and separately discussed for each one of the artists' paint brands included in the study (Flashe® - LeFranc&Bourgeois; Heavy Body - Liquitex®; Brera - Maimeri®).

As already described in Chapter 2 (section 2.3.1); a total of 45 samples were subjected to the ageing, which consisted in 20 cycles simulating water absorption through the capillary rise mechanism.
Apart from monitoring the samples as the cycles were carried out (through both naked eye and Light Microscopy[27] examinations), the effects of the ageing were evaluated using different analytical techniques.
In particular, Mid-Near FTIR reflection spectroscopy was used for assessing the chemical composition of paint layers' surfaces (monitoring, for example, the exudation process of the surfactants) and Mid-IR active thermography was used for detecting the delaminations of the paint layers. When being affected by this decay typology, the paint layers were completely peeled from the support, allowing the study of the support-paint interface through different FTIR spectroscopy techniques.
Due to the considerable amount of data, only the most relevant results are presented in detail, while the others are summarized in tables.

The results concerning the Rising Damp Ageing will be further discussed in section *3.1.2.3 Discussing results*.

FLASHE® PAINTS (LeFranc&Bourgeois)

GENERAL REMARKS

In figures 3.1-25/26/27 and 3.1-30, the aged samples are compared with the reference ones: some variations were detected through both, naked eye and Light Microscopy examinations. These variations held over time (pictures were taken some weeks after the end of the ageing).

A certain yellowing was detected in the case of the White samples (especially next to the edges). Ultramarine Blue, Yellow Ochre and Armor Green samples instead, underwent a certain darkening. The surfaces of the aged Blue and Yellow samples looked also rougher than those of the unaged ones. No significant variation were instead detected for the Ruby Red samples.

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[27] The examinations were carried out using the Olympus SZX9 Microscope.

It is to remember that, while carrying out the cycles, the paint layers of the White, Ultramarine Blue and Yellow Ochre mock-ups were clearly permeable to liquid water.

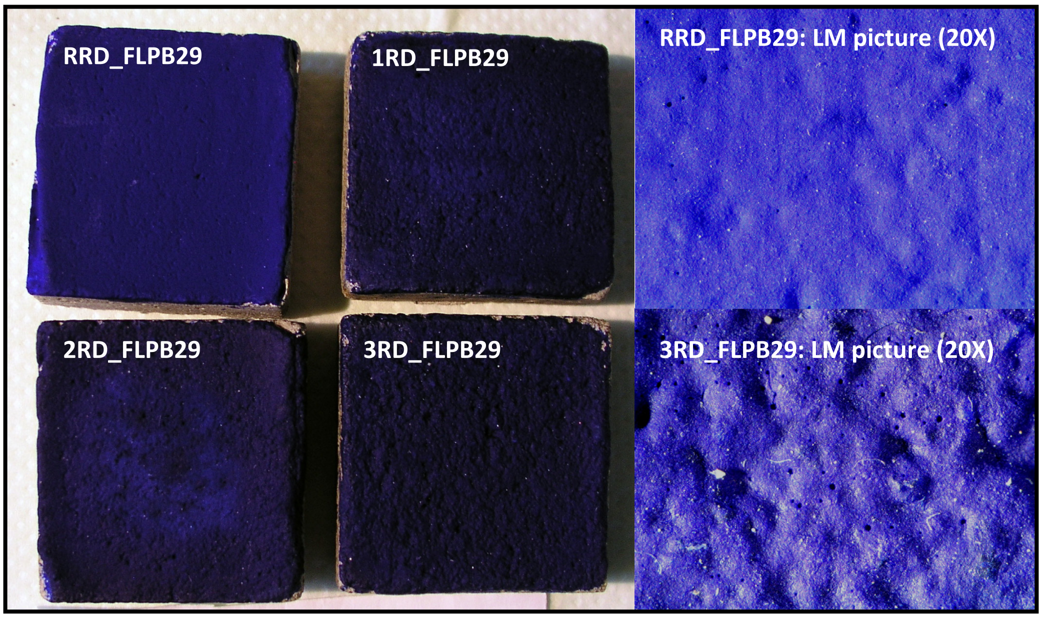

Fig.3.1-25: Samples cast using the Ultramarine Blue (PB29) Flashe® paint, after 20 rising damp cycles. As clearly seen in the Light Microscopy pictures, the paint layers of aged samples look darker an rougher than that of the unaged one (RRD, Reference Rising Damp). Sample 2RD locally underwent a thinning of the paint layer (central lighter areas).

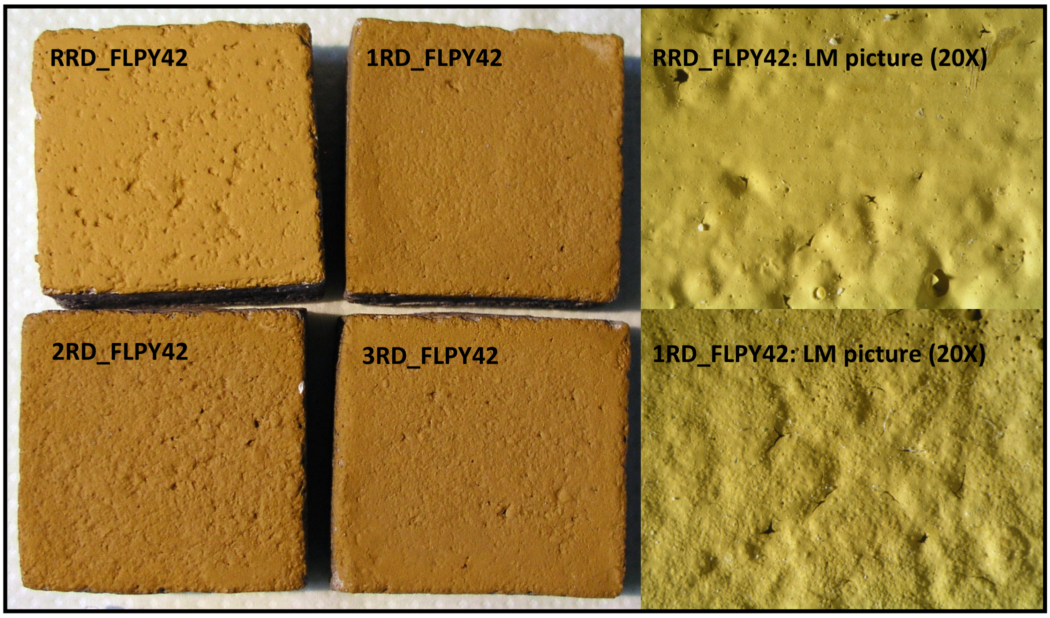

Fig.3.1-26: Samples cast using the Yellow Ochre (PY42) Flashe® paint, after 20 rising damp cycles. As also highlighted in the LM pictures, the aged samples look slightly darker and show a rougher surface than the reference one (RRD, Reference Rising Damp).

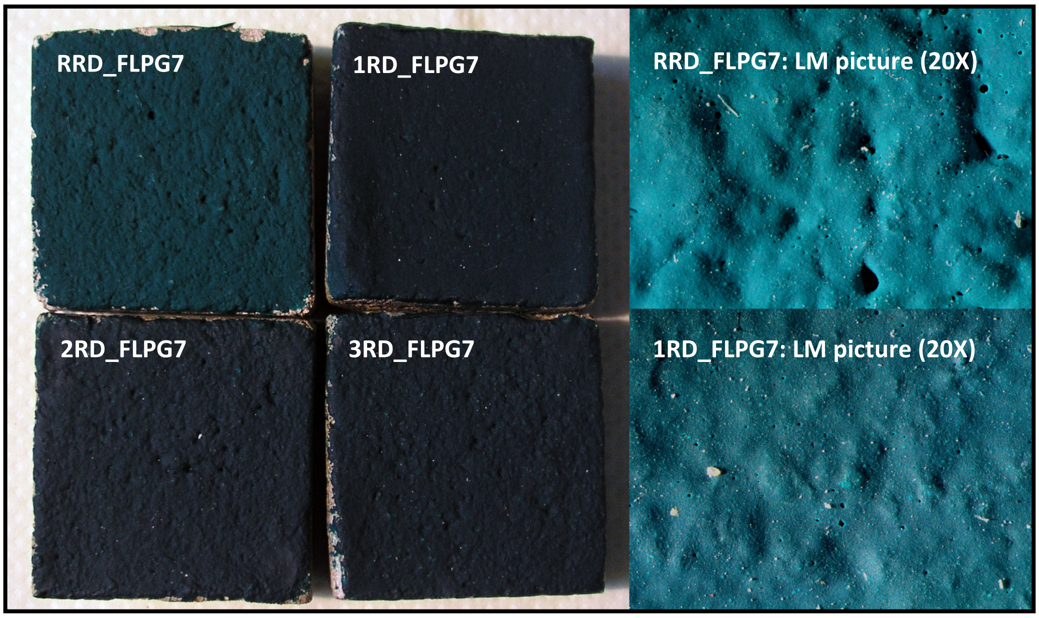

Fig.3.1-27: Samples cast using the Armor Green (PG7) Flashe® paint, after 20 rising damp cycles. The aged samples look darker than the RRD (Reference Rising Damp) one, which was not subjected to the ageing.

Mid-Near FTIR REFLECTION SPECTROSCOPY ANALYSIS

At the end of the ageing, the chemical composition of samples' surfaces was assessed using Mid-Near FTIR reflection spectroscopy.

As pointed out when presenting the *Investigation techniques* (section 2.4.1.1), the reflection spectra collected from the surface of real objects are affected by large distortions, both in bands shape and position. In order to make the interpretation of the spectra from the aged surfaces easier, the reflection spectra of the reference samples were collected as well.

By way of example, only the spectrum of the White sample (RRD_FLPW6) is shown here (Fig. 3.1-28): to highlight the reflection spectral distortions, it is compared with the respective Mid-FTIR ATR spectrum.[28]

The main absorptions related to the vinyl binder (p(VAc-VeoVA)) are marked by dotted lines. As pointed out elsewhere,[29] in the MIR spectral region, the principle diagnostic features shown by the reflection spectrum of a vinyl binder are: two derivative shaped bands around 1025 cm^{-1} and 1045 cm^{-1} due to C-C stretching of the polymer backbone; a mixed derivative/inverted band around 1240 cm^{-1} related to the C-O-C symmetric

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[28] The elaboration of the spectrum, collected using the Vertex 70 spectrometer in ATR mode, included the conversion from Attenuated Total Reflection to Absorbance.

[29] Karhim's PhD thesis (2009-10)

stretching;[30] a derivative shaped band at about 1375cm^{-1}; a derivative shaped band around 1740 cm^{-1} (C=O stretching) and some derivative distortions associated with the C-H stretching vibrations.

The straight lines mark the features assigned to the extender (calcium carbonate, $CaCO_3$): the ν_2 band (around 873 cm^{-1}) and the ν_3 band (around 1400 cm^{-1}) are inverted and appear as minima; the ν_1+ν_3 band (at approximately 2515 cm^{-1}) and the ν_1+ν_4 feature (around 1796 cm^{-1}) are also present and particularly pronounced. These latter combination bands are diffuse reflectance dependant, so that they remain positively shaped.

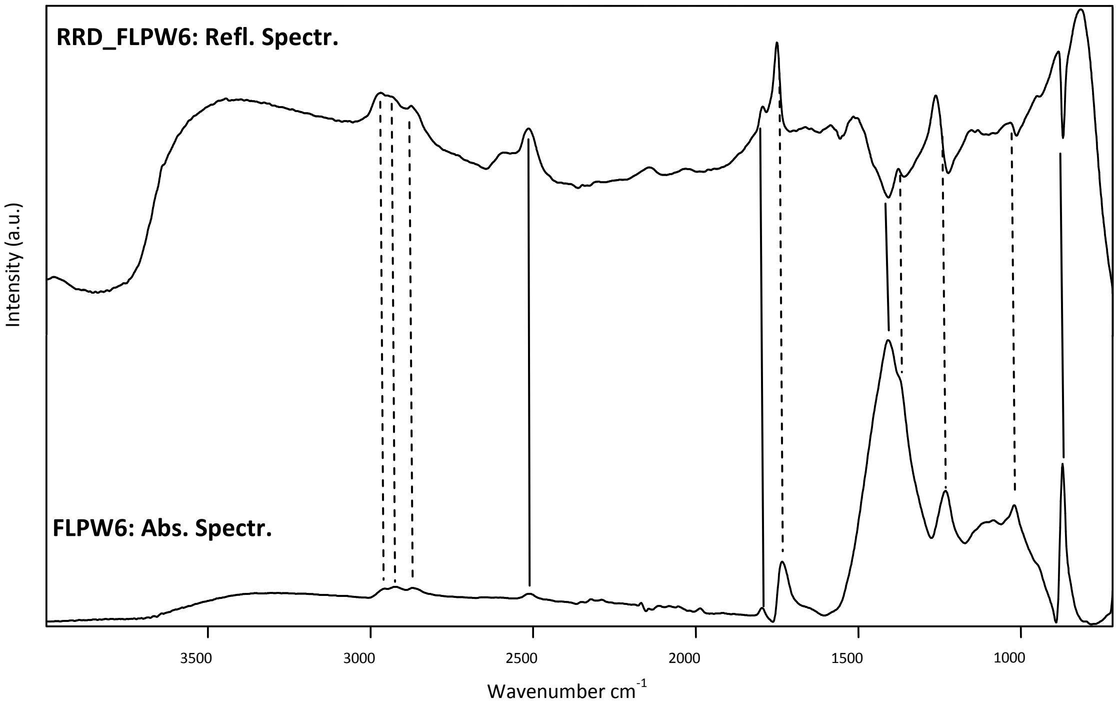

Fig. 3.1-28: Comparing the corrected Mid-FTIR ATR spectrum (FLPW6, below) with the Mid-reflection spectrum (RRD_FLPW6, above) from the reference White Flashe® paint. Dotted lines mark the features of the vinyl binder while straight lines those assigned to the calcium carbonate extender.

The data collected from the surface of the samples using FTIR reflection spectroscopy are summarized in the following table (Tab.3.1-31), which also displays the results coming from the other analytical techniques: the surfaces of the samples were examined through naked-eye (using also raking-light) and Light Microscopy; Mid-IR active thermography was used to detect the delaminations of the paint layers; to assess the cause of these delaminations, FTIR spectroscopy analysis were carried out (using different set-ups) to investigate the film-support interface.

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[30] The feature at about 1240 cm^{-1} is present in both acrylic and vinyl polymers, but it may be distinguished upon the nature of the distortion: the mixed derivative/inverted shape of the band is diagnostic for the vinyl resin.

ID Cod	Examinations	Mid-IR Thermography FTIR Spectroscopy Support-Paint layer Interface	Surface Reflection Spectroscopy
1RD_FLPW6	Surface yellowing; from the 17th cycle on local paint layer delaminations	Local Delaminations Support-Paint Layer Interface: gypsum	Gypsum (?)
2RD_FLPW6			-
3RD_FLPW6			Gypsum close to yellow areas
1RD_FLPB29	Darkening; increment of surface roughness.	No delaminations	-
2RD_FLPB29	Darkening; increment of surface roughness, local paint layer thinning.		Gypsum (only close to the edges)
3RD_FLPB29	Darkening; increment of surface roughness		Gypsum
1RD_FLPY42	Slight darkening	No delaminations	Gypsum
2RD_FLPY42			
3RD_FLPY42			
1RD_FLPV19	-	No delaminations	-
2RD_FLPV19			Traces of gypsum (?)
3RD_FLPV19			Traces of gypsum (?)
1RD_FLPG7	Darkening	No delaminations	-
2RD_FLPG7			
3RD_FLPG7			

Tab. 3.1-31: The table summarizes the main results coming from the ageing of Flashe® samples (20 distilled water absorption cycles simulating the rising damp mechanism). The variations detected through naked eye and Light Microscopy examinations are reported, together with the results of Mid-IR active thermograhy, Mid-Near FTIR reflection spectroscopy and FTIR spectroscopy analysis carried out at the paint layer-support interface. Hyphen is used when no changes were detected. The question mark is used when the interpretation is uncertain.

No evidences of paints' water soluble components (e.g. the APE surfactant, the cellulose derivative) were detected on the surface of the samples.

Comparing the Mid-Near FTIR reflection spectrum of the White reference sample (RRD_FLPW6) with the spectra of the aged samples, some minor changes were seen: the spectra from 1RD_FLPW6 and 3RD_FLPW6 samples (yellow areas) presented an additional small band around 1120 cm^{-1}, probably due to the stretching of a SO_4 group.

As displayed in figure 3.1-29, the presence of gypsum ($CaSO_4 \cdot 2H_2O$) was detected on the surfaces of the three Yellow Ochre samples.
The most diagnostic features of gypsum are highlighted by arrows. Apart from the strong asymmetric stretching of the SO_4 group appearing as an inverted band around 1150 cm^{-1}, the presence of gypsum is revealed by some of its second-order modes, that

are not distorted by reflection (SO_4^{2-} and OH overtones in the 1900÷2700 cm^{-1} region an combinations bands in the 5000÷6000 cm^{-1} region). [31]

The combination $\nu_1+\nu_3$ gives rise to a system of bands positioned at 2114 and 2132 cm^{-1}. The $2\nu_3$ band is instead covered by a strong and broad band at 2230 cm^{-1}, possibly due to the combination of bending and libration modes of water ($\nu_1+\nu_L$).

In addition to these sulfate combination features, the bands due to the combinations of water stretching ($\nu_1$and/or ν_3) and bending modes (ν_2) are shown at 5140 and 5054 cm^{-1}. Other modes related to water vibrations (ν_2 doublet around 1620 and 1685 cm^{-1}; and the broad band in the stretching region usually characterized by features at 3240, 3405, 3494 and 3550 cm^{-1}) or sulfate vibrations (ν_4 about 603 and 670 cm^{-1}) are here barely detectable.

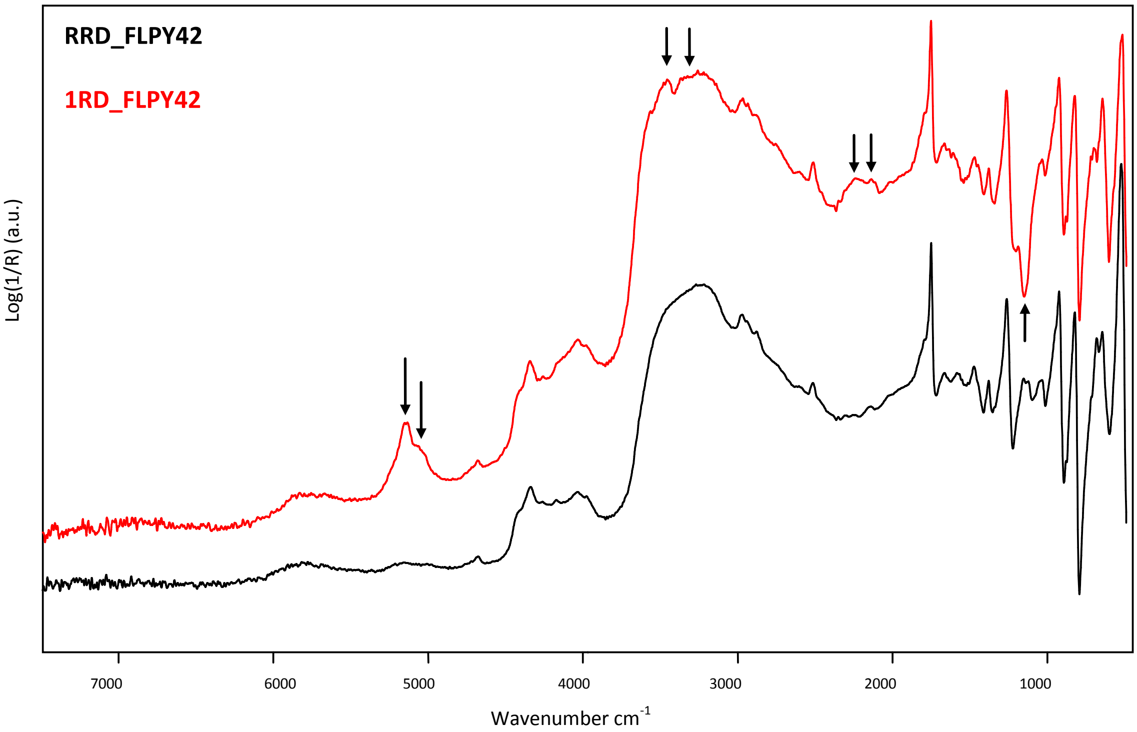

Fig. 3.1-29: Comparing the Mid-Near Reflection spectra collected from unaged (RRD_FLPY42, black) and aged (1RD_FLPY42, red) Yellow Ochre samples (Flashe®). Arrows point out those features related to gypsum ($CaSO_4 \cdot 2H_2O$).

The presence of gypsum was detected also on the surface of two of the Ultramarine Blue samples, 3RD_FLPB29 and 2RD_FLPB29 (only next to the edges in this latter case).

No relevant variations were instead detected on the surfaces of the Armor Green and Ruby Red samples.

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[31] Rosi *et al.* (2010) pointed out that, using FTIR reflection spectroscopy, second-order modes (being highly specific, reliable and less affected by overlapping with organic binders' bands) can be properly used for identifying sulfate hydration phase, allowing distinctions between gypsum, bassanite and anhydrite.

PAINT LAYERS' DELAMINATIONS

Raking light examinations and Mid-IR active thermography pointed out that, the only Flashe® samples undergoing a partial delamination of the paint layer were those cast using the White paint. This decay typology started with the 17th rising damp cycle and worsened during the last three cycles, leading to the situation shown in figure 3.1-30.
The delaminations actually affected very small areas (diameters in the 40μm÷120μm range), and were barely detectable through Mid-IR thermography.[32]

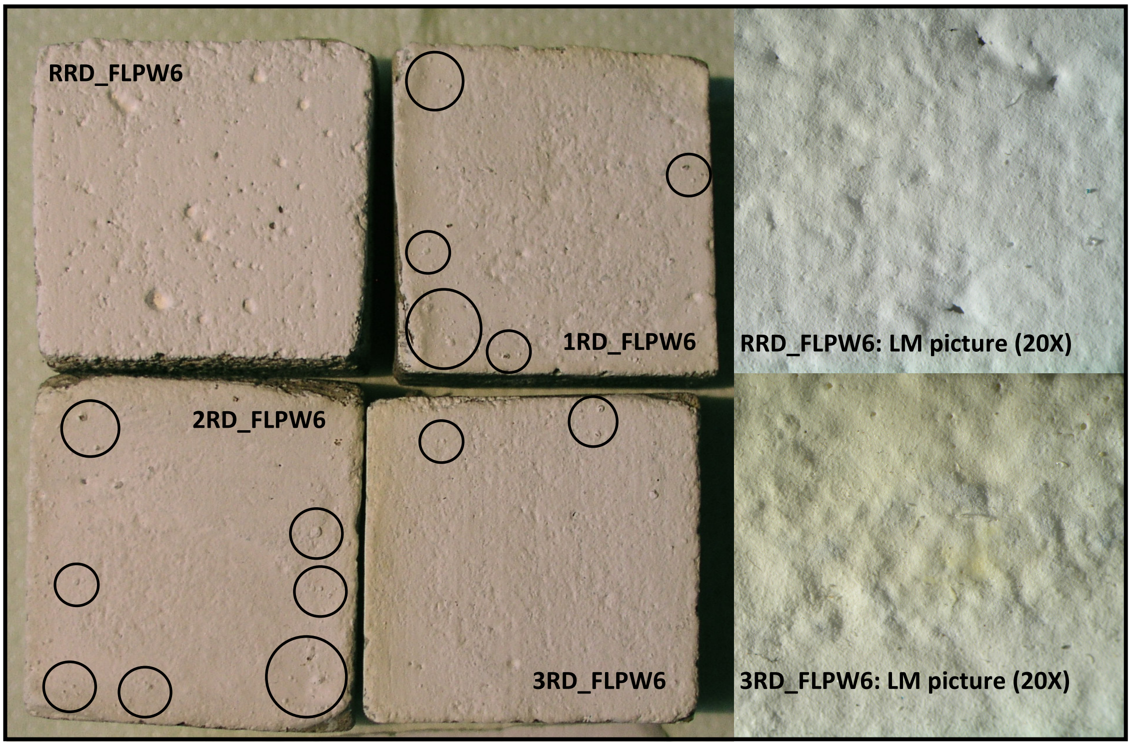

Fig.3.1-30: Samples cast using the White (PW6-PW5) Flashe® paint, after 20 rising damp cycles. The black circles point out some of the delaminations (affecting very small areas). Samples 1RD (upper horizontal edge) and 3RD (left vertical edge) show some surface yellowing. This yellowing is clearly seen in the LM pictures. The RRD (Reference Rising Damp) sample was not subjected to the ageing.

In order to assess the cause of delaminations, the interface between the mortar support and the paint layer was investigated using different FTIR spectroscopy techniques. When areas affected by the delamination were large enough, the paint layer was completely peeled off and the interface was explored through μFTIR reflection spectroscopy.
This was the case of 2RD_FLPW6 sample.
The main absorptions presented by the spectra acquired both, on the back of the peeled paint layer and on the surface of the support, are related to the cement-lime mortar support components (cement-lime binder and sand).

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[32] The thermal response is influenced by the chemical composition of the paint layer (mainly due to pigments nature and thermal conductivity). In this case, the poor quality of the images stacked from the video acquired during the cooling process is due to the low thermal conductivity of Titanium White pigment, as well as to the small dimension of the delaminated areas (small air volumes beneath the paint layer).

No evidences of organic additives (like surfactant) were detected, with some features in the spectrum collected from the mortar support which are instead due to gypsum.

In order to better investigate the interface, further FTIR spectroscopy analysis were carried out: the back of the delaminated paint layer was analyzed using ATR-FTIR spectroscopy; the mortar support was partially scraped and analyzed through Transmission FTIR spectroscopy (this latter spectrum is shown in figure 3.1-31).[33]

In both cases the presence of gypsum was confirmed.

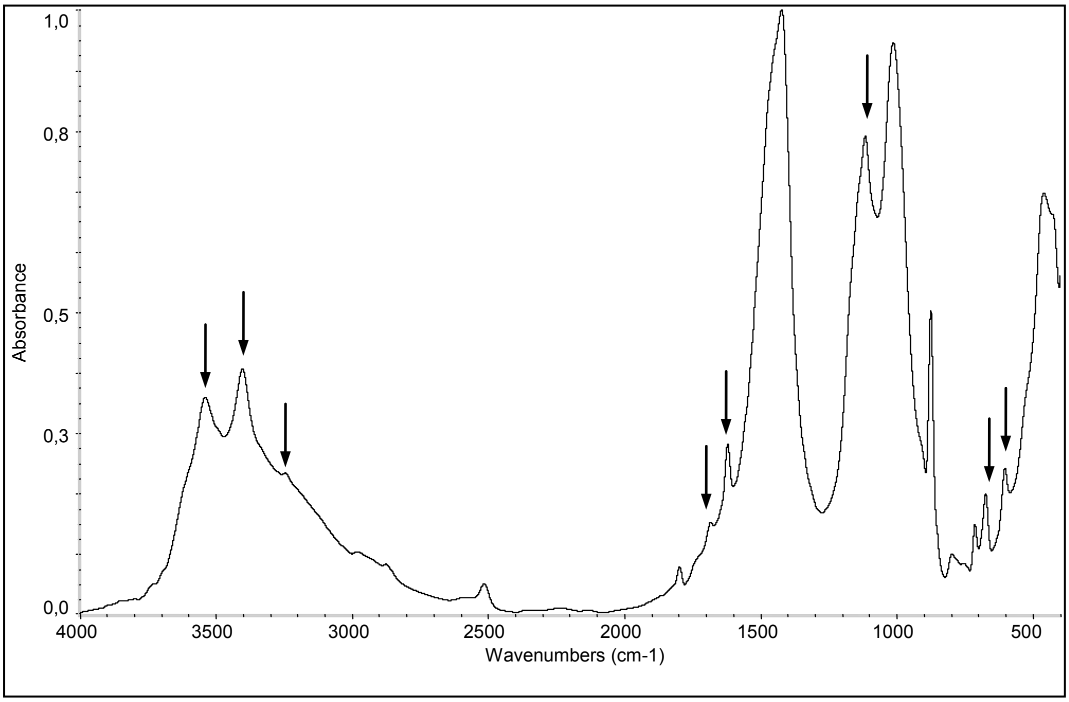

Fig.3.1-31: 2RD_FLPW6 sample, FTIR spectrum of the mortar beneath one of the delamination. Arrows point out those features related to gypsum ($CaSO_4 \cdot 2H_2O$).

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[33] The FTIR transmission analysis were carried out on KBr micropellets, using a Nicolet Nexus 670 spectrometer (spectral range: 4000-400 cm^{-1}, 64 scans, resolution of 4 cm^{-1}).

HEAVY BODY PAINTS (Liquitex®)

GENERAL REMARKS

The main variations detected through naked eye and Light Microscopy examinations for the Heavy Body-Liquitex® samples are displayed in figures 3.1-32/33/34/39 and 3.1-41). As already seen for Flashe® samples, these variations held over time.

Apart from local delaminations, no significant variations were detected for the Titanium White samples.

The ageing of 1RD_LQPB29 sample (Ultramarine Blue paint) was stopped at the end of the 3rd rising damp cycle, because of the surface appearance of a patchy translucent layer. The other blue samples (2RD and 3RD) were instead subjected to 20 rising damp cycles, which caused a partial thinning of the paint layers and the surface appearance of some white material.

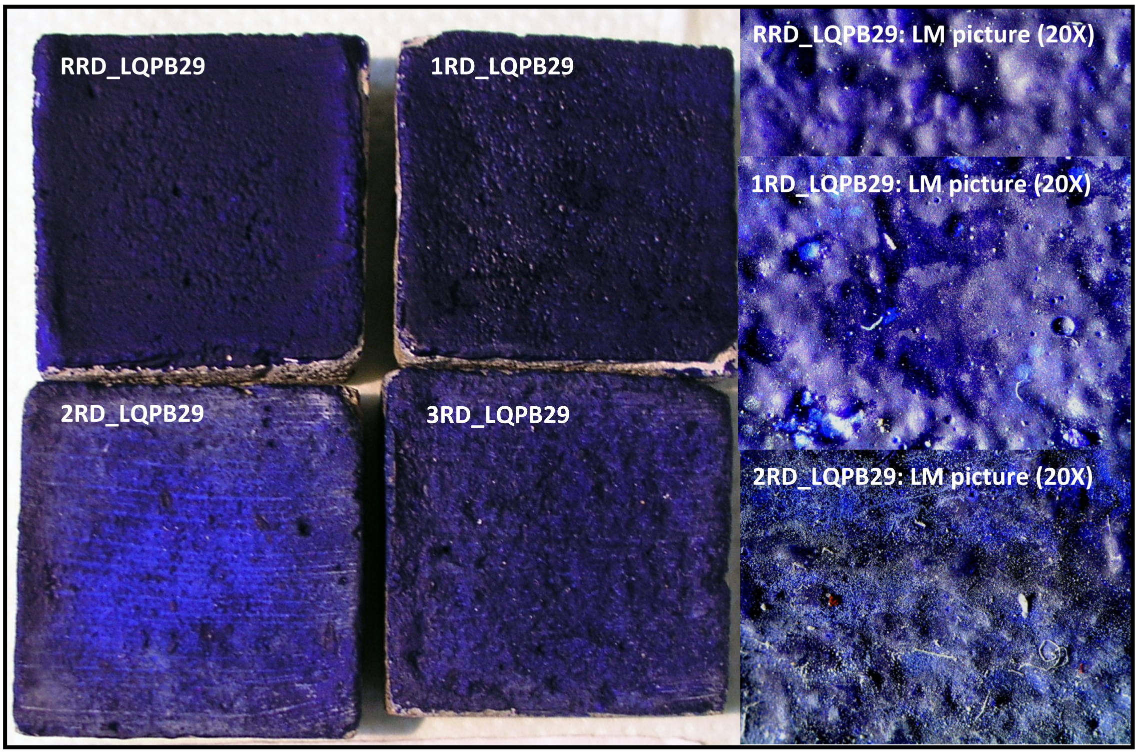

Fig.3.1-32: Samples cast using the Ultramarine Blue (PB29) Heavy Body-Liquitex® paint, after 20 rising damp cycles. Starting from the 3rd cycle, patchy layers of a translucent material (later identified as an APE surfactant) appeared on the surface of sample 1RD. The other samples (2RD and 3RD) locally underwent a thinning of the paint layer (lighter areas) and showed some white material on their surfaces (later identified as a mixture of calcium carbonate and gypsum).

The ageing of 1RD_LQPY42 sample (Transparent Raw Sienna paint) was stopped at the end of the 12th rising damp cycle, because of the surface appearance of some white material (see Fig. 3.1-41). A total of 20 cycles were instead carried out for the other yellow samples (2RD and 3RD), with the ageing resulting in: matter paint layers, the surface appearance of some white material and local delaminations.

Upon ageing, the surfaces of the samples cast with the Quinacridone Crimson paint (PV19), became matter and slightly lighter than that of the unaged sample. Light Microscopy examinations actually pointed out the presence of both, translucent areas and some white material.

Even though no relevant macroscopic variations were detected for the Phthalocyanine Green samples (PG7), Light Microscopy examinations pointed out that the surfaces of the aged samples were matter than that of reference one and were characterized by some white material.

During the ageing, the paint layers of all the samples showed a certain permeability to liquid water: while carrying out the rising damp cycles, drops of water were actually seen on the surfaces of the samples .

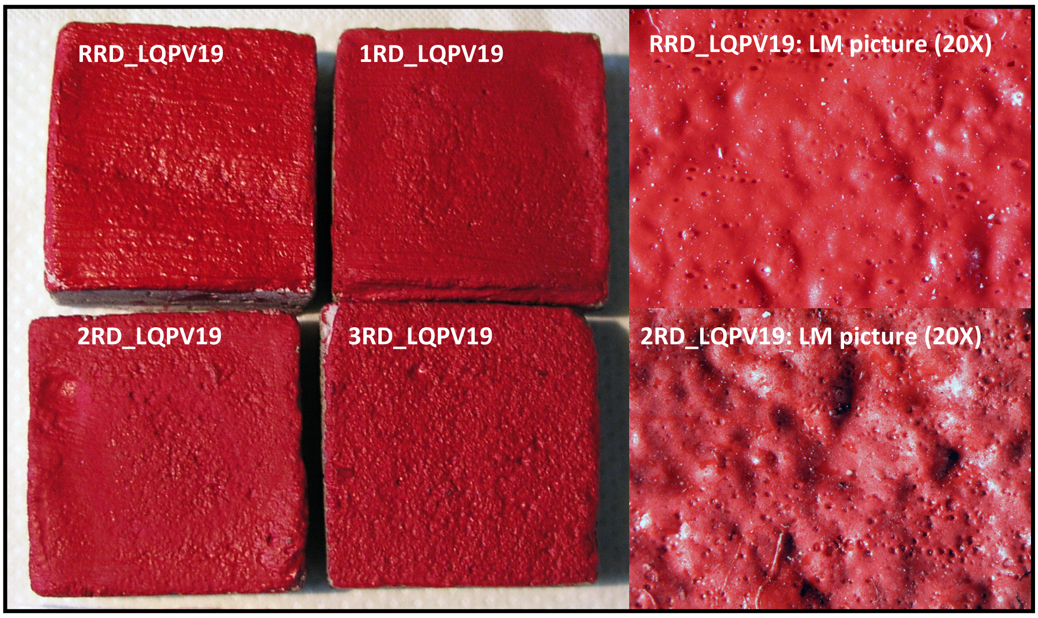

Fig.3.1-33: Samples cast using the Quinacridone Crimson (PV19) Heavy Body-Liquitex® paint, after 20 rising damp cycles. As can be seen in the Light Microscopy pictures, the paint layers of aged samples look matter and slightly lighter than that of the reference sample. Moreover, aged surfaces are affected by the presence of some translucent material (mainly ascribable to an APE surfactant) together with some white material (especially in the case of 2RD sample, later identified as calcium carbonate).

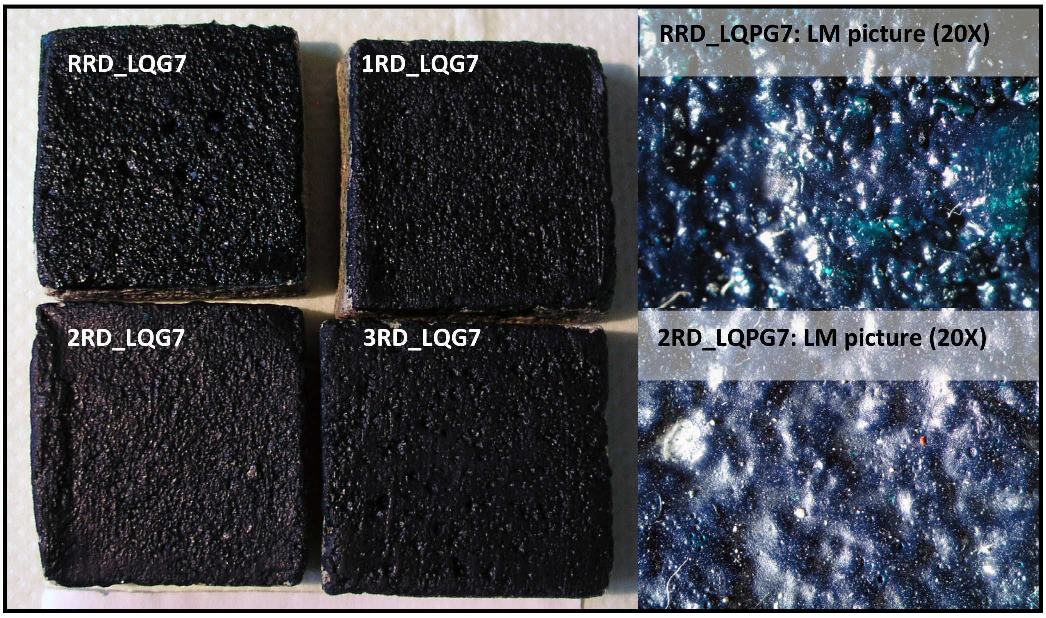

Fig.3.1-34: Samples cast using the Phthalocyanine Green (PG7) Heavy Body-Liquitex® paint, after 20 rising damp cycles. The ageing does not result in decay features which can be detected at a macroscopic level but, Light Microscopy examinations, point out that the surfaces of the aged samples are slightly matter and affected by the presence of some white material.

Mid-Near FTIR REFLECTION SPECTROSCOPY ANALYSIS

Even in this case, the variations of the surface chemical composition were assessed through Mid-Near FTIR reflection spectroscopy. The reflection spectra were collected from aged and reference samples.

The reflection spectrum from the Titanium White reference (RRD_LQPW6) is presented in figure 3.1-35. To highlight the spectral distortions, it is compared with the corresponding Mid-FTIR ATR spectrum, with the main absorptions related to the acrylic binder (p(*n*BA-MMA)) marked by dotted lines.

As pointed out elsewhere,[34] when considering the MIR spectral region, the principle diagnostic features shown by the spectrum of an acrylic binder acquired in reflection mode are: two derivative shaped band around 1025 cm^{-1} and 1065 cm^{-1} due to the C-C stretching of the polymer backbone;[35] a derivative shaped band around 1150 cm^{-1} related to –C(=O)-O asymmetric stretching; a derivative shaped band at about 1175 cm^{-1} due to C(=O)O-C asymmetric stretching;[36] two derivative bands around 1240 cm^{-1} and 1270 cm^{-1} related to C-O-C symmetric and asymmetric stretching;[37] a derivative shaped band around 1390 cm^{-1} due to the methyl symmetric bending of COOR moieties; a

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[34] Karhim's PhD thesis (2009-10)

[35] These two absorptions are not always detected due to medium-strength vibration. In this case only the latter was detected (at 1065 cm^{-1}).

[36] Not always seen for Heavy Body (Liquitex®)paints.

[37] In this case only the first was detected (at 1240 cm^{-1}).

derivative shaped band around 1733 cm^{-1} (C=O stretching), and some derivative bands associated with the C-H stretching vibrations.

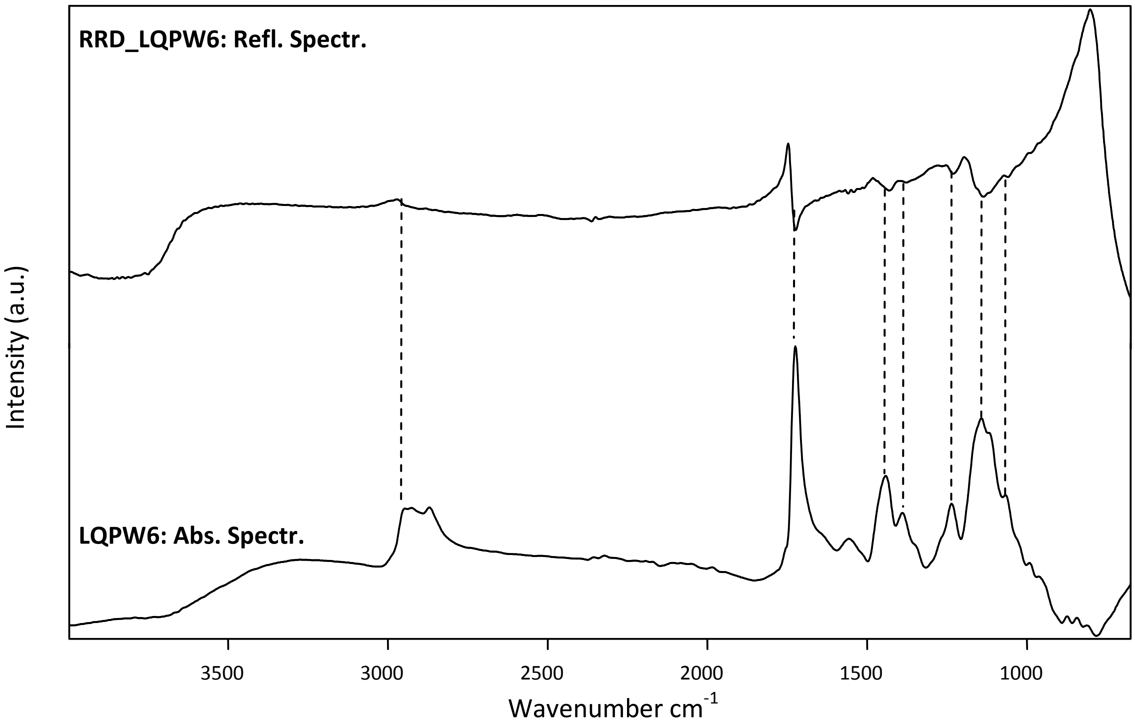

Fig. 3.1-35: Comparing the corrected Mid-FTIR ATR spectrum (LQPW6, below) with the Mid-reflection spectrum (RRD_LQPW6, above) from the reference Titanium White, Heavy Body-Liquitex® paint. Dotted lines mark the main features assigned to the acrylic binder.

The data collected from the surface of the samples using FTIR reflection spectroscopy are summarized in the following table (Tab.3.1-32), which also displays the results gathered using the other analytical techniques. Even in this case, the paint surfaces were examined through naked-eye (using also raking-light) and Light Microscopy; Mid-IR active thermography was used to detect the delaminations of the paint layers and FTIR spectroscopy analysis were carried out to investigate the film-support interface.

ID Cod	Observations	Mid-IR Thermography FTIR Spectroscopy Support-Paint layer Interface	Surface MIR-Reflectance Spectroscopy
1RD_LQPW6	Delaminations from the 17th cycle on	Delaminations Support-Paint Layer Interface: gypsum	Gypsum; APE surfactant (traces)
2RD_LQPW6			$CaCO_3$, gypsum; APE surfactant (traces)
3RD_LQPW6			$CaCO_3$; Gypsum
1RD_LQPB29	Ageing stopped at the 3rd cycle because of the appearance of some transluscent material on the surface	No delaminations	APE surfactant; CaCO3
2RD_LQPB29	Thinning of the paint layer; discoloration; white material on the surface		Central area: $CaCO_3$ and Gypsum(?) Close to the edges: different amounts of $CaCO_3$ and Gypsum (close to one of the edges traces of APE surfactant?)
3RD_LQPB29			Central area: $CaCO_3$ and Gypsum; traces of APE surfactant (?) Close to the edges: different amounts of $CaCO_3$ and Gypsum; (close to one of the edges traces of the APE surfactant)
1RD_LQPY42	Ageing stopped at the 12th cycle because of the appearance of white material on the surface	No delaminations	$CaCO_3$ and Gypsum (the latter especially close to the edges)
2RD_LQPY42	Delaminations from the 15th cycle on; the surface becomes matter	Delaminations Support-Paint Layer Interface: gypsum	$CaCO_3$ and Gypsum (the latter especially close to the edges)
3RD_LQPY42			Gypsum and some $CaCO_3$ (close to one of the edges)
1RD_LQPV19	The surface becomes matter; white and glossy material on the surface	No delaminations	APE surfactant and slight amounts of $CaCO_3$
2RD_LQPV19	White and glossy material on the surface		APE surfactant and higher amounts of $CaCO_3$ (central lighter area and close to the edges)
3RD_LQPV19	The surface becomes matter; white and glossy material on the surface		APE surfactant and slight amounts of $CaCO_3$
1RD_LQPG7	White and glossy material on the surface	No delaminations	APE surfactant; traces of $CaCO_3$
2RD_LQPG7		No delaminations	APE surfactant; traces of $CaCO_3$
3RD_LQPG7		No delaminations	APE surfactant and $CaCO_3$ (especially close to the edges)

Tab. 3.1-32: The table summarizes the main results coming from the ageing of Heavy Body-Liquitex® samples (20 distilled water absorption cycles simulating the rising damp mechanism). The variations detected through naked eye and Light Microscopy examinations are reported, together with the results of Mid-IR thermograhy, Mid-Near FTIR Reflection Spectroscopy and FTIR spectroscopy analysis carried out at the paint layer-support interface. The question mark is used when the interpretation is uncertain. APE= Alkylphenol Ethoxylate.

Mid-Near FTIR reflection analysis pointed out that, after the rising damp cycles the surface of the samples could be affected by the presence of three main compounds: an Alkylphenol Ethoxylate (APE) surfactant, gypsum and calcium carbonate.

The surfactant was detected on the surface of some samples, especially where patchy layers of a translucent material have been previously seen through naked eye and/or Light Microscopy examinations (it is the case of Quinacridone Crimson and Phtalocyanine Green samples, or of 1RD_LQPB29 Ultramarine Blue sample).

Figure 3.1-36 shows a portion of the spectra collected for two of the Quinacridone Crimson samples: while the spectrum of the reference (RRD_LQPV19, blue) presents only the features of the bulk film constituents, the spectrum of the aged sample (3RD_LQPV19, red) clearly shows the bands of the APE surfactant.

Due to the *reflectance effect*, these bands have an inverted shape, appearing as minima rather than maxima. Each minima is however in good agreement with the maxima of the absorption bands displayed by the spectrum of the paint water extracts (black).[38]

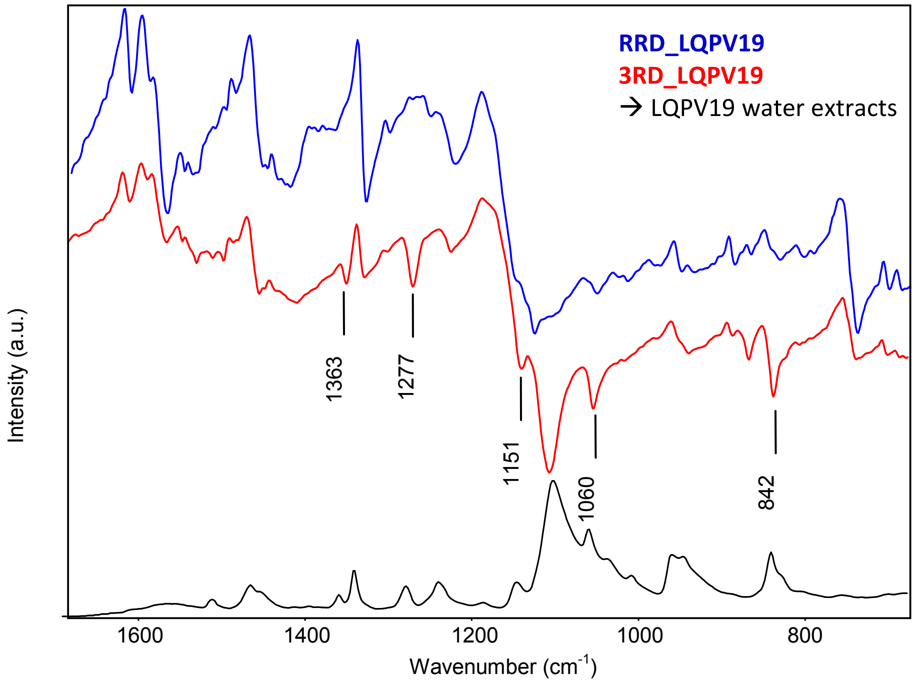

Fig. 3.1-36: Reflection Mid-FTIR spectra from Quinacridone Crimson samples. In comparison to the reference unaged sample (RRD_LQPV19, blue), the aged one (3RD_LQPV19, red) shows the typical features of the APE surfactant (in good agreement with the spectrum collected from the water extracts of the paint.

At the end of the ageing, the features related to the surfactant are clearly detectable only on the surfaces of Quinacridone Red and Phthlocyanine samples, while can be barely seen for the other samples.

It is possible that:

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[38] Data are moreover consistent with Ormsby *et al.*, 2009

- at the beginning the exudation process is promoted by water absorbing into the support and wetting the paint layers (e.g. in the case of 1RD_PB29 blue sample, 3 cycles are enough for leading to the process).
- later, as water continues to go through the paint layer, the surfactant is partially re-dissolved, and driven back into the paint film and/or the support.

This process was suggested also by the results collected from the Ultramarine Blue samples. As shown in figure 3.1-37, while the features related to the surfactant are clearly detectable on the surface of the sample that underwent 3 rising damp cycles (1RD_LQPB29, red spectrum), the same features disappear in the spectrum acquired, at the end of the 20 cycles (3RD_LQPB29, black spectrum).

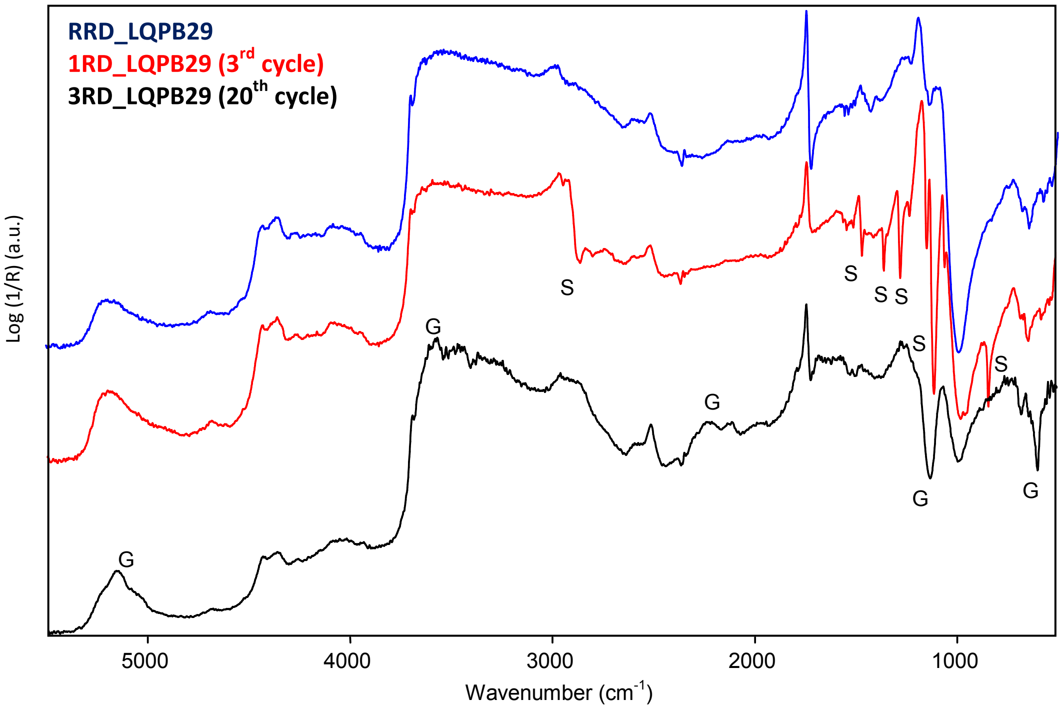

Fig. 3.1-37: Comparing the Mid-Near reflection spectra collected from unaged (RRD_LQPB29, blue) and aged Ultramarine Blue samples. The red spectrum, acquired at the end of the 3rd cycle on the surface of 1RD_LQPB29 sample, shows the features of an APE surfactant (marked by S). The black spectrum, acquired at the end of the 20th cycle on the surface of 3RD_LQPB29 sample, shows the features of gypsum (marked by G).

At the end of the ageing, calcium carbonate and gypsum[39] were often detected on the surface of the samples. This is for instance the case of 3RD_LQPB29 Ultramarine Blue sample (Fig 3.1-37) or of 1RD_LQPY42 Transparent Raw Sienna sample (Fig 3.1-38).
The presence of these compounds (as in the case of the gypsum detected on the surfaces Flashe® samples) could be due to the cement-lime mortar supports.

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[39] Sometimes absorptions related to a sulfate anion were detected but it was not possible to assign them to gypsum or to other compounds (it is the case of Titanium White samples and of some Ultramarine Blue samples).

These are actually characterized by slight amounts of water soluble components (calcium hydroxide and various sulfates)[40] which could be dissolved [41] by the rising water. As the aqueous solution went through the paint layers (which turned out to be permeable to liquid water), it led to surface carbonation and crystallization of soluble salts.

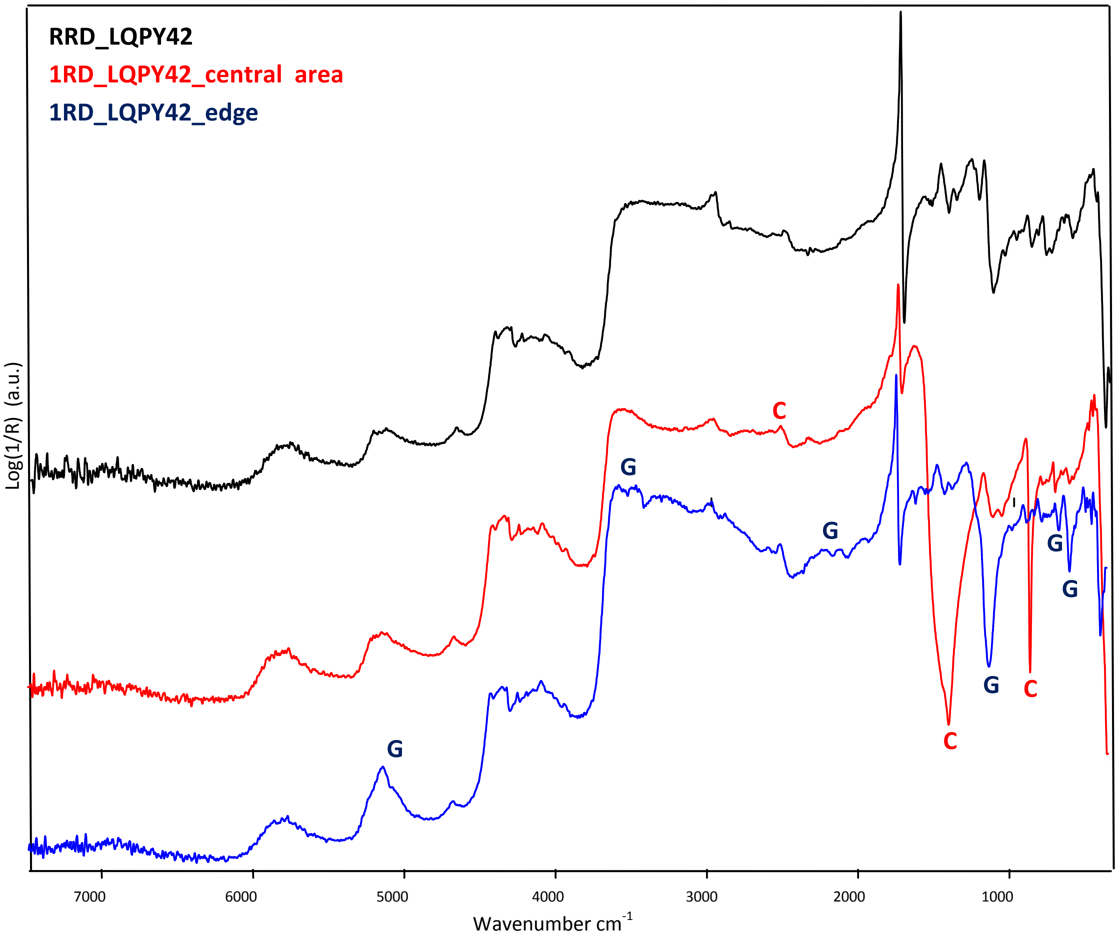

Fig. 3.1-38: Mid-Near reflection spectra collected from Transparent Raw Sienna samples: in comparison to the unaged sample (RRD_LQPY42, black) the spectrum, collected from the central area of the aged sample (1RD_LQPY42, red) shows the main features of calcium carbonate (marked with C) and slight amounts of a sulfate compound (probably gypsum). The spectrum, collected from the surface of the aged sample, close to one of the edges (1RD_PY42, blue), shows the main features of gypsum (marked by G).

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[40] Hughes., *et al.*, 1995.

[41] The solubilities (grams per 100 cc) in cold water of these inorganic compounds are: 0.241 for gypsum ($CaSO_4{\cdot}2H_2O$), 0.3 for bassanite ($CaSO_4{\cdot}1/2H_2O$), 0.25 for syngenite ($K_2Ca(SO_4)_2{\cdot}H_2O$), 0.209 for anhydrite ($CaSO_4$), 0.185 for calcium hydroxide($Ca(OH)_2$). Weast (ed.), 1976.

PAINT LAYERS' DELAMINATION

Raking light examinations and Mid-IR thermography analysis pointed out that some of the samples cast using Heavy Body- Liquitex® paints, underwent a partial delamination of the paint layer.

This decay typology was detected since the 17th rising damp cycle in the case of the Titanium White samples, since the 15th cycle for the Transparent Raw Sienna samples.

The lifting worsened during the last cycles, leading to the situation shown in figures 3.1-39 and 3.1-41.

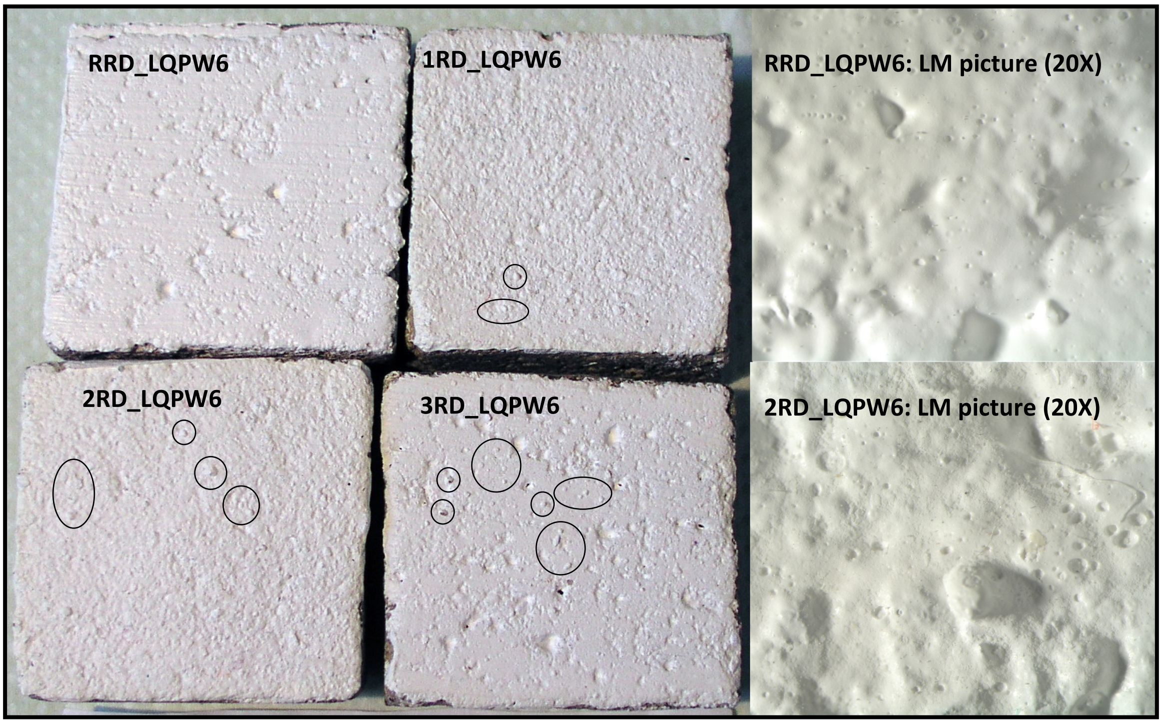

Fig.3.1-39: Samples cast with Titanium White (PW6) Heavy Body-Liquitex® paint, after 20 rising damp cycles. The black circles point out some of the delaminations (affecting very small areas). As shown in LM pictures (20X, on the right), aged and unaged surfaces are very similar.

As far as the Titanium White samples, the delaminations affected very small areas (diameters in the 50 µm ÷ 150 µm range), that were barely detectable using Mid-IR thermography.

In order to better assess the causes of the delaminations, the paint layers were completely peeled off and the interfaces between the mortar support and the paint layers were investigated using different FTIR spectroscopy set-ups:

- µFTIR reflection spectroscopy was used for exploring both the paint layers back and the mortar surface;
- ATR-FTIR spectroscopy was used for studying the back of the delaminated paint layers;

- transmission FTIR spectra (KBr micropellets) were collected for studying the surface of the mortar supports.

All the results suggested that delaminations are due to the sub-superficial crystallization of gypsum. In figure 3.1-40 the Mid-Near reflection spectrum acquired on the back of 2RD_LQPW6 paint layer is shown, together with the spectrum collected for the surface of the mortar support (beneath the delaminated area).

No evidences of paints' water soluble components (e.g. the APE surfactant) were detected at the interface.

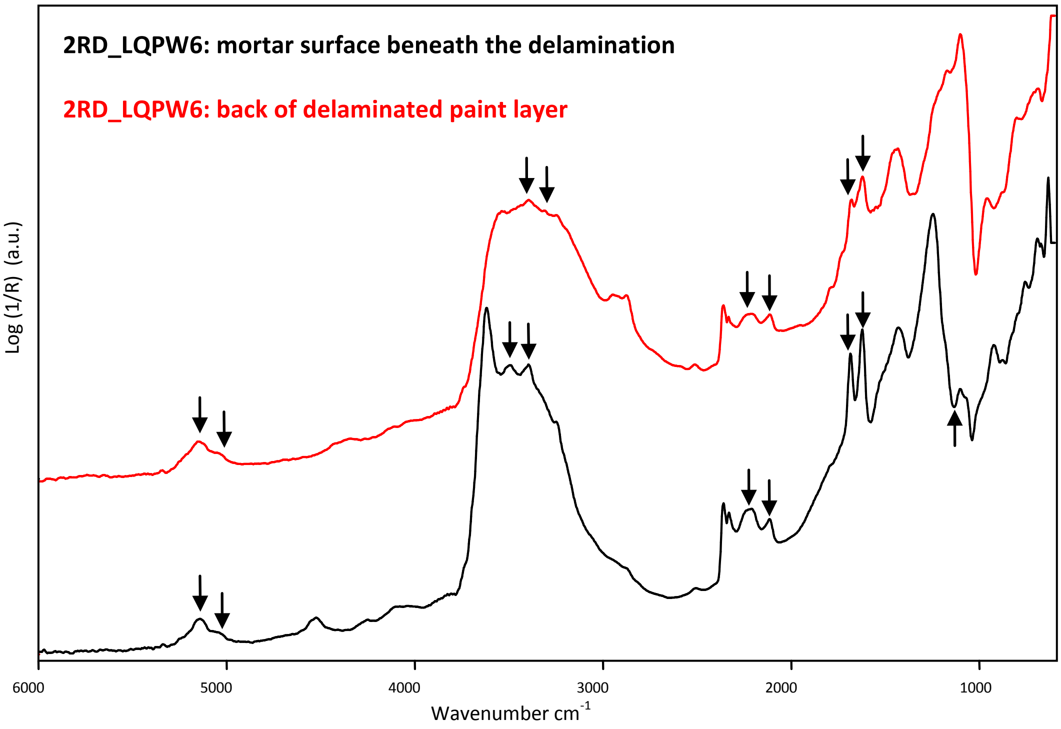

Fig. 3.1-40: Studying the interface between the support and the paint layer of 2RD_LQPW6 sample, through Mid-Near μFTIR reflection spectroscopy: in red the spectrum collected on the back of the delaminated paint layer, in black that collected on the surface of the mortar support. Arrows point out those features related to gypsum ($CaSO_4 \cdot 2H_2O$).

Figure 3.1-41 , presents the Transparent Raw Sienna samples at the end of the ageing. Even though some of the paint layer delaminations were detectable through careful naked eye and raking light examinations, their exact location was revealed by Mid-IR thermography inspections (as displayed in figure 3.1-42).

As better described in chapter 2 (section 2.4 *Investigation Techniques*) a pulse heating[42] was applied on samples surfaces, and the thermal maps sequence of the surface heat

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[42] Samples' surfaces was orthogonally illuminated with a tungsten 500W lamp, from 100 mm of distance. A pulse length of 15 s provided a temperature gradient of about 7°C that, though allowing the exact detection of subsurface defects, did not affect the properties of the paint layer: the heating lead to a

decay was acquired. The surface temperature value was affected by the reflection of the thermal waves from subsurface features, causing those anomalies that allowed the detection of defects (e.g. subsurface voids or delaminations).

In this case, thanks to the excellent resolution and high precision in the measurement of heath and temperatures provided by the thermocamera, it was possible to detect very small anomalies and to discriminate between defects down to sub-millimetric scale (diameters ranging between 50 µm and 225 µm).

It is to remember that: the larger are the delaminated areas, the larger is the volume of air underneath the paint layer. For this reason, the cooling process of these areas will last longer and, when studying the thermal maps frozen during the heath decay, delaminations involving larger volume of air will turn out as areas of higher surface temperature.

Even in this case, the support-paint layer interface was studied through different FTIR spectroscopy techniques (as already explained for white samples).
Again, data suggested that delaminations are due to sub-crystallization of gypsum and not to the presence of surfactants or other organic additives.

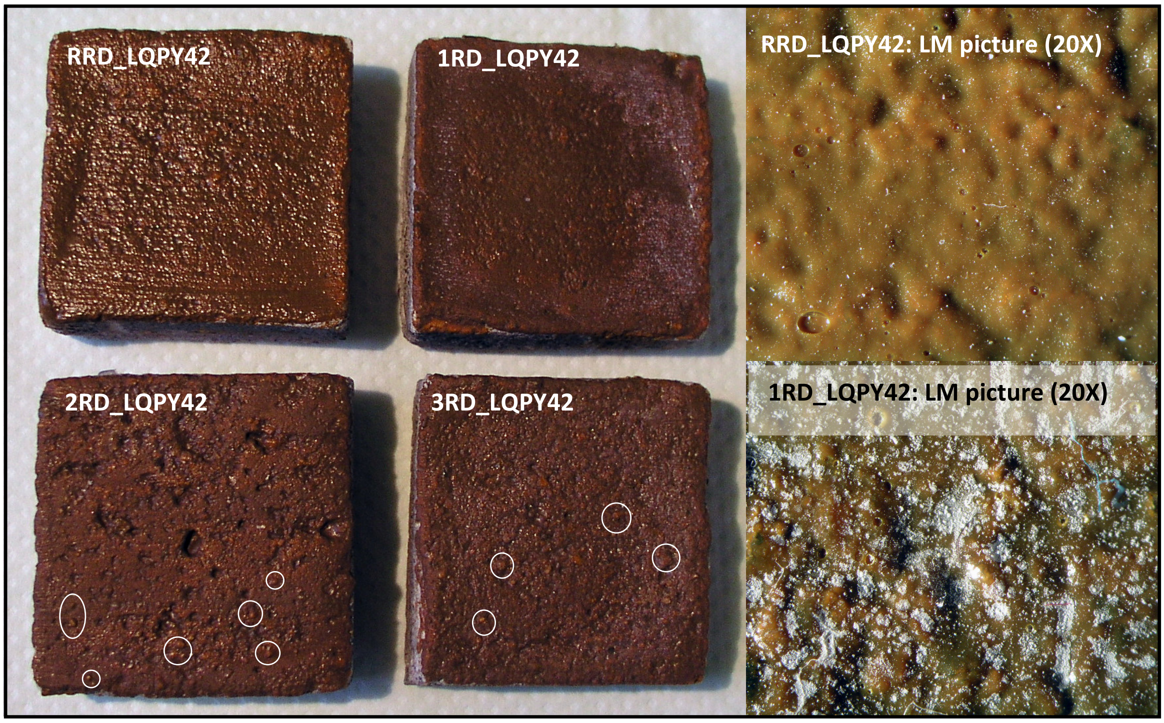

Fig.3.1-41: Samples cast using the Transparent Raw Sienna (PY42) Heavy Body-Liquitex® paint, after 20 rising damp cycles. The white circles point out some of the delaminations (affecting very small areas). As displayed in the LM pictures, the surface of 1RD sample was affected by some white material (later identified with calcium carbonate and gypsum).

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maximum of 30°C, and the cooling was very fast (the surface came back to room temperature in less than 20 s).

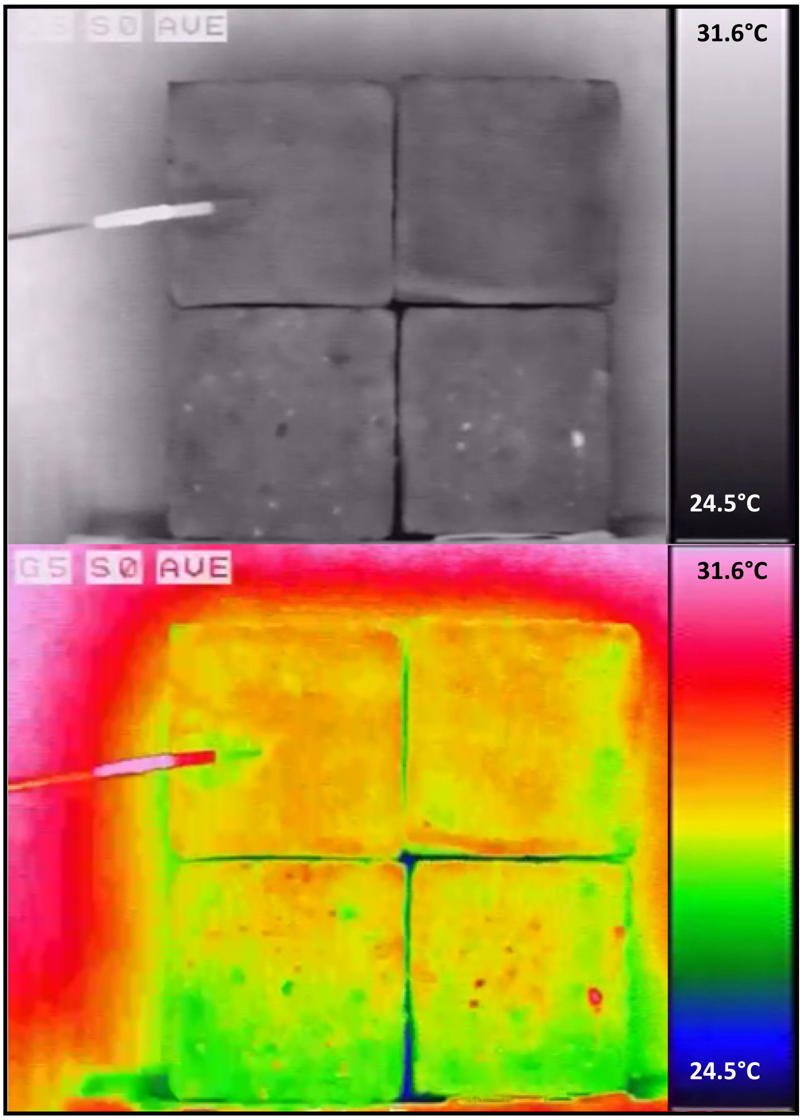

Fig. 3.1-42: Heavy Body-Liquitex®, Transparent Raw Sienna samples examined through Mid-IR active thermography. Studying the thermal maps frozen at the beginning of the cooling process it is possible to exactly detect paint layer delaminations, discriminating between defects differing in dimension (the higher the temperature, the larger the defect).

BRERA PAINTS (Maimeri®)

As a consequence of the rising damp cycles, the samples cast using Brera (Maimeri®) paints did not undergo significant decay processes.
Comparing the aged samples with the reference ones, no variations in the surface appearance were detected (nor at macroscopic nor at microscopic level).
By way of example, the comparison of the Ultramarine unaged sample to the aged ones is shown in figure 3.1-43. The macroscopic differences in the surface roughness are due to the different properties of the mortar supports.

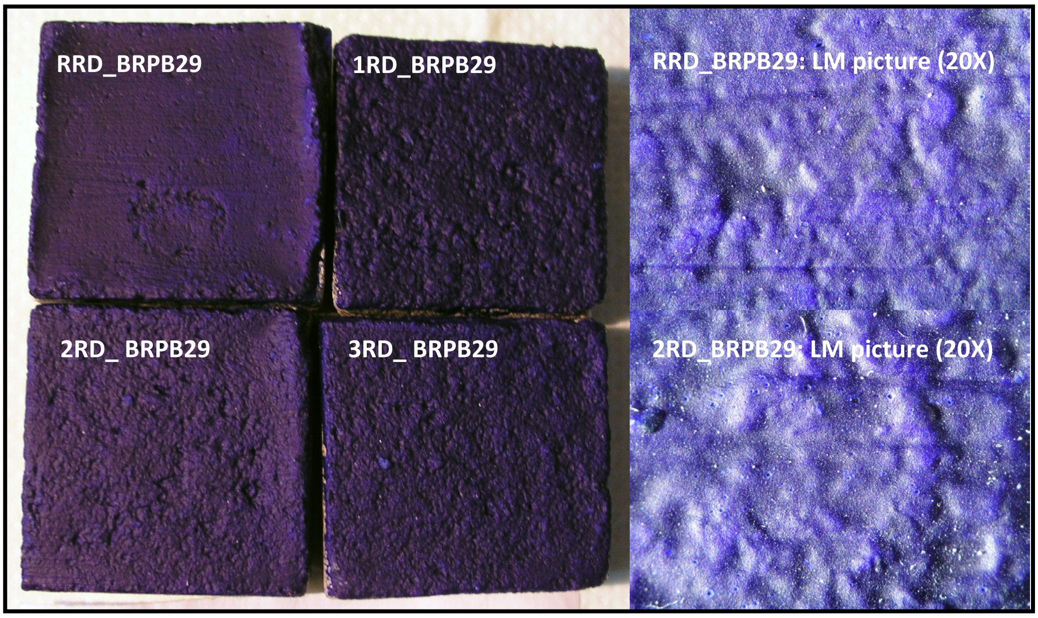

Fig.3.1-43: Samples cast using the Ultramarine (PB29) Brera (Maimeri®) paint after 20 rising damp cycles. As shown in the LM pictures, there are no significant differences in the appearance of the aged (2RD) and unaged (RRD) samples. The differences of surface roughness detectable in the raking-light macroscopic picture (on the left) are due to different roughness of the mortar supports.

Mid-Near FTIR reflection spectroscopy was used to detect the variations of surface chemical composition. The reflection spectrum from the Titanium White reference sample (RRD_BRPW6) is shown in figure 3.1-44. As usual, to better visualize the spectral distortions, the reflection spectrum is compared with the corresponding Mid-FTIR ATR spectrum, with the main absorptions related to the styrene-acrylic binder (p(*n*BMA-2EHA-styr)) marked by dotted lines.

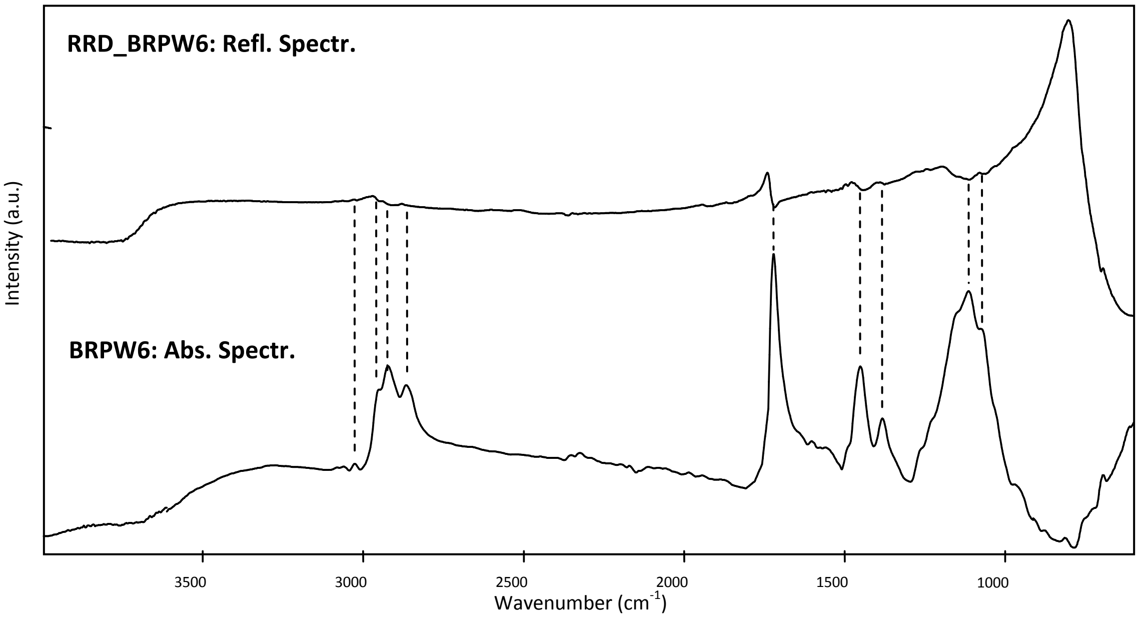

Fig.3.1-44: Comparing the corrected Mid-FTIR ATR spectrum (BRPW6, below) with the Mid-reflection spectrum (RRD_BRPW6, above) collected for the reference Titanium White, Brera-Maimeri® paint. Dotted lines highlight the features related to the styrene-acrylic binder.

When considering the MIR spectral region, the principle diagnostic features shown by the spectrum of the styrene-acrylic binder acquired in reflection mode are: two derivative shaped bands around 700 cm^{-1} and 760 cm^{-1} due to aromatic C-H out-of-plane bending;[43] two derivative shaped bands around 1070 cm^{-1} and 1120 cm^{-1} respectively related to the C-C stretching and C-O stretching of the acrylic monomer; a derivative shaped band around 1390 cm^{-1} due to the methyl symmetric bending in COOR acrylic monomer; a derivative shaped band around 1455 cm^{-1} due to the methyl asymmetric bending coupled with methylene bending (acrylic monomer); a derivative shape band around 1725 cm^{-1} (C=O stretching); some derivative bands associated with aliphatic C-H stretching vibrations (around 2925 cm^{-1} and 2955 cm^{-1}) and some positive absorptions due to aromatic stretching vibrations (e.g. that at 3030 cm^{-1}).

The spectra collected on the surfaces of the aged samples perfectly overlap the reference ones, there is no evidence of surfactant/organic additives exudation nor of salt crystallization on paint surface. As an example, the FTIR reflection spectra of RRD_BRPB29 and 2RD_BRPB29 samples are compared in figure 3.1-45.

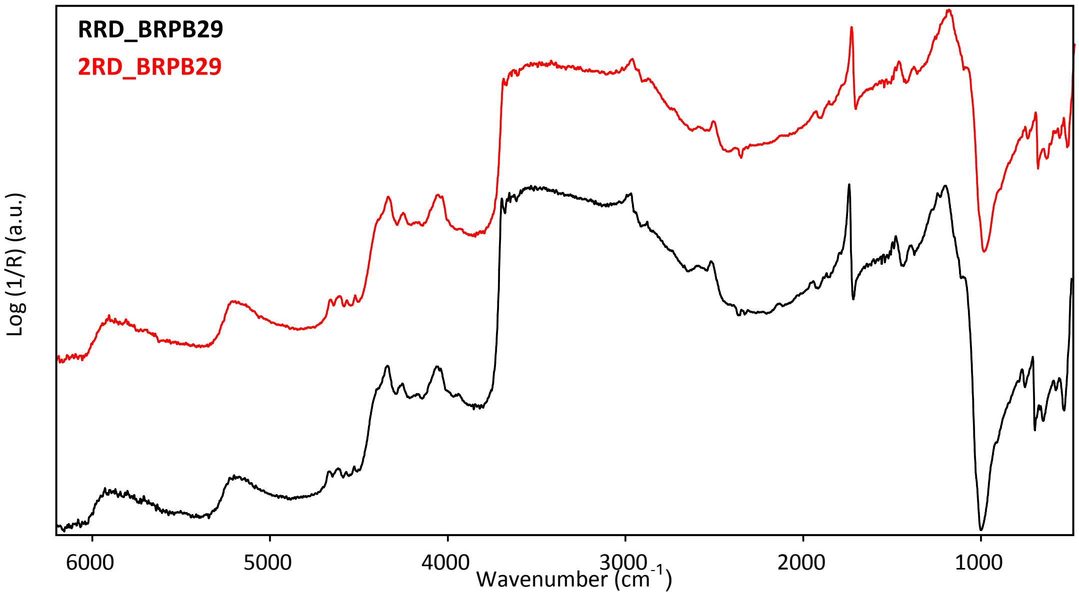

Fig. 3.1-45: The Mid-Near reflection spectra of the unaged (RRD_BRPB29, black) and aged Ultramarine samples (2RD_BRPB29, red) do not present significant differences.

In addition, raking light examinations and Mid-IR thermography analysis did not point out any paint layer delamination.

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[43] These two absorption cannot be seen in spectra shown in Fig 3.1-44 because of the overlapping of the broad absorption due to the Titanium White pigment.

3.1.2.2 UV-light stability testing

As described in Chapter 2 (section *2.3.2 UV-light stability testing*), a total of 15 samples were subjected to 800h of UV-light exposure (UVA-340 lamps, temperature 45°C).
During the ageing process, the occurrence of any chemical or physical variation was assessed through different analytical techniques: FTIR spectra were collected every 100h; colorimetric measurements were carried out every 200h; while the paint layer morphology was studied using Light and Scanning Electron Microscopy, every 400h.

The results of the UV-light stability tests are presented, and briefly discussed for each one of the artists paints’ brand included in the study (Flashe®-LeFranc&Bourgeois; Heavy Body- Liquitex®; Brera-Maimeri®).

A more detailed discussion of the results is given later in the text (section *3.1.2.3 Discussing results*).

FLASHE® PAINTS (LeFranc&Bourgeois)

FTIR SPECTROSCOPY ANALYSIS

The degradation processes affecting poly(vinyl acetate) resins can be followed using FTIR spectroscopy analysis.

As described in Chapter 1 (section *1.2.3.2 Photooxidative processes*), the main degradation reactions affecting a vinyl resin are:

- acetate hydrolysis
- photooxidative reactions, evolving through a series of intermediate (carboxylic acids, peracids, ketones, lactones) and radicals, which lead to chain-scissions (among which, side-chain reactions leading to the loss of methyl groups) and cross-linking reactions.

The occurrence of the first degradation mechanism is revealed by a general decrease in the intensity of the polymer absorption bands (the release of acetic acid turns out in a general loss of polymer) and the appearance of OH stretching absorptions due to the formation of poly(vinylalcohol). The evolution of the acetate hydrolysis reaction can be followed[44] evaluating the ratios: $C{=}O^{1743}/C\text{-}O^{1240}$, $C{=}O^{1743}/CH_3{}^{1374}$ and $C{=}O^{1743}/C\text{-}H^{2968,\,2935}$

The second degradation mechanism is revealed by the appearance of new absorption features: additional C=O stretching (leading to the broadening of the original ester band), O-H stretching of hydroxide and hydroperoxides (peracids) and absorptions related to C=C bonds (cross-linking). The occurrence of side-chain reactions leading to the loss of methyl groups can be also evaluated considering the C=O/C-H ratio, the

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[44] Melo, *et al.*, 2006

variations in the C-H stretching region (mainly the ν_{as} CH_3 around 2970cm^{-1}) and the changes in the intensity of the CH_3 bending absorption (around 1373 cm^{-1}).

Considering the ageing conditions used (UVA-340 lamps, temperature 45°C) the second type of degradaion was more expected than the acetate hydrolysis.

Comparing the spectra collected from Flashe® paint samples before and after ageing,[45] negligible differences were detected.

As shown in figure 3.1-46, this was particularly true for those paints formulated with organic pigments (Ruby Red, PV19 and Phthalo Green,PG7).

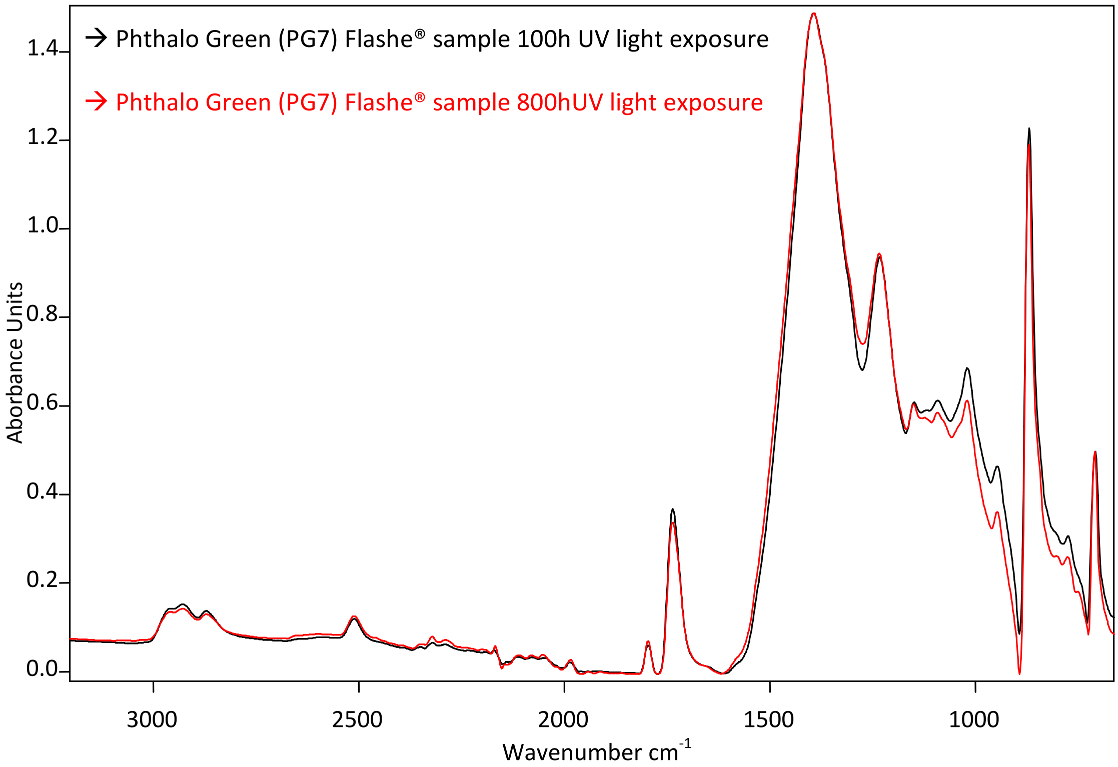

Fig. 3.1-46:Comparing two of the FTIR spectra collected from the Flashe® Phthalo Green sample at different steps of the UV-light ageing. In black the spectrum collected after 100h, in red that collected after 800h of exposure. Among the minimal spectral changes detected: slight decrements in the intensity of the absorptions due to the binder.

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[45] To monitor the chemical variations affecting the paints as a consequence of UV-light exposure, the spectra were collected from little amounts of paint scraped from the surface of the mock-ups simulating mural paintings. The Vertex 70 Fourier Transform Infrared spectrometer (Bruker Optik GmbH), equipped with ATR accessory, was used. For all the spectra the processing, carried out using OPUS 5.0 software, included: ATR→ABS conversion, automatic base line correction (Rubberband method, 64 baseline points), automatic smoothing and scale normalization. The results presented in this thesis come from a qualitative comparison of the spectra. A semi-quantitative evaluation of the degradation process will be presented in future publications.

When considering the paints based on inorganic pigments instead (White,PW5-PW6, Ultramarine Blue, PB29 and Yellow Ochre,PY42, paints), the spectral variations were slightly more pronounced.[46]

As far as the White and Yellow Ochre samples, a general decrease of the intensity in the absorptions of the polymer, suggested the occurrence of ester cleavage reactions, which probably develop according to a Norrish Type II mechanism (release of acetic acid going with the formation of double bonds in the main chain).

As can be seen in figure 3.1-47, the Ultramarine Blue (PB29) sample is the only one showing a decrement in the absorptions bands ascribed to the polymer together with a slight increase in the intensity of the OH stretching absorption and a broadening of the carbonyl band at low wavenumbers. These spectral variations probably relate to the development of photooxidative reactions.

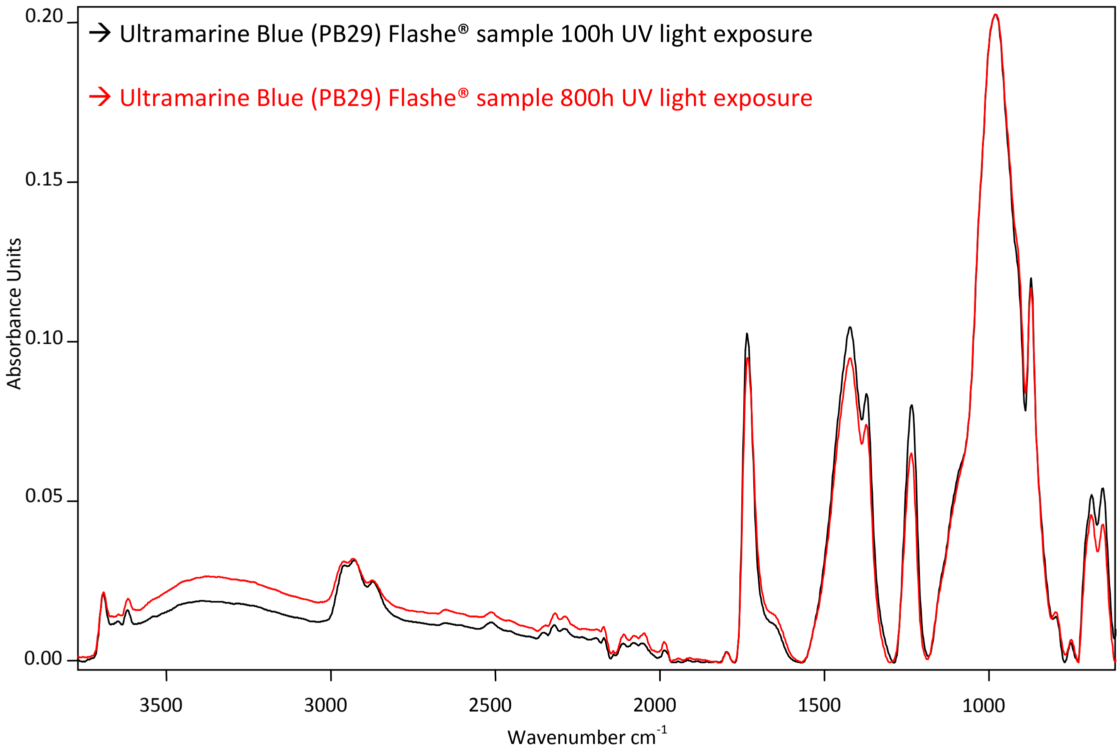

Fig. 3.1-47:Comparing two of the FTIR spectra collected from the Flashe® Ultramarine Blue sample at different steps of the UV-light ageing. In black the spectrum after 100h, in red that collected after 800h of exposure. Besides the decrements in the intensity of the absorptions due to the binder, an increment in the OH stretching region and a slight broadening of the carbonyl band are detected.

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[46] It is possible that the presence of metal ions due the inorganic pigments (that are TiO_2 and ZnS-$BaSO_4$ for the White paint, $2Na_2Al_2Si_2O_6 \cdot NaS_2$ for the Ultramarine Blue paint and $FeO(OH) \cdot H_2O$ for the Yellow Ochre paint) slightly affects the photochemical stability of the polymer.

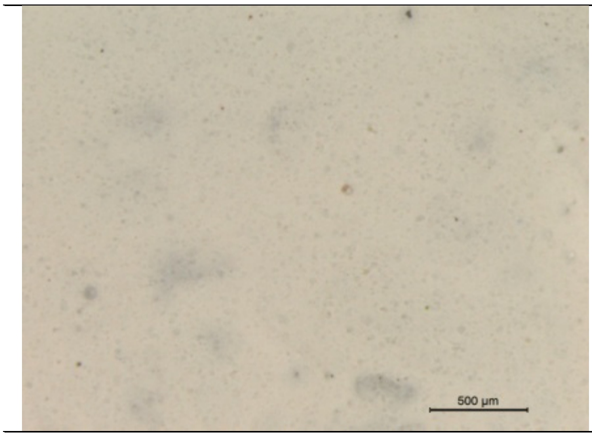
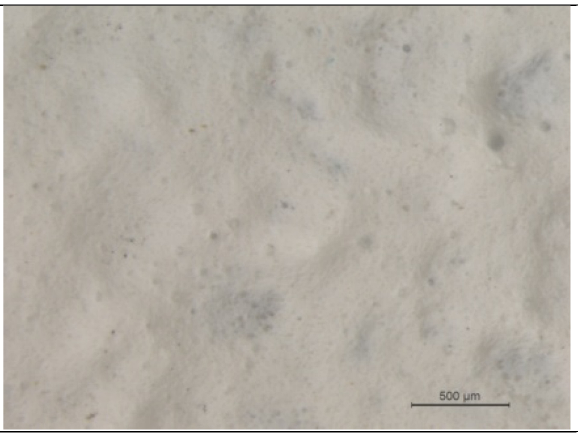
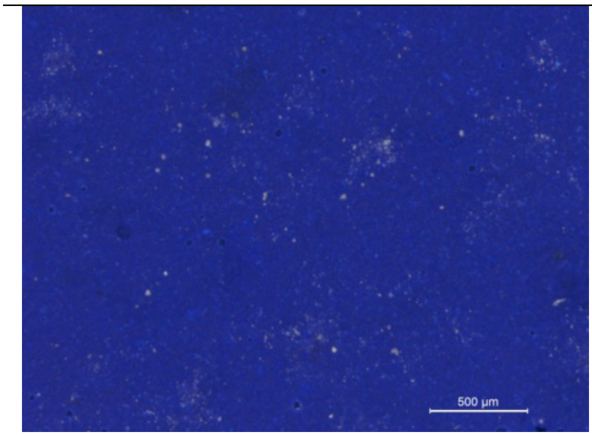
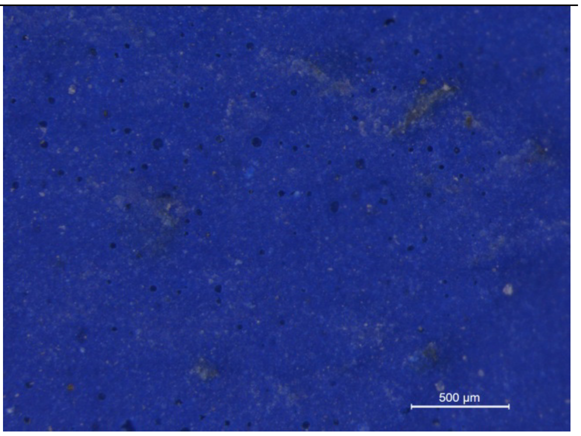
MORPHOLOGICAL VARIATIONS

During the ageing process, the morphology of Flashe® paint layers was monitored using Light Microscopy (8X, 25X and 50X) and Scanning Electron Microscopy (100X, 500X, 1000X and 5000X).

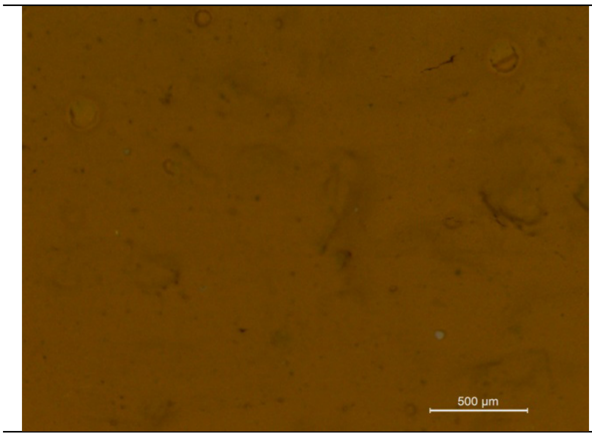
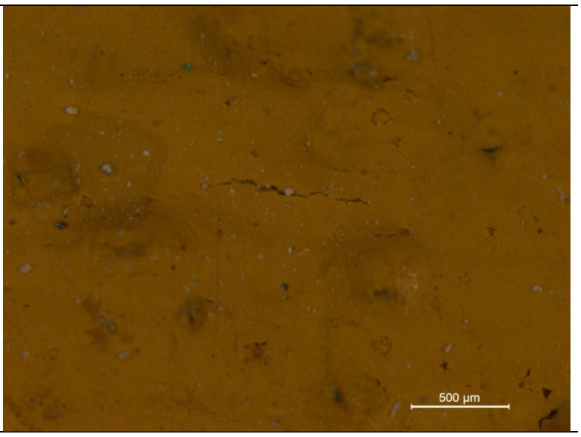
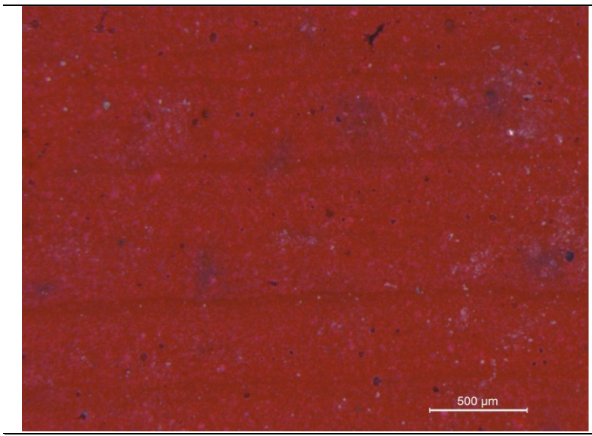
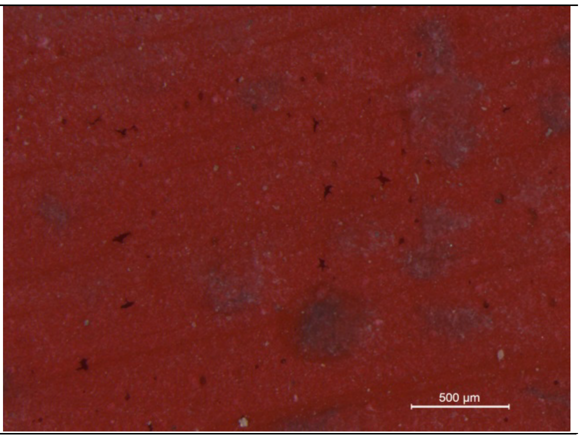
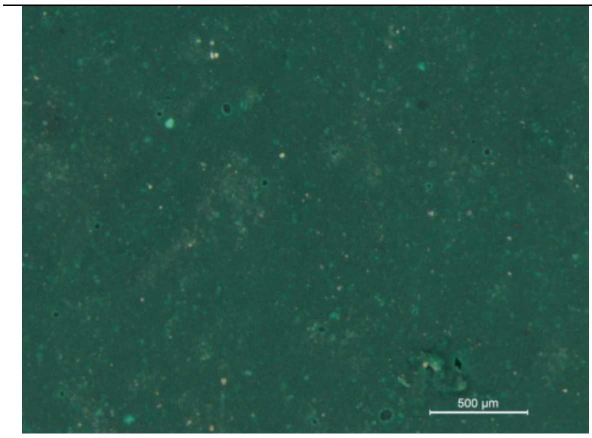
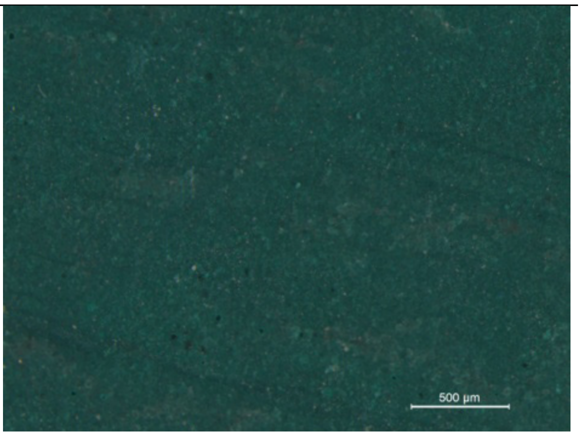
As shown in table 3.1-33, if comparing the appearance of the surfaces before and after 800h of UV-light exposure, only some minor variations were detectable at low magnifications.

Even though still homogeneous, the aged layers looked slightly rougher than the unaged ones. The presence of cracks and pin-holes did not increase significantly, nor significant variations of paints' hiding properties were detected.

Even if not clearly appreciable in the pictures, a certain discoloration was perceived for Ultramarine Blue (PB29), Ruby Red (PV19) and Phthalo Green (PG7) samples (see *Colorimetric Measurements*).

<table>
<tr><th colspan="2">FLASHE ®(LeFranc and Bourgeois) - WHITE -</th></tr>
<tr><td>0h of ageing (25X-LM)</td><td>800h of ageing- (25X-LM)</td></tr>
<tr><td>
</td><td>
</td></tr>
<tr><th colspan="2">FLASHE ®(LeFranc and Bourgeois) – ULTRAMARINE BLUE -</th></tr>
<tr><td>0h of ageing (25X-LM)</td><td>800h of ageing- (25X-LM)</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

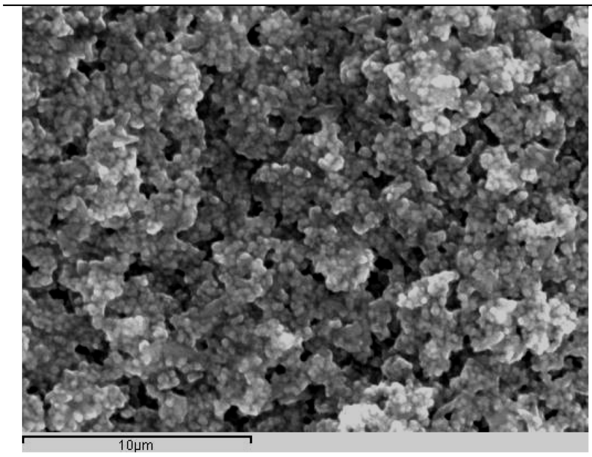
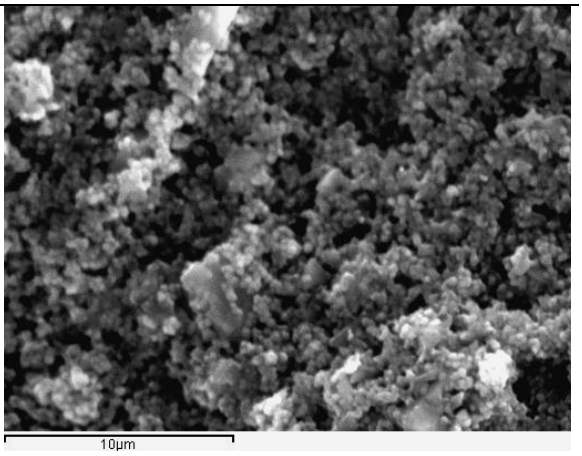
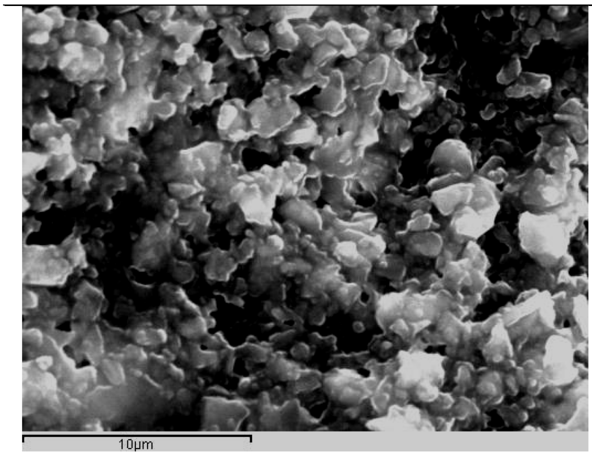
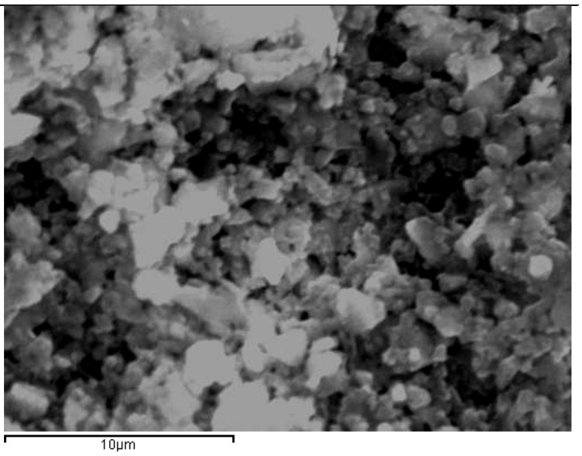
Tab.3.1-33: The surfaces of Flashe® samples before and after 800h of UV-light exposure (LM pictures, 25X) (the table continues in the following page).

FLASHE ® (LeFranc and Bourgeois) – YELLOW OCHRE -	
0h of ageing (25X-LM)	800h of ageing- (25X-LM)
	
FLASHE ® (LeFranc and Bourgeois) – RUBY RED -	
0h of ageing (25X-LM)	800h of ageing- (25X-LM)
	
FLASHE ® (LeFranc and Bourgeois) – ARMOR GREEN -	
0h of ageing (25X-LM)	800h of ageing- (25X-LM)
	

Tab.3.1-33: The surfaces of Flashe® samples before and after 800h of UV-light exposure (LM pictures, 25X)

As shown in table 3.1-34, it was possible to better evaluate the morphological variations of the paint layers examining the surfaces at higher magnifications (using SEM).[47]

At the end of the ageing, pigments and extenders were not well embedded in the polymer matrix anymore (thus suggesting that the vinyl binder had been partially degraded by the UV-light exposure).

<table>
<tr><th colspan="2">FLASHE ® (LeFranc and Bourgeois) - WHITE -</th></tr>
<tr><td>0h of ageing (5000X-SEI)</td><td>800h of ageing- (5000X-SEI)</td></tr>
<tr><td> </td><td> </td></tr>
<tr><td colspan="2">FLASHE ® (LeFranc and Bourgeois) – ULTRAMARINE BLUE -</td></tr>
<tr><td>0h of ageing (5000X-SEI)</td><td>800h of ageing- (5000X-SEI)</td></tr>
<tr><td> </td><td> </td></tr>
</table>

Tab.3.1-34: Comparison of Flashe® samples surface before ageing and after 800h of UV-light exposure (SEM pictures, Secondary Electrons, 5000X): evidences of polymer binder degradation (the table continues in the following page).

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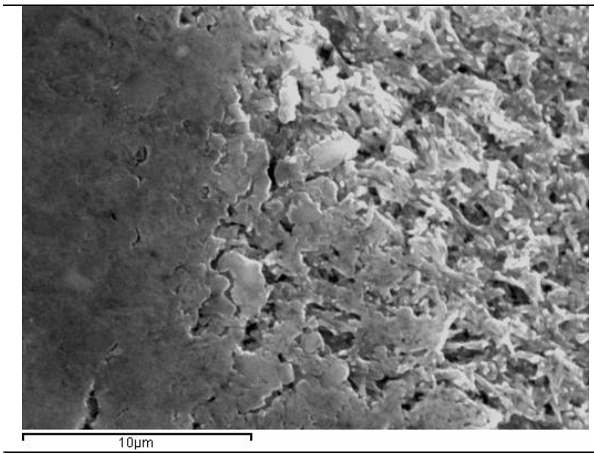
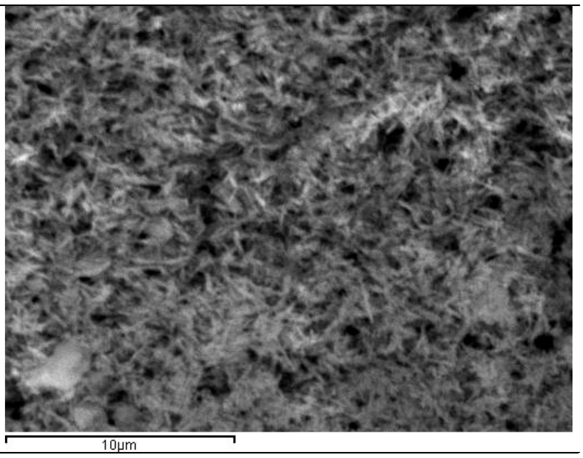
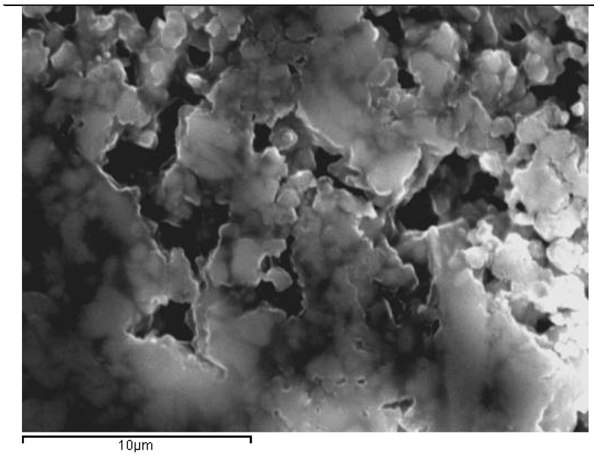
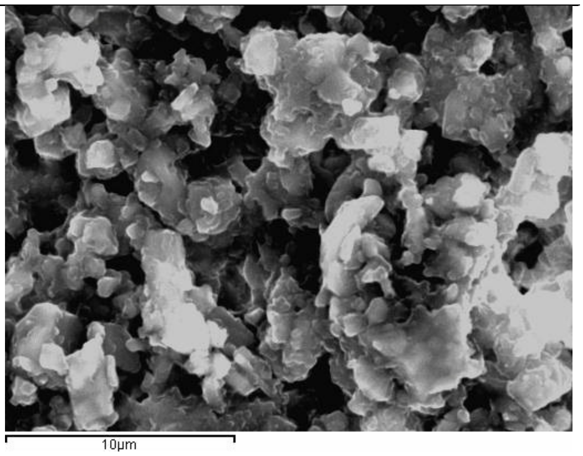
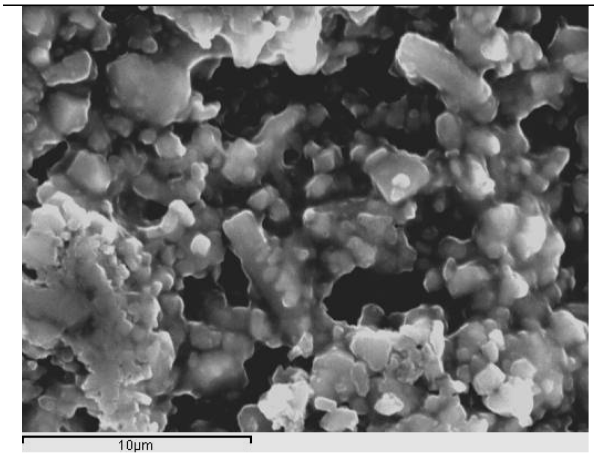
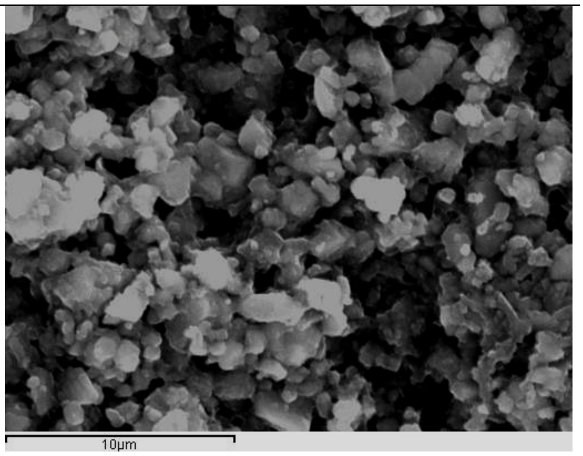
[47] Studying the aged surfaces by SEM, the occurrence of chemical variations was also assessed through Energy Dispersive X-ray (EDX) analysis. The spectra were collected according to the same methodology used to characterize the unaged samples (considering areas, 500X, BSE). Since no relevant results came from the comparison of the data acquired from unaged and aged samples, the spectra are not displayed here. Anyway, this suggests that the UV-light exposure did not significantly affect the chemical composition of the paint layers' inorganic components. This was true for all the samples included in the study: the Flashe® (Lefranc&Bourgeois) ones, the Haevy Body (Liquitex®) ones and the Brera (Maimeri®) ones.

<table>
<tr><th colspan="2">FLASHE ® (LeFranc and Bourgeois) – YELLOW OCHRE -</th></tr>
<tr><td>0h of ageing (5000X-SEI)</td><td>800h of ageing- (5000X-SEI)</td></tr>
<tr><td> </td><td> </td></tr>
<tr><th colspan="2">FLASHE ® (LeFranc and Bourgeois) – RUBY RED -</th></tr>
<tr><td>0h of ageing (5000X-SEI)</td><td>800h of ageing- (5000X-SEI)</td></tr>
<tr><td> </td><td> </td></tr>
<tr><th colspan="2">FLASHE ® (LeFranc and Bourgeois) – ARMOR GREEN -</th></tr>
<tr><td>0h of ageing (5000X-SEI)</td><td>800h of ageing- (5000X-SEI)</td></tr>
<tr><td> </td><td> </td></tr>
</table>

Tab.3.1-34: Comparison of Flashe® samples surface before ageing and after 800h of UV-light exposure (SEM pictures, Secondary Electrons, 5000X): evidences of polymer binder degradation.

COLORIMETRIC MEASUREMENTS

During the UV-light ageing process, the color of the painted surfaces was measured, according to the method described in Chapter 2 (section 2.4.5 *Colorimetric Measurements*).[48]

In table 3.1-35 the total color variations, expressed as ΔE^*_{ab}, are shown together with the variations of the three colorimetric values (ΔL^*, Δa^* and Δb^*). These latter variations were calculated as differences between the values collected during the ageing (200h, 400h,600h and 800h) and before the ageing.

At the end of the 800h of exposure, the color variations for the white and yellow samples were negligible and probably not directly connected to a decay process ($\Delta E^*_{ab} < 1$). In the case of the White sample (PW6-PW5), the color changed in a consistent way, with the calculated ΔE^*_{ab} slightly increasing as the ageing went on and a color variation due to a slight darkening (decrement in L*) and yellowing (increment in b*) of the surface. In the case of the Yellow Ochre sample (PY42) instead, data changed in a not linear way.

The color variations detected for the red and green samples were slightly higher and detectable to naked eye examinations.

In particular, for the Ruby Red (PV19) sample, the ΔE^*_{ab} reached a value of 8.5 and, even if the color did not change in a completely linear way, data suggested a slight increment of L* and a certain decrement of a* and b* (the color lightened and shifted toward green and blue, and so to a colder palette).

For the Armor Green (PG7) sample, the ΔE^*_{ab} reached a value of 6. Even in this case the variations were not linear but the total color variation seemed to come from a decrement of b* and an increment of L* and a* (the color lightened and slightly shifted toward blue and red).

The sample affected by the most significant color variation was that cast with the Ultramarine Blue (PB29) paint.

200h of UV light exposure, were enough to induce a significant color change (ΔE^*_{ab} 7.60), detectable to naked eye examinations. Extending the ageing, the color variation increased, with the ΔE^*_{ab} reaching a value of 18 after 800h of exposure. The color changed in a consistent way, with an increment of L*, a decrement of a*, and b* that did not change significantly (due to the exposure the surface became lighter and more greenish).

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[48] Measurements were taken in 3 different areas of each samples. A set of 3 spectra was collected for each area so that, the final colorimetric values, came from an average of 9 acquisitions.

WHITE (PW6-PW5)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	0.29	0.02	0.06	0.30	0.31	0.01	0.02	0.31
400	0.27	-0.04	0,30	0.41	0.23	-0.04	0.28	0.37
600	-0.58	0.06	0.23	0.63	-0.63	0.06	0.23	0.68
800	-0.74	0.06	0.39	0.84	-0.74	0.05	0.37	0.83

ULTRAMARINE BLU (PB29)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	4.70	-5.65	-1.95	7.60	4.78	-5.87	-1.76	7.77
400	6.67	-9.95	-1.06	12.03	6.83	-10.35	-0.68	12.42
600	9.07	-12.72	-1.71	15.71	9.17	-13.01	-1.24	15.97
800	10.38	-14.77	-1.47	18.11	10.54	-15.03	-0.98	18.38

YELLOW OCHRE (PY42)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	0.33	-0.04	0.98	1.03	0.31	-0.04	0.92	0.97
400	0.69	0.09	0.31	0.76	0.63	0.09	0.31	0.71
600	0.87	0.03	-0.40	0.96	0.74	0.05	-0.26	0.79
800	0.60	-0.12	0.25	0.66	0.55	-0.11	0.28	0.63

RUBY RED (PV19)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	0.59	0.40	-4.08	4.14	0.48	0.38	-3.67	3.72
400	1.34	-0.90	-7.55	7.72	1.52	-1.42	-7.53	7.81
600	0.68	-0.77	-6.07	6.15	0.71	-1.08	-6.05	6.19
800	0.56	-2.91	-7.97	8.50	1.55	-2.96	-7.60	8.30

ARMOR GREEN (PG7)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	2.13	-0.52	0.22	2.20	2.16	-0.35	0.26	2.20
400	5.12	5.27	-2.44	7.74	5.19	5.73	-2.54	8.14
600	4.72	3.68	-1.16	6.10	4.75	4.03	-1.17	6.33
800	5.01	3.12	-0.99	5.99	5.06	4.43	-1.01	6.19

Tab. 3.1-35: The color variations induced by the UV light ageing of the samples cast with Flashe® paints. The total color variation (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from values acquired both including and excluding specular reflectance (SCI and SCE methods).

HEAVY BODY PAINTS (Liquitex®)

FTIR SPECTROSCOPY ANALYSIS

The degradation processes affecting acrylic resins can be followed using FTIR spectroscopy analysis.

Considering the ageing conditions used (UVA-340 lamps, temperature 45°C) the acrylic binder was expected to undergo the following degradation processes (section *1.2.3.2 Photooxidative processes*):

- loss of low molecular weight material (decrements in the intensity of the C-H stretching absorption; decrements of C-O and C-C stretching absorptions, especially for those bands around 1240 cm^{-1}, 1160 cm^{-1}, 1145 $cm^{-1}$and 1065 cm^{-1})
- chain scissions, followed by the formation of terminal and inner C=C bonds (revealed by the appearance of absorption features in the 1640 ÷ 1630cm^{-1} and 1680 ÷ 1660 cm^{-1} regions, respectively)
- photooxidation leading to new functionalities such as hydro-peroxides, alcohol groups, unsatured ketones and γ-lactones (increments of the OH stretching absorptions in the 3600÷3100 cm^{-1} range; broadening of the carbonyl band, in the 1705 cm^{-1} region due to unsatured ketones and at 1780 cm^{-1} due to γ-lactones)
- coupling reactions with the formation of cross-linked structures (C=C inner bonds)

In addition, the alkaline environment produced by $CaCO_3$, H_2O and CO_2 which originates on mortar surface, may induce the hydrolysis of the ester side chain of the polymer leading to the formation of carboxylate groups, revealed by the appearance of an absorption at about 1598 cm^{-1}. Due to the low R.H. value (lower than 40%), this degradation process is less expected.

Among the Heavy Body-Liquitex® paints included in the study, those containing the inorganic pigments (Titanium White, PW6; Ultramarine Blue, PB29 and Transparent Raw Sienna, PY42) were more affected by the UV-light ageing conditions.

Comparing the reference spectra with those collected at the end of the 800h of UV light exposure, an increment of the absorption in the OH stretching region, and a slight broadening of the carbonyl band at lower wavelengths were detected. These variations suggested the occurrence of photooxidative processes resulting in the formation of new hydroxyl and carbonyl functionalities.
In the case of the Ultramarine Blue sample (PB29), the occurrence of the shoulder at about 1784 cm^{-1} is possibly related to the formation of γ-lactones (figure 3.1-48).

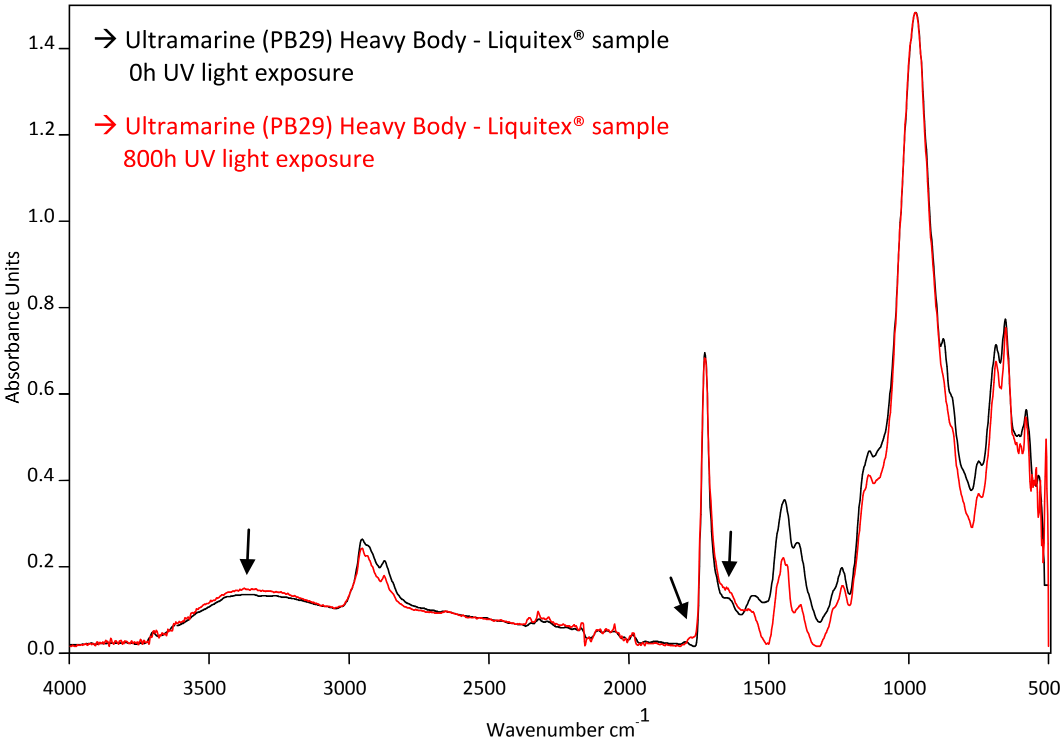

Fig. 3.1-48:Comparing the FTIR spectra from the Heavy Body-Liquitex® Ultramarine Blue sample before (black) and after 800h of UV-light exposure (red). Besides the decrements in the intensity of the absorptions due to the binder, a slight increment in the OH stretching region and a slight broadening of the carbonyl band are observed (this latter variation indicates the formation of γ-lactones and unsatured ketones).

As shown in figure 3.1-49, in the case of the Transparent Raw Sienna sample (PY42), the spectral variations suggested the occurrence of chain-scission processes resulting in terminal C=C bonds: the intensity of the absorptions related to the methyl stretching vibrations decreases (ν_{as} CH_3 at 2954 cm^{-1} and ν_s CH_3 at 2877 cm^{-1}); the intensity of the the methylene stretching vibrations increases (ν_{as} CH_2 at 2921 cm^{-1} and ν_s CH_2 at 2841cm^{-1});a new absorption ascribable to terminal C=C bonds occurs at 1638 cm^{-1}.

There were no evidences of the formation of carboxylate compounds.

On the contrary, for the Titanium White, Ultramarine Blue and Transparent Raw Sienna samples a decrement in the absorption around 1558 cm^{-1} was detected . This possibly suggested the degradation of an organic additive initially exuded on paint surfaces (likely an anionic dispersant, such as a salt of polyacrylic acids).[49]

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[49] This result was consistent with those reported by Doménech-Carbó *et al.*, 2011.

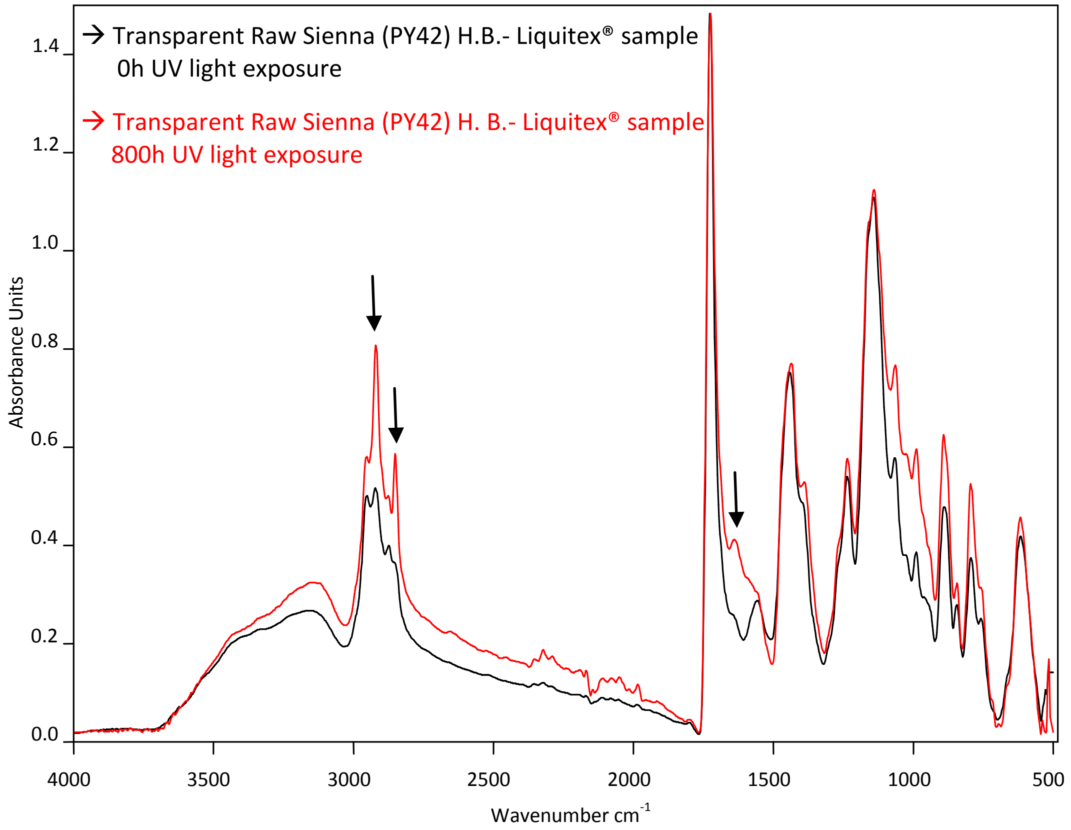


Fig.3.1-49:Comparing the FTIR spectra from the Heavy Body-Liquitex® Transparent Raw Sienna sample before (black) and after 800h of UV-light exposure (red). The changes detected in the CH stretching region and the band at 1638 cm^{-1} (terminal C=C bond) are possibly due to chain scission processes.

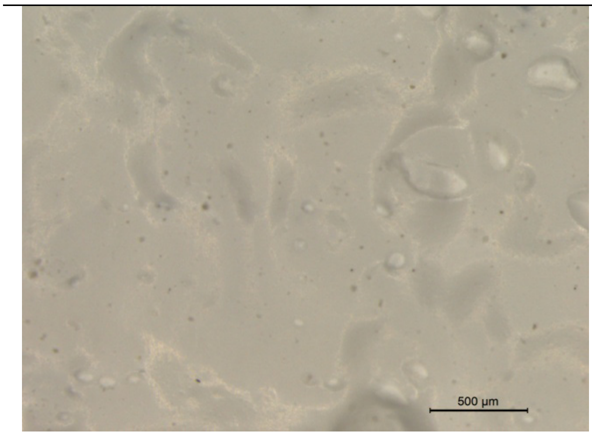
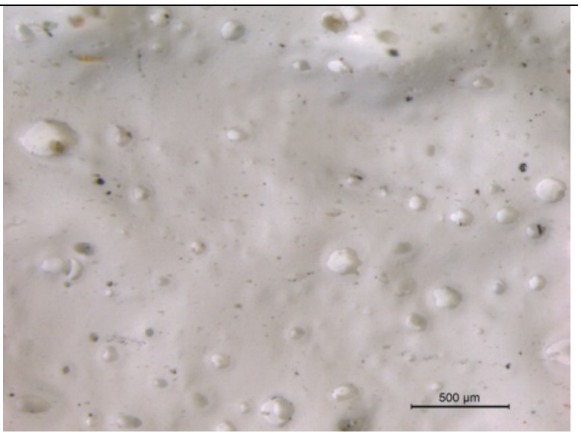
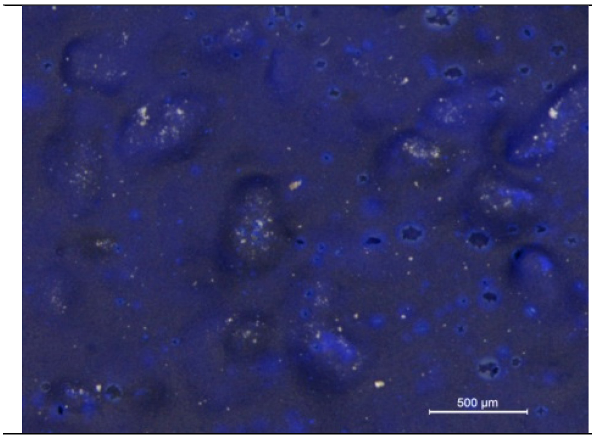
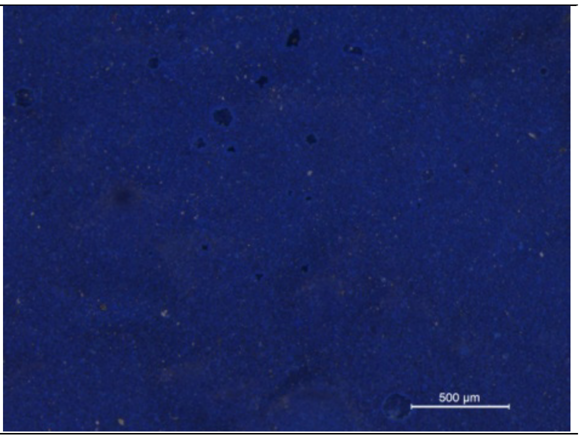
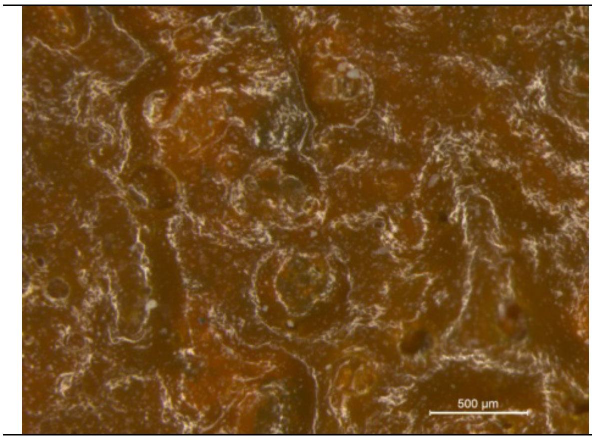
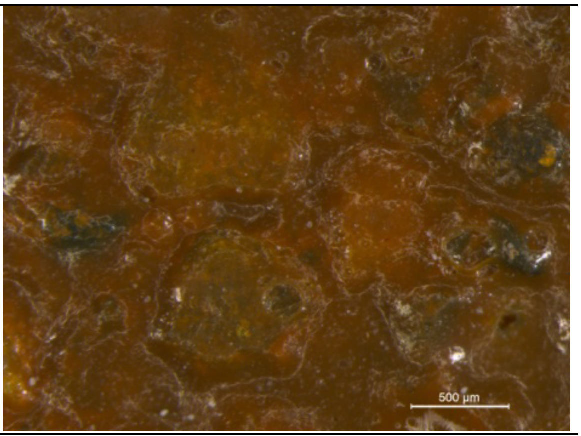
MORPHOLOGICAL VARIATIONS

The morphology of the Heavy Body (Liquitex®) paint layers was monitored using Light Microscopy (8X, 25X and 50X) and Scanning Electron Microscopy (100X, 500X, 1000X and 5000X).

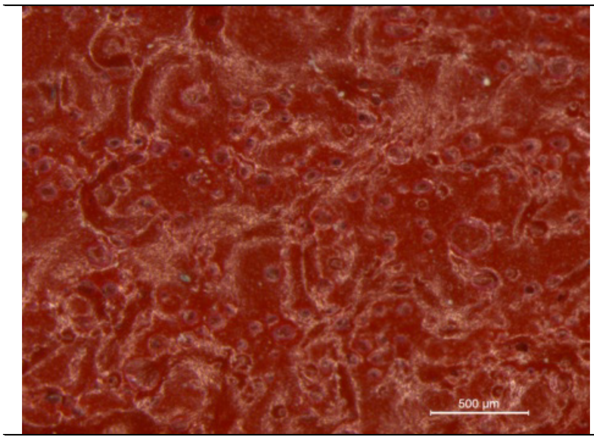
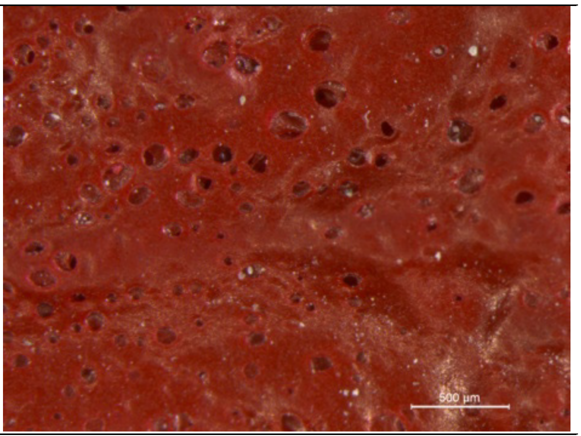
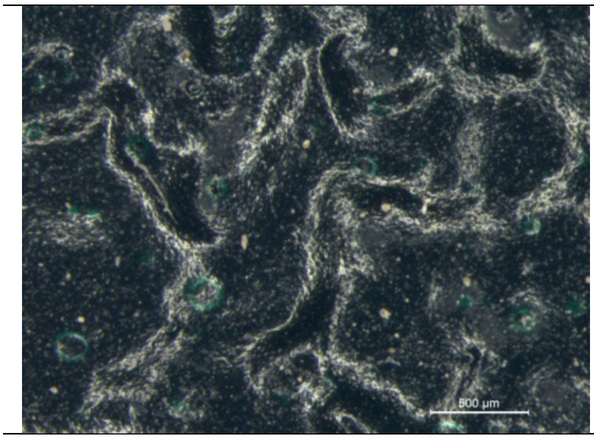
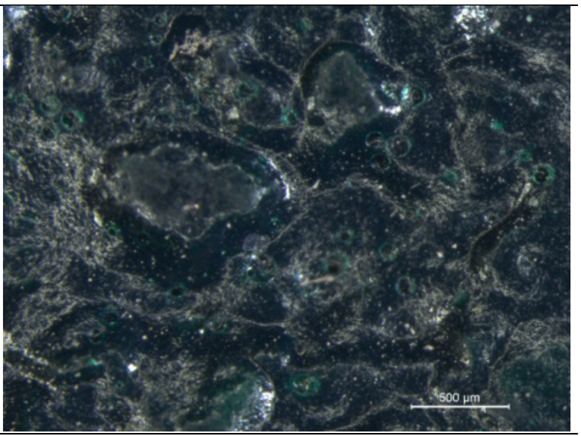
Even in this case, only some minor variations were detected when examining the surfaces at low magnifications (table 3.1-36).

The Ultramarine Blue (PB29) sample was the only one to be affected by evident changes: the painted surface became lighter and matter after 800h of UV light exposure. Slighter reductions in the surface gloss were perceived also for the Transparent Raw Sienna (PY42) and the Quinacridone Crimson (PV19) samples. The other samples did not suffer relevant variations.

There were no evidences of cracks, new pin-holes or of significant variations in paints' hiding properties.

HEAVY BODY (Liquitex®) - TITANIUM WHITE -	
0h of ageing (25X-LM)	800h of ageing- (25X-LM)
	
HEAVY BODY (Liquitex®) - ULTRAMARINE BLUE (Green Shade)-	
0h of ageing (25X-LM)	800h of ageing- (25X-LM)
	
HEAVY BODY (Liquitex®) – TRANSPARENT RAW SIENNA -	
0h of ageing (25X-LM)	800h of ageing- (25X-LM)
	

Tab.3.1-36: The surfaces of Heavy Body (Liquitex®) samples before and after 800h of UV light exposure (LM pictures, 25X). (the table continues in the following page).

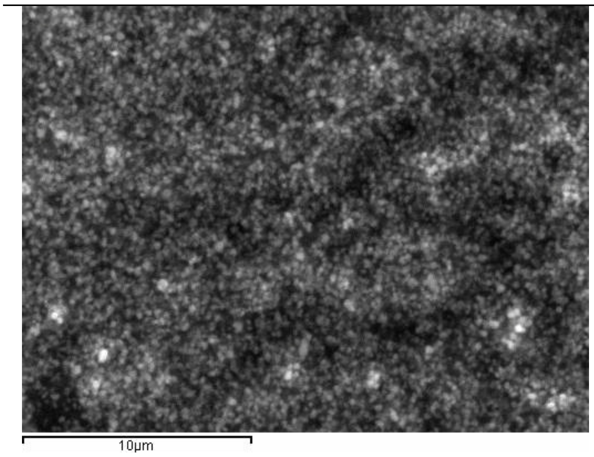
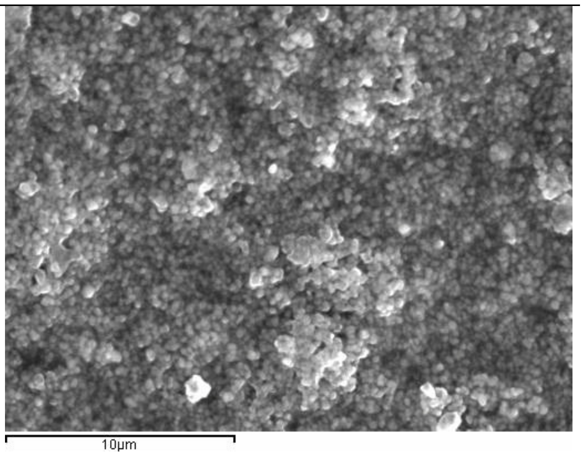
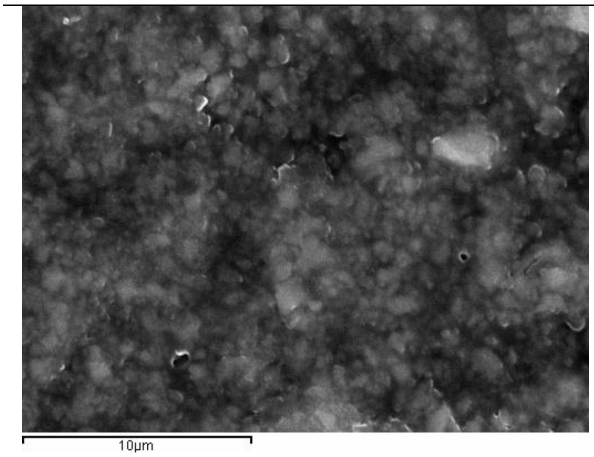
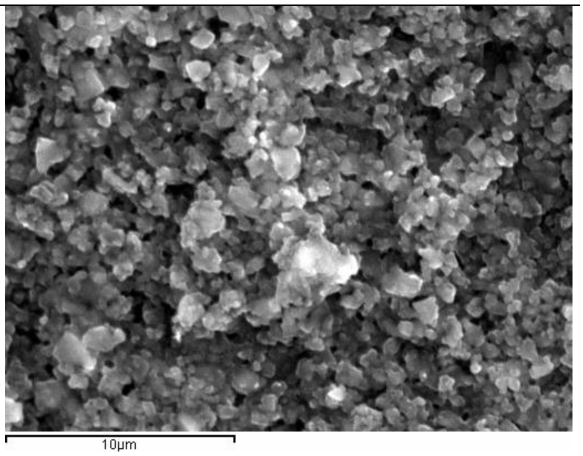
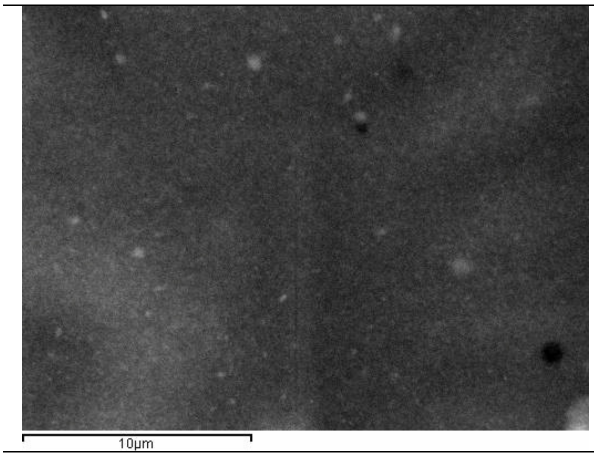
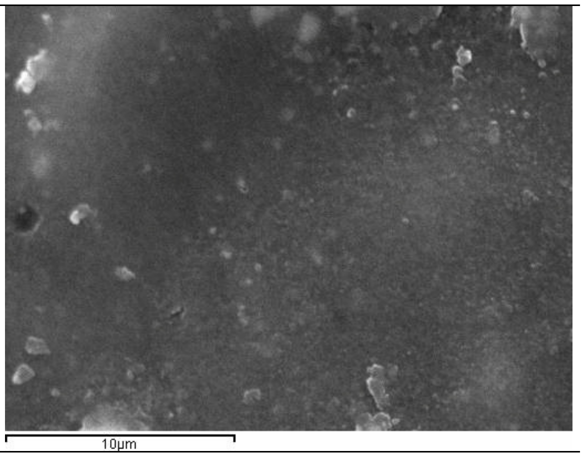
HEAVY BODY (Liquitex®) - QUINACRIDONE CRIMSON -	
0h of ageing (25X-LM)	800h of ageing- (25X-LM)
	
HEAVY BODY (Liquitex®) - PHTHALOCYANINE GREEN (Blue Shade)-	
0h of ageing (25X-LM)	800h of ageing- (25X-LM)
	

Tab.3.1-36: The surfaces of Heavy Body (Liquitex®) samples before and after 800h of UV light exposure (LM pictures, 25X).

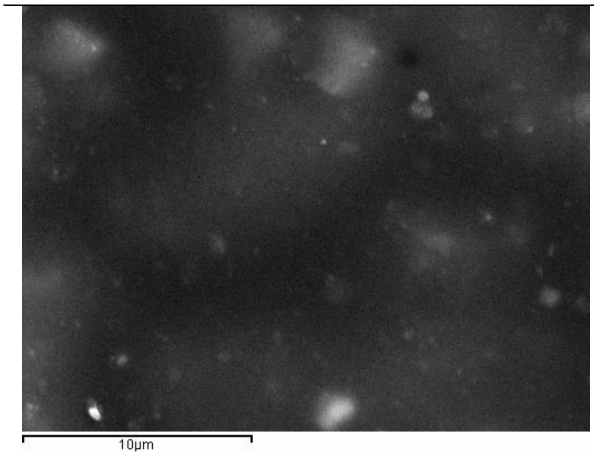
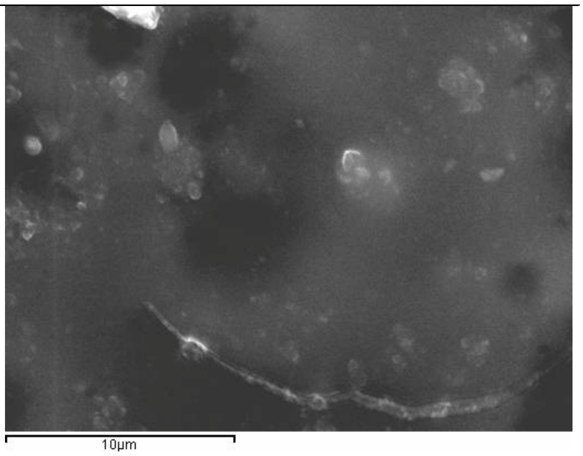
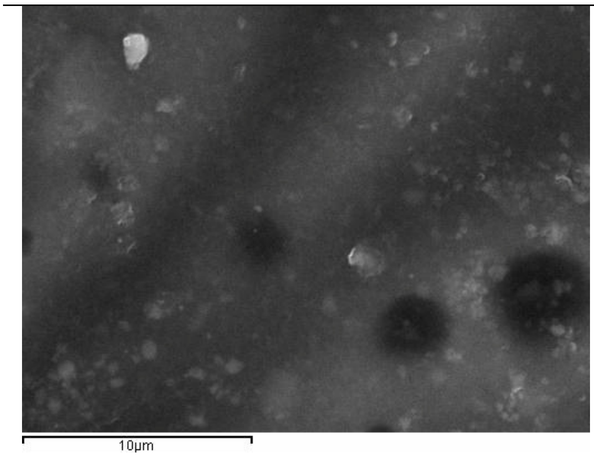
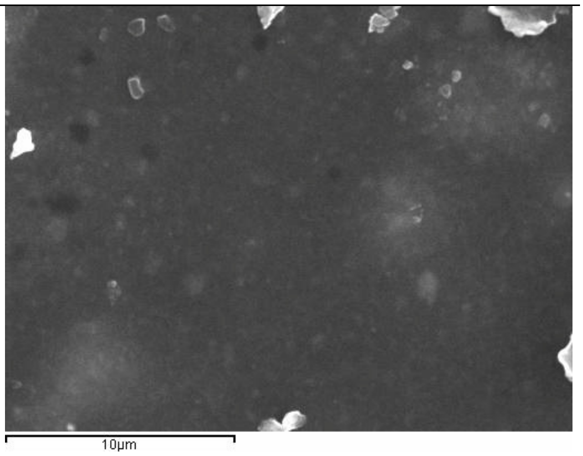
These considerations were mainly confirmed examining the surfaces at higher magnifications by SEM (table 3.1-37).

Despite the ageing, the paint layers of the Transparent Raw Sienna (PY42), Quincridone Crimson (PV19) and Phthalocyanine Green (PG7) samples were still characterized by high amounts of the polymer binder, and presented smooth, homogeneous and continuous surfaces.

More relevant variations were instead detected for those samples characterized by higher pigment volume concentrations. After the ageing, the surfaces of the Titanium White (PW6) and Ultramarine Blue (PB29) samples looked rougher, with the pigments that were not completely embedded in the polymeric binder anymore.

HEAVY BODY (Liquitex®) - TITANIUM WHITE -	
0h of ageing (5000X-SEI)	800h of ageing- (5000X-SEI)
	
HEAVY BODY (Liquitex®) - ULTRAMARINE BLUE (Green Shade)-	
0h of ageing (5000X-SEI)	800h of ageing- (5000X-SEI)
	
HEAVY BODY (Liquitex®) – TRANSPARENT RAW SIENNA -	
0h of ageing (5000X-SEI)	800h of ageing- (5000X-SEI)
	

Tab.3.1-37: The surfaces of Heavy Body (Liquitex®) samples before and after 800h of UV light exposure: SEM pictures, 5000X, secondary electrons (the table continues in the following page).

<table>
<tr><th colspan="2">HEAVY BODY (Liquitex®) - QUINACRIDONE CRIMSON -</th></tr>
<tr><td>0h of ageing (5000X-SEI)</td><td>800h of ageing- (5000X-SEI)</td></tr>
<tr><td> </td><td> </td></tr>
<tr><th colspan="2">HEAVY BODY (Liquitex®) - PHTHALOCYANINE GREEN (Blue Shade)-</th></tr>
<tr><td>0h of ageing (5000X-SEI)</td><td>800h of ageing- (5000X-SEI)</td></tr>
<tr><td> </td><td> </td></tr>
</table>

Tab.3.1-37: The surfaces of Heavy Body (Liquitex®) samples before and after 800h of UV light exposure: SEM pictures, 5000X, secondary electrons.

COLORIMETRIC MEASUREMENTS

Table 3.1-38 shows the color variations assessed, for the Heavy Body-Liquitex® samples during the ageing. The measurements were carried out according to the method previously described for Flashe® sample.

The color of the Titanium White (PW6), Transparent Raw Sienna (PY42) and Phthalocyanine Green (PG7) samples, did not change in a coherent way (e.g. for the Titanium White sample, the ΔE^*_{ab} at the end of the 800h of exposure was smaller than that calculated after 200h of ageing). Anyway, the color variations detected for these samples were negligible and probably not directly due to a decay process ($\Delta E^*_{ab} < 1$ for Titanium White; $\Delta E^*_{ab} < 3$ for Transparent Raw Sienna; $\Delta E^*_{ab} < 4$ for Phthalocyanine Green sample).

The color of the Quinacridone Crimson (PV19) sample instead changed in a quite coherent way, with the total color variation (ΔE^*_{ab}) which actually increased while extending the ageing. This color variation was related to slight decrements of L*, a* and b* (the color became darker and shifted toward green and blue, so to a colder palette).[50] Even if the ΔE^*_{ab} reached a value of 4 at the end of the 800h of exposure, this color variation was still not detectable to the naked eye.

TITANIUM WHITE (PW6)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	0.58	-0.05	0.02	0.58	0.50	-0.05	-0.02	0.50
400	0.05	-0.09	-0.05	0.12	-0.01	-0.10	-0.08	0.13
600	-0.21	0.08	0.33	0.40	-0.27	0.08	0.33	0.44
800	0.06	0.10	0.31	0.33	0.10	0.10	0.28	0.31

ULTRAMARINE BLU (Green Shade) (PB29)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	3.50	12.13	-12.94	18.08	3.79	10.61	-12.18	16.59
400	6.87	11.38	-16.77	21.40	7.27	9.15	-15.61	19.50
600	10.94	7.81	-19.44	23.63	11.28	5.55	-18.12	22.05
800	13.25	6.75	-21.52	26.16	13.63	4.43	-20.16	24.74

TRANSPARENT RAW SIENNA (PY42)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	0.94	0.49	0.55	1.19	1.05	0.40	0.15	1.13
400	1.07	0.72	0.81	1.53	1.17	0.65	0.38	1.39
600	1.58	-0.61	-2.08	2.68	1.89	-0.79	-2.93	3.57
800	0.97	-0.07	-0.22	0.99	1.23	-0.23	-1.14	1.69

QUINACRIDON CRIMSON (PV19)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	-1.07	-1.00	0.91	1.72	-1.05	-0.89	0.68	1.53
400	-1.49	-2.12	0.79	2.71	-1.34	-2.06	0.30	2.48
600	-0.61	-3.70	-0.33	3.76	-0.41	-4.01	-0.62	4.08
800	-1.54	-3.68	0.58	4.03	-1.26	-3.81	-0.13	4.01

PHTHALOCYANINE GREEN (Blue Shade) (PG7)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	-1.77	2.93	1.55	3.76	-1.54	2.34	1.01	2.98
400	-1.79	3.18	1.17	3.83	-2.09	3.52	1.57	4.38
600	-0.13	1.64	-1.37	2.14	0.17	1.46	-1.53	2.12
800	-0.64	1.69	-0.77	1.96	-0.55	1.42	-0.76	1.70

Tab. 3.1-38: The UV-light induced color variations of Heavy Body-Liquitex® samples. The total color variation (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from values acquired both including and excluding specular reflectance (SCI and SCE methods).

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[50] Data collected at the end of the 600h of ageing are probably affect by an error.

The only sample affected by a significant color variation was that cast with the Ultramarine Blue (Green Shade- PB29-) paint.

200h of UV light exposure, were enough to induce a significant color change (ΔE^*_{ab} 18) that was clearly detectable to the naked eye. Extending the ageing, the color variation increased, with the ΔE^*_{ab} reaching a value of 26 after 800h of UV-light exposure. The color changed in a consistent way, undergoing an increment of L*, decrements of a*and b* (the painted surface became lighter, more greenish and more bluish; the color shifted to a colder palette).

BRERA PAINTS (Maimeri®)

FTIR SPECTROSCOPY ANALYSIS

As for the other paint binders, the degradation processes affecting the styrene-acrylic polymers can be followed using FTIR spectroscopy analysis. Considering the ageing conditions used (UVA-340 lamps, temperature 45°C) the expected degradation mechanisms are those already discussed for the acrylic resins (loss of molecular weight material; chain scissions; loss of ester functionalities and formation of C=C terminal bonds; photooxidative processes leading to new hydroxyl, hydro-peroxides and carbonyl groups, partially ascribable to unsatured ketones and γ-lactones).

Further reactions expected to affect the styrene monomers are:

- phenyl ring opening reactions affecting the styrene units (decrements in the intensity of the features related to styrene: aromatic skeletal ring breathing around 1495 cm^{-1} and 1455 cm^{-1}; C-H out of plane bending around 755 cm^{-1} and 700 cm^{-1})

Only minimal differences were detected when comparing the spectra collected from the Brera-Maimeri® paint samples, at different steps of the ageing.

After 800h of UV light exposure, all the samples showed an increment of the absorptions in the hydroxyl stretching region and a slight broadening of the carbonyl absorption band towards lower wavelengths. These changes suggested the occurrence of photo-oxidative processes resulting in the formation of alcohol/hydroperoxide groups and of unsatured ketones. In most of the cases there were no clear evidences of other degradation processes (especially if considering those involving the styrene units).

The Ultramarine (PB29) sample underwent the most evident variations (figure 3.1-50). Besides the spectral changes described above (and common to all the samples), the spectrum collected for the Ultramarine sample showed some features possibly related to the formation of γ-lactones (absorption around 1780 cm^{-1}) and to the occurrence of phenyl ring opening reactions (the intensity of 700 cm^{-1} band slightly decreases).

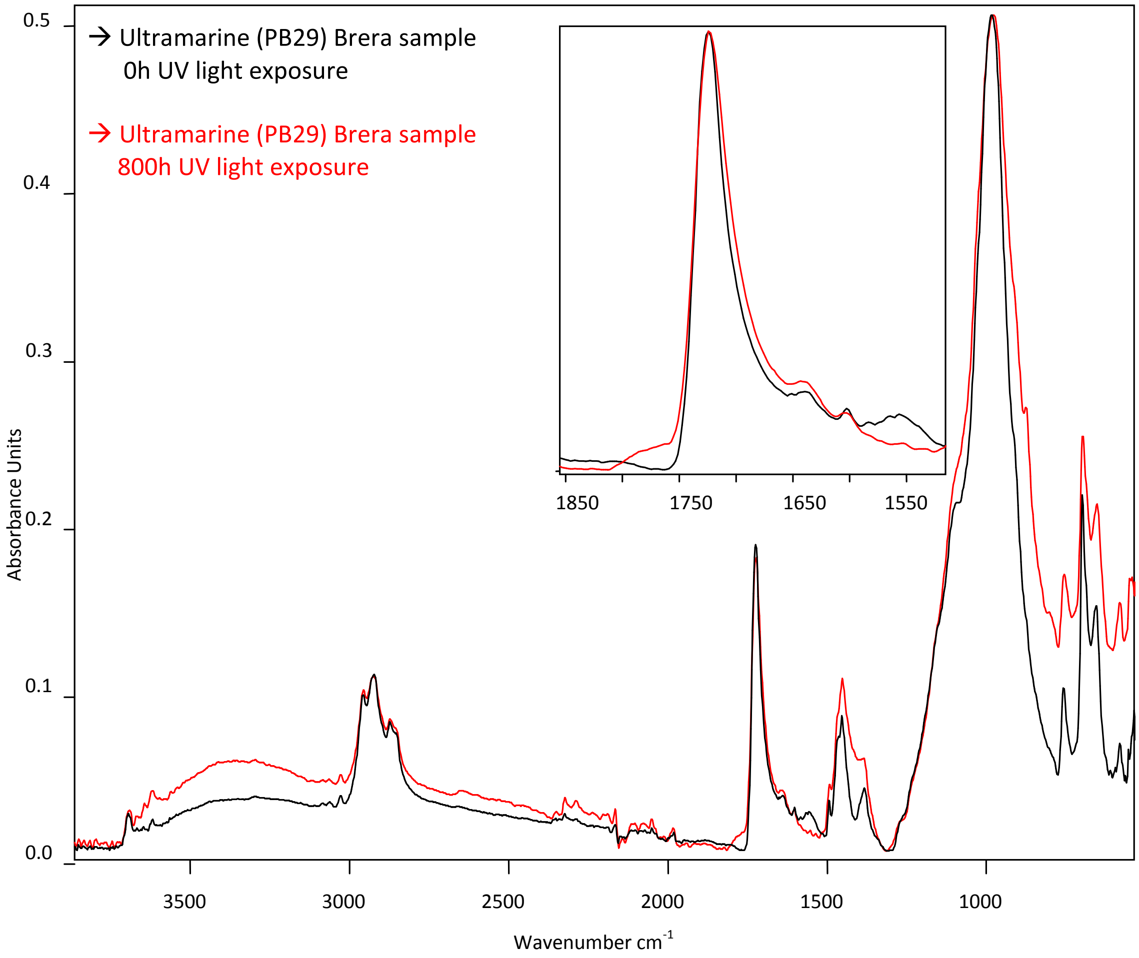


Fig. 3.1-50:Comparing the spectra from the Ultramarine (PB29) Brera-Maimeri® paint sample, before (black) and after 800h of UV-light exposure (red). Besides the increment in the OH stretching region, a slight broadening of the carbonyl band was observed (indicating both the formation of γ-lactones and unsatured ketones) .

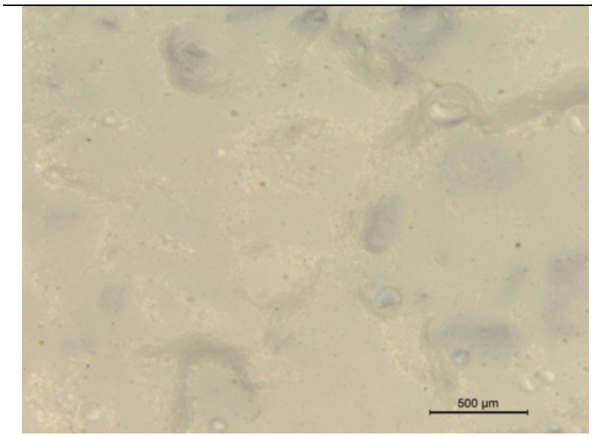
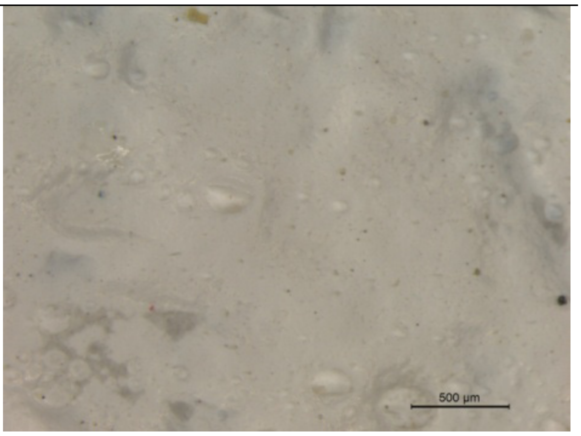
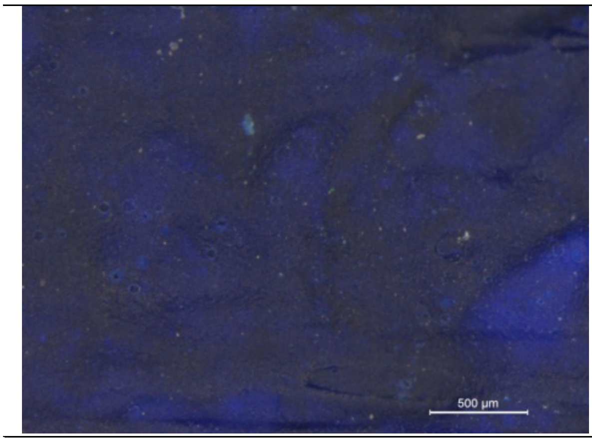
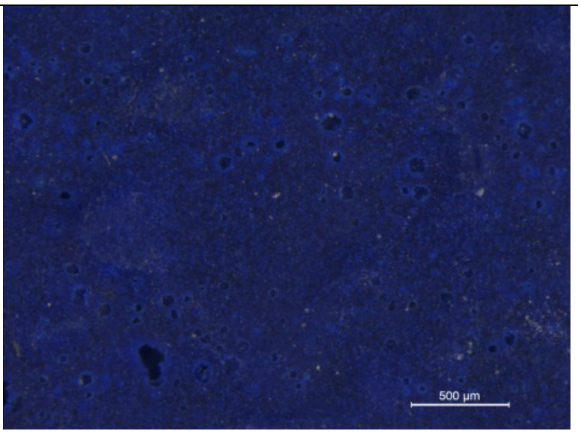
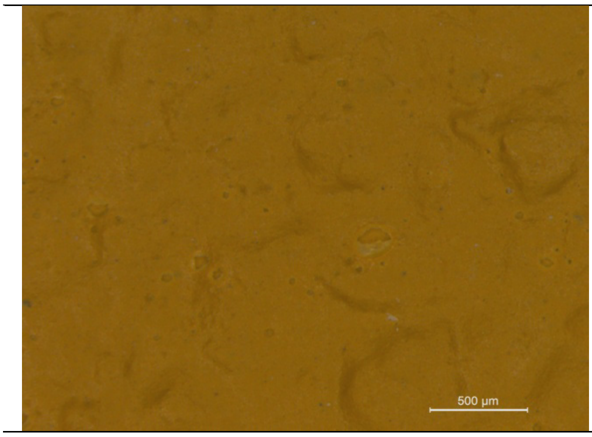
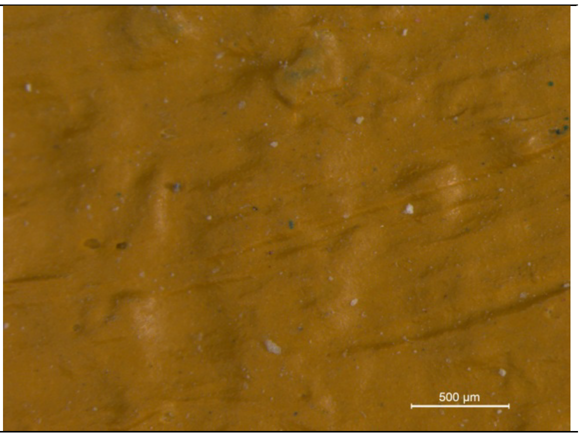
MORPHOLOGICAL VARIATIONS

The morphology of Brera (Maimeri®) paint layers was monitored using Light Microscopy (8X, 25X and 50X) and Scanning Electron Microscopy (100X, 500X, 1000X and 5000X).

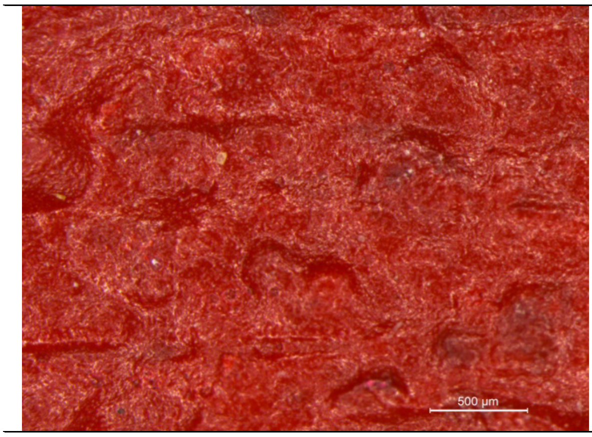
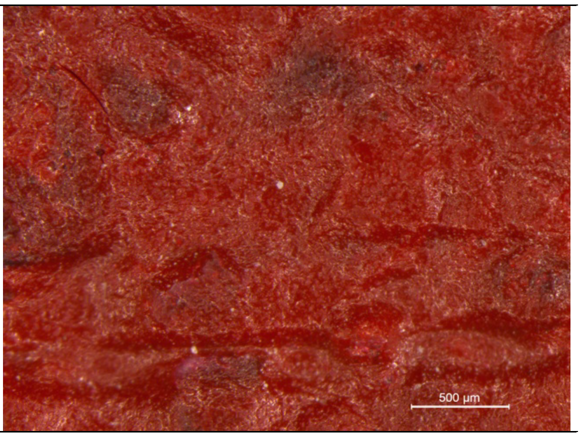
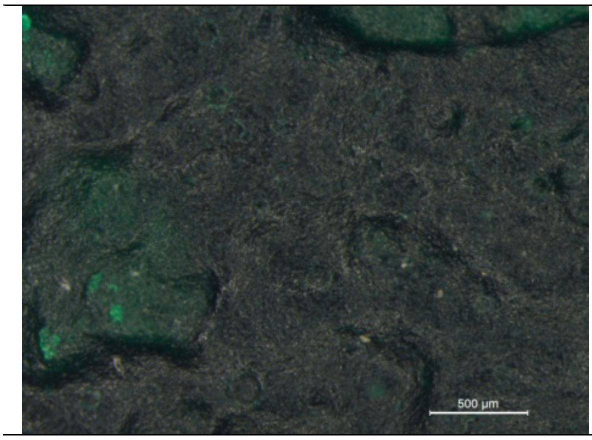
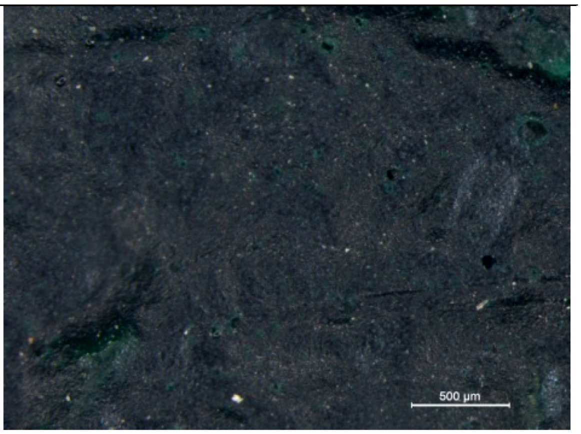
Again, only some minor variations due to the ageing were detected studying the surfaces at low magnifications (table 3.1-39).

The Ultramarine (PB29) sample was the only one showing evident changes: the surface became lighter and matter and was characterized by a greater number of pin-holes.

The other samples did not suffer relevant variations. There were no evidences of cracks, new pin-holes, significant color/gloss variations, or changes of the hiding properties.

<table>
<tr><th colspan="2">BRERA (Maimeri®) - TITANIUM WHITE -</th></tr>
<tr><td>0h of ageing (25X-LM)</td><td>800h of ageing- (25X-LM)</td></tr>
<tr><td>
</td><td>
</td></tr>
<tr><th colspan="2">BRERA (Maimeri®) - ULTRAMARINE-</th></tr>
<tr><td>0h of ageing (25X-LM)</td><td>800h of ageing- (25X-LM)</td></tr>
<tr><td>
</td><td>
</td></tr>
<tr><th colspan="2">BRERA (Maimeri®) – YELLOW OCHRE -</th></tr>
<tr><td>0h of ageing- (25X-LM)</td><td>800h of ageing- (25X-LM)</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

Tab.3.1-39: The surfaces of Brera (Maimeri®) samples before and after 800h of UV-light exposure (LM pictures, 25X) (the table continues in the following page).

<table>
<tr><th colspan="2">BRERA (Maimeri®) - PRIMARY RED MAGENTA -</th></tr>
<tr><td>0h of ageing (25X-LM)</td><td>800h of ageing- (25X-LM)</td></tr>
<tr><td> </td><td> </td></tr>
<tr><th colspan="2">BRERA (Maimeri®) - PHTHALO GREEN-</th></tr>
<tr><td>0h of ageing (25X-LM)</td><td>800h of ageing- (25X-LM)</td></tr>
<tr><td> </td><td> </td></tr>
</table>

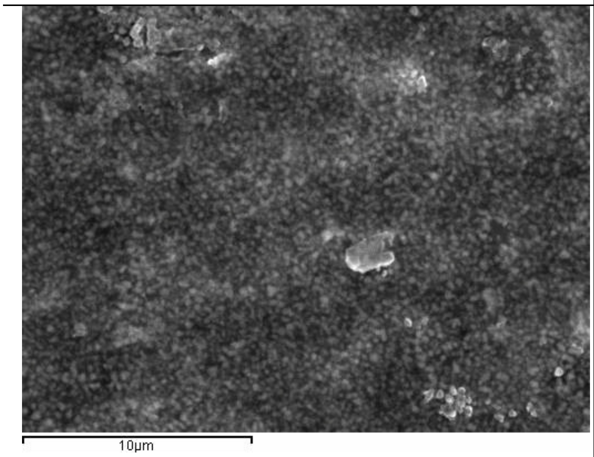
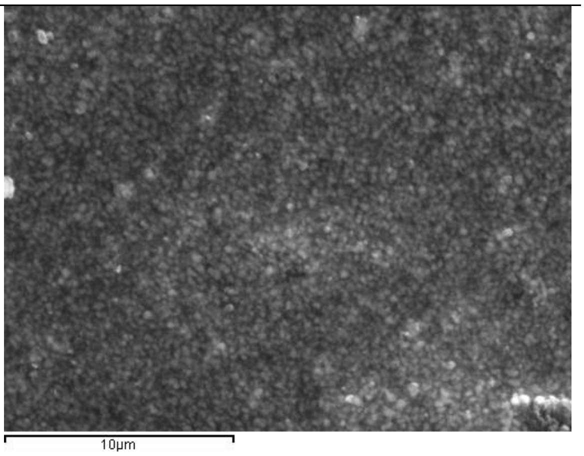
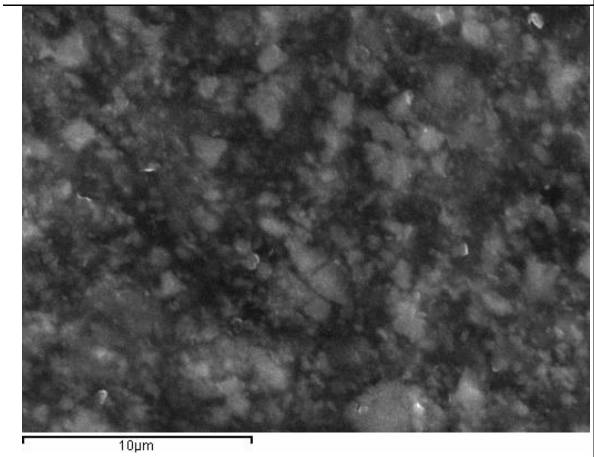
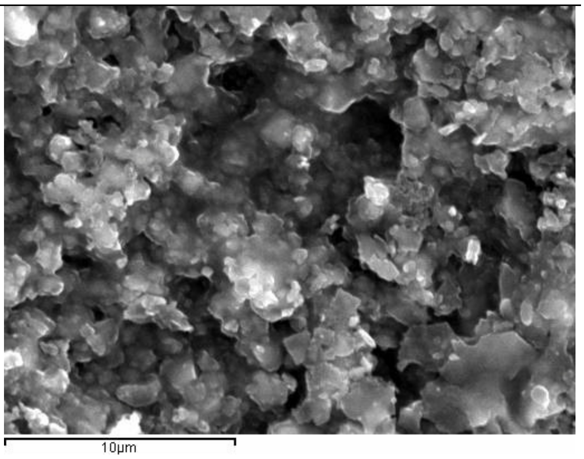
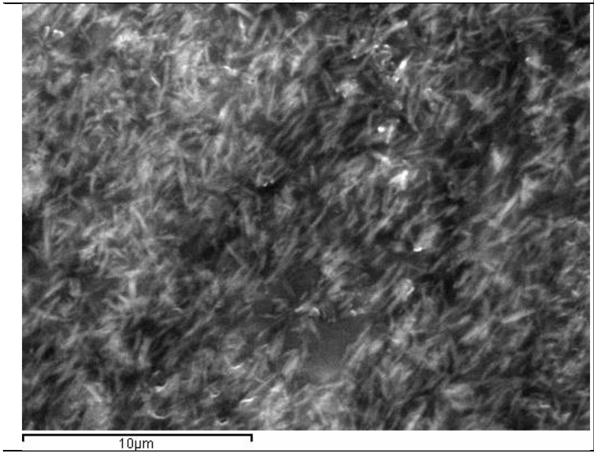
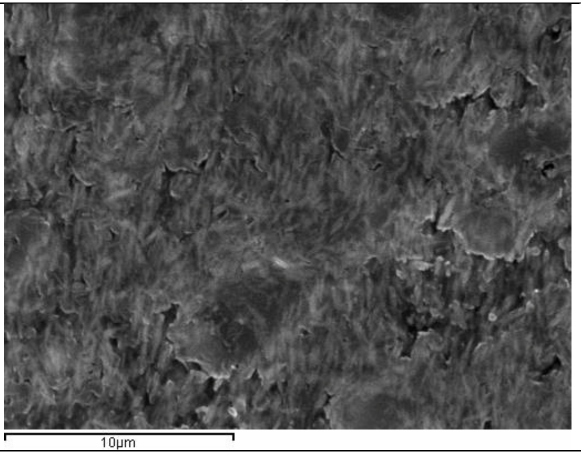
Tab.3.1-39: The surfaces of Brera (Maimeri®) samples before and after 800h of UV-light exposure (LM pictures, 25X).

The occurrence of paint layers' morphological variations was better assessed examining the surfaces using SEM (table 3.1-40).

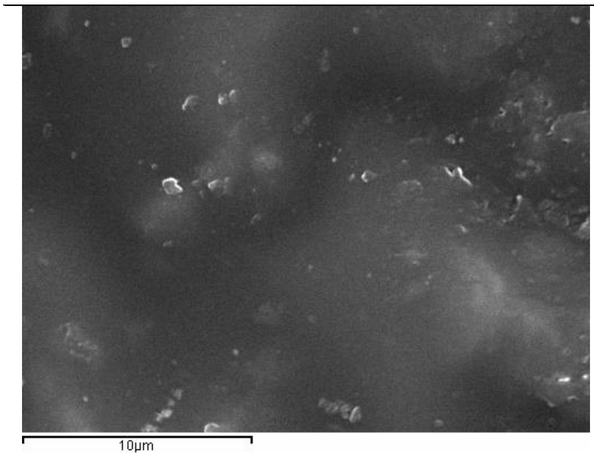
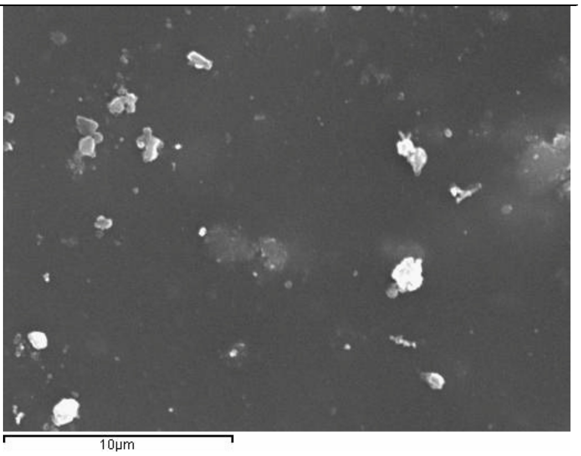
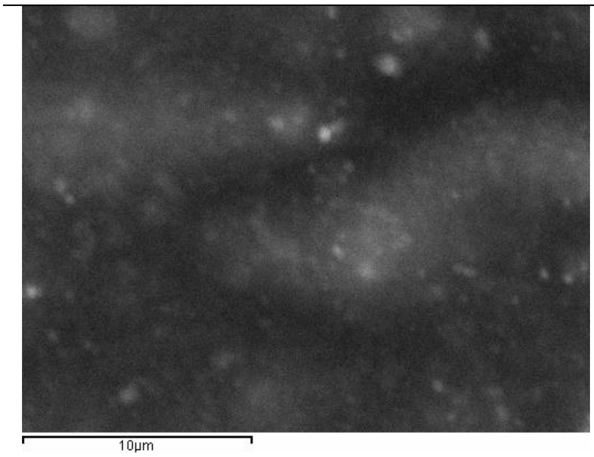
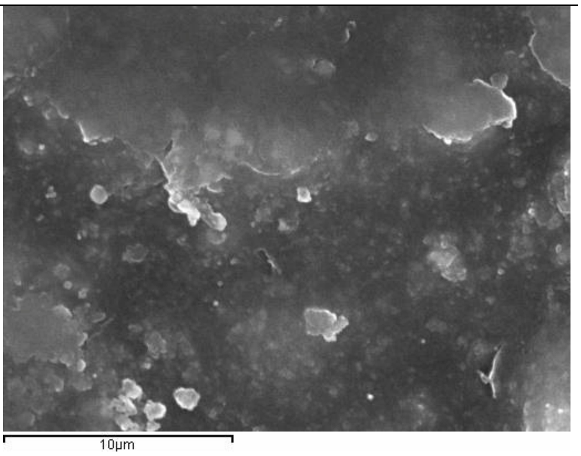
Even though, after ageing, the surface of the Ultramarine (PB29) sample looked definitely rougher, pictures taken at high magnifications showed that pigments and extenders are still covered by a thin layer of binder.

The Yellow Ochre (PY42) and Phthalo Green (PG7) samples turned out to be affected by small cracks (less than 10 µm in length).

No relevant variations were instead detected for the Titanium White (PW6) and Primary Red Magenta (PV19) samples.

<table>
<tr><th colspan="2">BRERA (Maimeri®) - TITANIUM WHITE -</th></tr>
<tr><th>0h of ageing (5000X-SEI)</th><th>800h of ageing- (5000X-SEI)</th></tr>
<tr><td> </td><td> </td></tr>
<tr><th colspan="2">BRERA (Maimeri®) - ULTRAMARINE-</th></tr>
<tr><th>0h of ageing (5000X-SEI)</th><th>800h of ageing- (5000X-SEI)</th></tr>
<tr><td> </td><td> </td></tr>
<tr><th colspan="2">BRERA (Maimeri®) – YELLOW OCHRE -</th></tr>
<tr><th>0h of ageing (5000X-SEI)</th><th>800h of ageing- (5000X-SEI)</th></tr>
<tr><td> </td><td> </td></tr>
</table>

Tab.3.1-40: The surfaces of Brera (Maimeri®) samples before and after 800h of UV-light exposure: SEM pictures, 5000X, secondary electrons. (the table continues in the following page)

BRERA (Maimeri®) - PRIMARY RED MAGENTA -	
0h of ageing (5000X-SEI)	800h of ageing- (5000X-SEI)
	
BRERA (Maimeri®) - PHTHALO GREEN-	
0h of ageing (5000X-SEI)	800h of ageing- (5000X-SEI)
	

Tab.3.1-40: The surfaces of Brera (Maimeri®) samples before and after 800h of UV-light exposure: SEM pictures, 5000X, secondary electrons.

COLORIMETRIC MEASUREMENTS

Table 3.1-40 shows the color variations assessed for Brera samples, at different steps of the UV-light ageing. The measurements were carried out according to the method previously described for Flashe® sample.

At the end of the ageing, the color variations detected for the white, yellow and green samples were negligible and probably not directly due to a decay process ($\Delta E^*_{ab} < 1$ for Titanium White and Yellow Ochre samples; $\Delta E^*_{ab} < 2$ for Phthalo Green sample).
The color of Titanium White sample (PW6) changed in a coherent way, with the calculated ΔE^*_{ab} slightly increasing as the ageing went on. The color variation was related to a slight darkening (decrement in L*) and yellowing (increment in b*) of the surface. The color of Yellow Ochre (PY42) and Phthalo Green (PG7) samples instead did not change in a coherent way.

In the case of the Primary Red Magenta (PV19) sample, the final color variation was higher but still not so pronounced to be detected when looking at the surface (ΔE^*_{ab} around 3, probably due to L*increment, a*and b*decrements).

The only sample that underwent a significant color variation was the Ultramarine one (PB29). In this case, 200h of UV light exposure, were enough to induce a color variation (ΔE^*_{ab}) of 8.50, which was detectable when looking at the paint surface. Extending the ageing, the color variation increased, with the ΔE^*_{ab} finally reaching a value of 13. The color changed in a coherent way, with increments of L*, a decrement of b*, and a* which did not change significantly (the color became lighter and more bluish).

TITANIUM WHITE (PW6)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	0.11	-0.04	0.06	0.14	0.09	-0.05	0.03	0.11
400	0.30	-0.02	0.30	0.42	0.29	-0.03	0.27	0.39
600	-0.05	0.00	0.65	0.66	-0.13	0.00	0.66	0.65
800	-0.67	-0.1	0.61	0.91	-0.66	-0.11	0.59	0.89

ULTRAMARINE (PB29)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	2.35	5.02	-6.44	8.50	2.57	4.00	-5.97	7.63
400	3.91	4.51	-8.10	10.06	4.27	2.88	-7.35	8.97
600	5.15	4.37	-9.58	11.72	5.48	2.73	-8.75	10.67
800	5.89	4.61	-10.66	13.02	6.22	2.96	-9.84	12.01

YELLOW OCHRE (PY42)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	0.11	0.06	0.44	0.45	0.13	0.05	0.34	0.37
400	0.09	-0.32	-1.35	1.39	0.13	-0.36	-1.58	1.63
600	0.07	-0.29	-1.00	1.05	0.11	-0.31	-1.29	1.33
800	0.21	-0.29	-0.48	0.60	0.24	-0.32	-0.61	0.73

PRIMARY RED MAGENTA(PV19)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	-0.93	-1.42	-0.33	1.73	-0.51	-1.96	-1.01	2.26
400	-0.53	-2.40	-1.19	2.73	-0.17	-2.95	-1.72	3.42
600	0.01	-3.37	-1.13	3.55	0.46	-4.04	-1.68	4.39
800	-0.53	-3.24	-0.76	3.37	-0.03	-3.94	-1.51	4.22

PHTHALO GREEN (PG7)

Ageing (h)	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔE^*_{ab}	ΔL*	Δa*	Δb*	ΔE^*_{ab}
200	0.12	0.40	-0.74	0.85	0.29	0.21	-0.77	0.85
400	0.39	0.16	-1.27	1.34	0.63	-0.01	-1.29	1.44
600	1.22	-1.02	-0.86	1.81	1.45	-0.60	-0.65	1.69
800	0.48	0.82	-1.06	1.42	0.69	1.11	-0.99	1.64

Tab. 3.1-41: The UV-light induced color variations of Brera-Maimeri® paints samples. The total color variation (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from values acquired both including and excluding specular reflectance (SCI and SCE methods).

3.1.2.3 Discussing results

RISING DAMP CYCLES

The ageing cycles simulating capillary absorption of water into the supports of the mural mock-ups, allowed a better definition of the degradation processes affecting real contemporary murals.

The use of reflection FTIR spectroscopy firstly contributed to the understanding of the phase-separation process of paints’ water-soluble components.

Those samples stored under laboratory conditions (thus simulating indoor works of art) did not show any evidences of early exudation phenomena. This could be due to the fact that paints were brushed on the mortar porous supports, which possibly absorbed some of the paints’ water-soluble components.[51] The spontaneous occurrence of the phase-separation process may nevertheless develop in periods of time longer than 18 weeks.

It was instead confirmed that, the phase-separation process is promoted by water which absorbed into the supports and wetted the relatively young (3 weeks) paint layers.[52]

The differences detected as far as the water induced phase-separation process are possibly due to the chemical composition of the paint layers themselves.
At the end of the 20 rising damp cycles, a polyethoxilate type surfactant (probably an alkylphenol ethoxilate one, of the Triton-X family) was detected on the surface of most of the samples cast with the acrylic Heavy Body (Liquitex®) paints.
The features related to this compound were particularly clear for the Quinacridone Crimson (PV19) and the Phthalocyanine Green (PG7) samples, they were instead less pronounced for the samples cast with paints based on inorganic pigments (PW6, PB29 and PY42).
This result is consistent with the reported use of non-ionic polyethoxylate surfactants as the best dispersing agents for organic pigments (Chapter 1, *1.2.1.4 Paints’ additives*).
Besides being characterized by the same typology of surfactants, the samples cast using Flashe®(LeFranc&Bourgeois) vinyl paints seemed not to undergo the exudation process.

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[51] It has been previously pointed out that the exudation is reduced if paints are applied on porous substrates. Ormsby, *et al.*, 2007

[52] The role played by water in speeding the exudation process of the surfactant was investigated through further testing. A sample was cast by brushing the Ultramarine Blue (Green Shade-PB29-) Heavy Body-Liquitex® paint over a fiber cement support. After few days, this sample was aged in a QUV-spray chamber, simulating outdoor ageing conditions. The sample was repeatedly exposed to an ageing cycle consisting of: 10 minutes of rain, 8h of UV light (340 nm, 60°C) and 4h of high humidity conditions leading to surface moisture (in the dark, 50°C). These ageing conditions caused an early exudation of the surfactant. Extending the ageing, the amount of surfactant detected on the surface of the sample decreased, probably as a consequence of both, re-dissolution by water (which gradually washed it away) and UV-light degradation. The role played by water in promoting the surfactant exudation process of young emulsion paints is after all well known by house-paint manufacturers (occurrence of *snail slime-lumacatura* phenomenon). (Umberto Dainese, San Marco Group S.p.a., Marcon (Ve), Italy; personal communication, spring 2010).

This could be due to:

- brand dependency reasons (the APE compound is not detected on the surface of the Flashe® samples because the vinyl formulations contain a lower amount of this surfactant with respect to the acrylic ones)
- different interactions between the paint components (the APE surfactant has a higher affinity for the vinyl binder rather than for the acrylic binder)
- the coalescence degree of the paint films (which, for Flashe®-L&B- films is actually poor, due to the presence of the calcium carbonate extender)
- the paint layer response to water (the acrylic paint layer are slightly permeable to water but less soluble than the vinyl ones).

Previous studies have actually pointed out that Flashe®-L&B- paint films are strongly sensitive to water.[53] It is therefore possible that, the overall effect of the rising damp on the vinyl paints is that of dissolving and redistributing the water-soluble components in the highly swollen film. This strong water swelling effect could be also the cause of the darkening and the increment of films' surface roughness, detected for some of the aged Flashe®-L&B- samples.

The permeability of the young acrylic and vinyl paint layers to liquid water was after all confirmed by the detection of gypsum and/or calcium carbonate on the surface of many Heavy Body-Liqutex® and Flashe®-L&B- samples.
The cement-lime mortar supports are presumably characterized by slight amounts of water soluble components (such as calcium hydroxide ad various sulfates) which could be dissolved by the rising damp. As the aqueous solution goes through the paint layers, it leads to the exudation of the paint water-soluble components and to the surface crystallization of soluble salts (with calcium carbonate due to calcium hydroxide carbonation).[54] This result is consistent with data coming from the characterization of real case studies. [55]

Neither the phase-separation nor the surface salt crystallization processes were detected for Brera (Maimeri®) samples. Their higher stability was presumably related to the higher hydrophobic nature of the paint layers, characterized by a styrene-acrylic binder.

The results seemed moreover to suggest that, as the ageing process is extended, the amount of exuded surfactant decreases. As a matter of fact, the APE surfactant, clearly

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[53] Zumbühl, *et al.*, 2007

[54] The potential surface carbonation cannot be appreciated for Flashe®-L&B- samples, due to the presence of the calcium carbonate extender.

[55] The surface presence of calcium carbonate was assessed during the restoration of the mural *Tuttomondo* by Keith Haring (*Rescue of a Mural Painting by Keith Haring in Pisa*, oral communication presented at the *Modern and Contemporary Mural* conference, Valencia, may 4-5, 2012). Similar results were gathered characterizing some of the case studies, later presented in Chapter 4 (e.g. the mural by Asdrubali, 1988).

seen on the surface of an Ultramarine Blue Heavy Body-Liquitex® samples after 3 rising damp cycles, was barely detectable at the end of the ageing (20 cycles).

It is possible that, the exuded compounds are then re-dissolved by the rising damp water and partially driven back into the paint layer during the drying process. However, no evidences of paint water-soluble components were detected at the film-support interface: when paint layer delaminations occurred they were due to sub-superficial crystallization of water soluble salts (mainly gypsum).

In order to better define the migration process of the paint water soluble components toward the support, further research should be carried out, using different analytical techniques and considering those samples that were not affected by delaminations. Since, the delaminations are due to the crystallization of soluble salts, the detection of the surfactant (presumably present in very low concentrations) could be prevented by the presence of the inorganic components. Some preliminary tests were carried out using confocal Raman spectroscopy [56] and micro Raman-spectroscopy [57] (the latter one used for investigating mock-ups' cross-sections) but they did not lead to satisfactory results. Further test should be carried out using confocal FTIR spectroscopy.

On the contrary, our trials confirmed that MIR active thermography is a powerful technique for detecting paint layer delaminations, down to a sub-millimetric scale.

Finally, the decay processes of contemporary murals are strongly influenced by the features of the support, which play an important role in causing both, surface chemical variations (temporary exudation of paint water-soluble components promoted by rising damp water, surface carbonation processes and crystallization of soluble salts such as gypsum) and delaminations of the paint layers from the support.

UV-LIGHT STABILITY TESTING

UV-light stability testing allowed a first evaluation of the suitability of the selected emulsion paints for creating out-door murals.

After 800 hours of exposure (UVA-340 light, 45°C), the chemical and physical properties of the paint layers underwent negligible or minor variations.

The development of the degradation processes was monitored using FTIR spectroscopy analysis, suggesting that:

- vinyl paints (Flashe®-LeFranc&Bourgeois) are likely to undergo ester cleavage reactions, which mainly develop according to a Norrish Type II mechanism (release

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[56] These preliminary tests were carried in collaboration with C.I.V.E.N. Venezia-Marghera (Dr. Francesco Enrichi). As far as the use of confocal Raman spectroscopy for following the phase-separation process of anionic surfactants: Belaroui, *et al.*, 2000.

[57] These preliminary tests were carried out in collaboration with Prof. Pietro Baraldi (Department of Chemistry, University of Modena and Reggio Emilia).

of acetic acid going with the formation of double bonds in the main chain). The occurrence of slight photooxidative reactions resulting in new carbonyl and hydroxyl functionalities was assessed only for one of the samples (Ultramarine Blue, PB29)

- acrylic paints (Heavy Body-Liquitex®) are likely to undergo chain scission reactions (resulting in new therminal C=C bonds) and photooxidative reactions leading to new hydroxyl and carbonyl functionalities, among which γ-lactones. The first process was possibly detected for the Transparent Raw Sienna sample (PY42), the second for the Ultramarine Blue one (PB29)
- styrene-acrylic paints (Brera-Maimeri®) are likely to undergo photooxidative reactions, mainly affecting the acrylic monomers and leading to new hydroxyl and carbonyl functionalities (among which γ-lactones, as in the case of the Ultramarine, PB29, sample). The occurrence of degradation processes involving the styrene units (such as phenyl opening reactions) was not clearly detected.

The spectral variations between unaged and aged samples were generally low, suggesting a good photooxidative stability of the tested paints.
The features ascribable to the degradation of the three binders, were slightly more pronounced for those paints consisting of inorganic pigments (especially the PB29 one), suggesting a potential catalytic effect due to the pigments themselves.[58]

Notwithstanding the fact of being applied on cement-lime mortar supports, the paints did not seem to undergo degradation processes leading to the formation of carboxylate compounds (generally promoted by the presence of water).[59]

The photooxidative degradation of the exuded organic additives (mainly non-ionic surfactants) has been also reported as one of the processes which commonly affect emulsion paints.[60] Since no evidences of organic additives were detected on the paint surfaces at the beginning of the ageing, it was not possible to evaluate their potential degradation. Only three Heavy Body-Liquitex® samples (Titanium White, Ultramarine Blue and Transparent Raw Sienna) were initially characterized by an absorption band, possibly ascribable to an anionic surfactant (at about 1558 cm^{-1}). At the end of the ageing, the intensity of this band decreased, suggesting the degradation of the additive.[61]

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[58] It is possible that the presence of the metal ions characterizing the inorganic pigments (which are TiO_2 in white paints; $2Na_2Al_2Si_2O_6 \cdot NaS_2$ in blue paints and $FeO(OH)\cdot H_2O$ in yellow paints) slightly affects the photochemical stability of the polymers.

[59] Favaro, *et al.* 2007

[60] Learner, Chiantore and Scalorone, 2002; Doménech-Carbó, *et al.* 2011; Pintus, Wei and Schreiner, 2012

[61] This result is consistent with those reported by Doménech-Carbó, *et al.* 2011.

The results detected using FTIR spectroscopy were totally consistent with the slight color and morphological variations assessed through colorimetric measurements, Light Microscopy (LM) and Scanning Electron Microscopy (SEM) examinations.

The degradation of the binder led to slight variations in the paint layer morphology: apart from being affected by microscopic cracks (less than 10 µm in length, detected only for the Yellow Ochre and Phthalo Green Brera-Maimeri® samples), the paint surfaces became rougher and matter, with the pigments/extenders which were not well embedded in the polymer matrix anymore.

Again, these morphological variations (which reflect the chemical degradation of the binders) were mainly detected for the paints containing the inorganic pigments. This could be partially due to pigment particles size and Pigment Volume Concentration reasons.[62]

The paint layers affected by the most relevant variations were those containing the artificial Ultramarine Blue pigment (PB29).

The blue samples also showed a significant discoloration,[63] clearly detectable to the naked eye, and corresponding to final color variations (ΔE^*_{ab}) higher than 10 (with L*, a* and b* variations suggesting that the colors became lighter and colder).
It is reasonable to suppose that, as the polymer resins undergo the degradation processes, the binder layers which cover the pigments become thinner and the pigments gradually extend outside the films. The rougher is the film surface, the greater is the scattering reflection of light, which contributes to the lighter appearance of the aged samples.

Comparing the color variations of the three blue samples:

- the acrylic Heavy Body-Liquitex® was the less stable, showing a ΔE^*_{ab} of 18 after only 200 hour of exposure and reaching a ΔE^*_{ab} of 26 at the end of the ageing
- the vinyl Flashe®-L&B sample showed a ΔE^*_{ab} of 7.6 after 200 hour of exposure, and reached a ΔE^*_{ab} of 18 at the end of the ageing
- the Brera-Maimeri® sample was the most stable, showing a ΔE^*_{ab} of 8.5 after 200 hour and reaching a ΔE^*_{ab} of 13 at the end of the 800 hours.

A better comparison of the results is presented in figure 3.1-51, which allows a qualitative evaluation of paints' discoloring rates during the different steps of the ageing.

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[62] See the results of the preliminary paints' characterization (section *3.1.1.3 Discussing Results*).

[63] A certain discoloration of acrylic paints based on the artificial Ultramarine Blue pigment was reported by Pintus*,* Wei and Schreiner*,* 2012

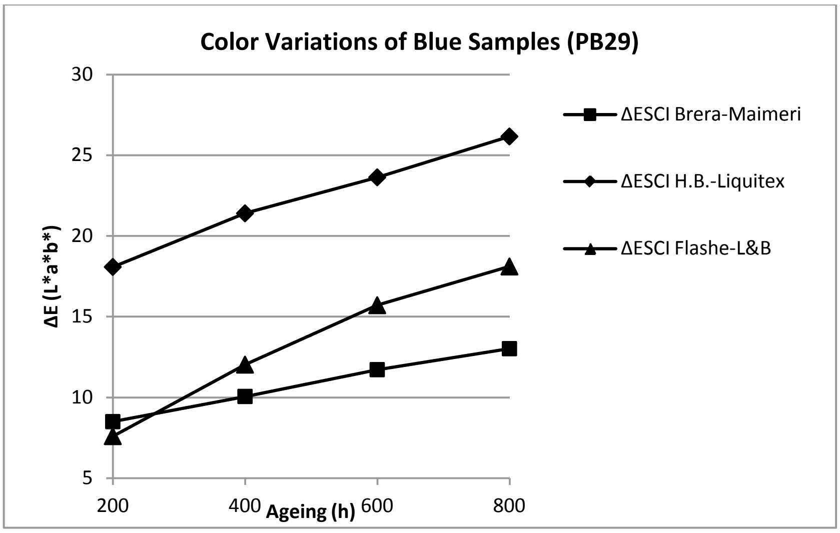

Fig.3.1-51: Comparison of the color variations (expressed as ΔE*ab) of the three paints containing the artificial Ultramarine Blue pigment (PB29), at different steps of the ageing (values including the specular components of light).

The color of the other samples did not change significantly after 800 hours of artificial ageing. The majority of the samples actually showed a negligible final color variation ($\Delta E^*_{ab} < 2$). Even though some minor variations (ΔE^*_{ab} around 4) were detected for two of the samples containing the Quinacridone Red (PV19) pigment,[64] these color changes were not detectable to naked eye examinations.
The color variations of Flashe®-L&B- Armor Green and Ruby Red samples were slightly higher (ΔE^*_{ab} of 6 and 8.5 respectively), but still barely detectable to the naked-eye.

Comparing the overall lightfastness properties of the three paint brands, Flashe®-L&B-vinyl paint turned out to be the most prone to discoloration.
This could relate to the presence of the calcium carbonate filler ($CaCO_3$, R.I. 1.6),[65] which tends to extend outside the film as the vinyl binder decays. Since the refraction index of air is lower than that of calcium carbonate, the degradation of the binder leads to an enhancement of the hiding power of the extender, resulting in a general lightening of the paint surface.

Finally, the three paint typologies were confirmed to be affected by minor photooxidative degradation processes, which could result in morphological variations and discoloration of the paint layers. These variations are more pronounced for paints consisting of inorganic pigments (usually characterized by bigger particle sizes with respect to the organic ones) and characterized by high pigment volume concentrations (due, for instance, to the presence of extenders).

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[64] These were the Quinacridone Crimson, Heavy Body-Liquitex® and Primary Red Magenta, Brera-Maimeri®.

[65] Radcliffe, 1964:58

Titanium White (PW6), Mars Yellow (PY42) and Ultramarine Blue (PB29) inorganic pigments could also play an active role in promoting the degradation of the binders.
Moreover, since paints containing the Ultramarine Blue (PB29) pigment were particularly prone to discoloration, they were confirmed not to suit outdoor use.

Even though the performances of the paints should be evaluated after longer periods of exposure (better if simulating both UV-light and rain weathering conditions), the results suggest that paints consisting of pure acrylic binders (the Heavy Body-Liquitex®) are slightly more stable than the styrene-acrylic (the Brera-Maimeri®) and the vinyl (Flashe®-L&B) ones.

3.2 Inpainting treatments: evaluation of innovative materials and methods

The second part of this thesis was undertaken with the aim of exploring the visual, handling and ageing properties of different paints which could be used for retouching acrylic/vinyl murals.

At first, Aquazol 200® and Laropal A81® resins were selected as possible media to test. Even if a number of studies have been recently published about these polymers, their use in the context of wall painting is still scarce, one of the innovative purposes of this research was to assess the properties of Aquazol 200® and Laropal A81® resins when applied on a cement-lime mortar support.

Considering the positive and negative aspects of working with the retouching formulations prepared with these media, and as they relate to the practical treatment of mural paintings, some artists' emulsion paints were later included in the study.

3.2.1 Preliminary characterization

Before testing the durability of the retouching paints, the chemical and physical properties of each inpainted area were assessed.

As already described in Chapter 2 (*2.2 Casting procedure*), each one of the samples was inpainted using six different formulations:

1) the reference artists' emulsion paint (P)

2) the reference artists' emulsion paint added with 2% by weight of the Europium (III) complex (PEu)

3) the formulation containing the Laropal A81® resin as the binder (Lr)

4) the same Laropal A81® formulation added with 2% by weight of the Europium (III) complex (LrEu)

5) the formulation containing the Aquazol 200® resin as the binder (Aq)

6) the same Aquazol 200® formulations added with 2% by weight of the Europium (III) complex (Aq Eu)

In the case of the blue samples,[66] two additional formulations were tested:

7) the artists' emulsion paint, diluted or added with some extenders in order to match the discolored reference paint (DsP)

8) the previous formulation added with 2% by weight of the Europium(III) complex (DsPEu).

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[66] It is to remember that the three blue samples (FLPB29, LQPB29 and BRPB29) were the only one which suffered a significant discoloration after 400h of UV-light exposure.

The preliminary characterization was carried out:

- taking pictures of the overall samples under visible and UV light (Wood's lamp, λ 365 nm, no filters);
- studying the morphology of the different retouching paint layers using Light Microscopy and, if of interest, Scanning Electron Microscopy;[67]
- assessing the color of each inpainted area in a quantitative way through Colorimetric Measurements;
- chemically characterizing each retouching formulation through FTIR spectroscopy.

The data collected during this preliminary characterization became the starting point for evaluating the ageing process of the retouching formulations.

They also allowed a comparison between the properties of the different retouching formulations: the evaluation of the match (in term of both color and texture) between the reference paints and the inpainted areas suggested how to potentially modify the 'recipes' used (e.g. varying the pigment volume concentration; varying the amounts of certain pigments to reach a better color match).

Another aim of this preliminary characterization was to assess if it was possible to discriminate between reference paints and inpainted areas when examining the surfaces under UV light. In this way, the real need of adding or not the luminescent Europium (III) complex to enhance the discernibility of the treatments was preliminary evaluated.

Finally, the potential influence of the Europium (III) complex on the color and morphological properties of the retouching formulations was assessed.

A selection of the most relevant results is presented in the following pages.

3.2.1.1 Chemical characterization

All the retouching formulations included in the study were preliminary characterized through FTIR spectroscopy measurements.[68]

The spectra showed the typical features characterizing the components included in the retouching formulations.

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[67] LM examinations were carried out using the Leica DMR microscope, SEM examination using the Jeol JSM 6300 electron microscope. In this latter case, only a selection of the treated surfaces were studied: BRPW6PEu, BRPB29PEu, BRPY42PEu, BRPV19PEu, BRPG7PEu, BRPW6Lr, BRPW6LrEu, BRPW6Aq and BRPW6AqEu.

[68] To assess the chemical composition of the retouching formulations, the spectra were collected from little amounts of paint, scraped from the surface of the mock-ups. The Vertex 70 Fourier Transform Infrared spectrometer (Bruker Optik GmbH), equipped with ATR accessory, was used. For all the spectra, the processing was carried out using OPUS 5.0 software and included: ATR→ABS conversion, automatic base line correction (Rubberband method, 64 baseline points), automatic smoothing and scale normalization.

As already described in Chapter 2 (sections *2.1.3 Retouching materials*, and 2*.2.3.1 Retouching formulations*) these components are: Laropal A81® or Aquazol 200® resins; Titanium White (PW6), Ultramarine Deep (PB29), Mars Yellow (PY42), Quinacridone Rose (PV19) and Phthalo Green (PG7) pigments; calcium carbonate ($CaCO_3$) and/or silica (SiO_2) extenders; the Europium (III) complex.

The reference spectra of these materials are reported in Appendix 2 (where the theoretical molecular structures of the organic components are presented as well).

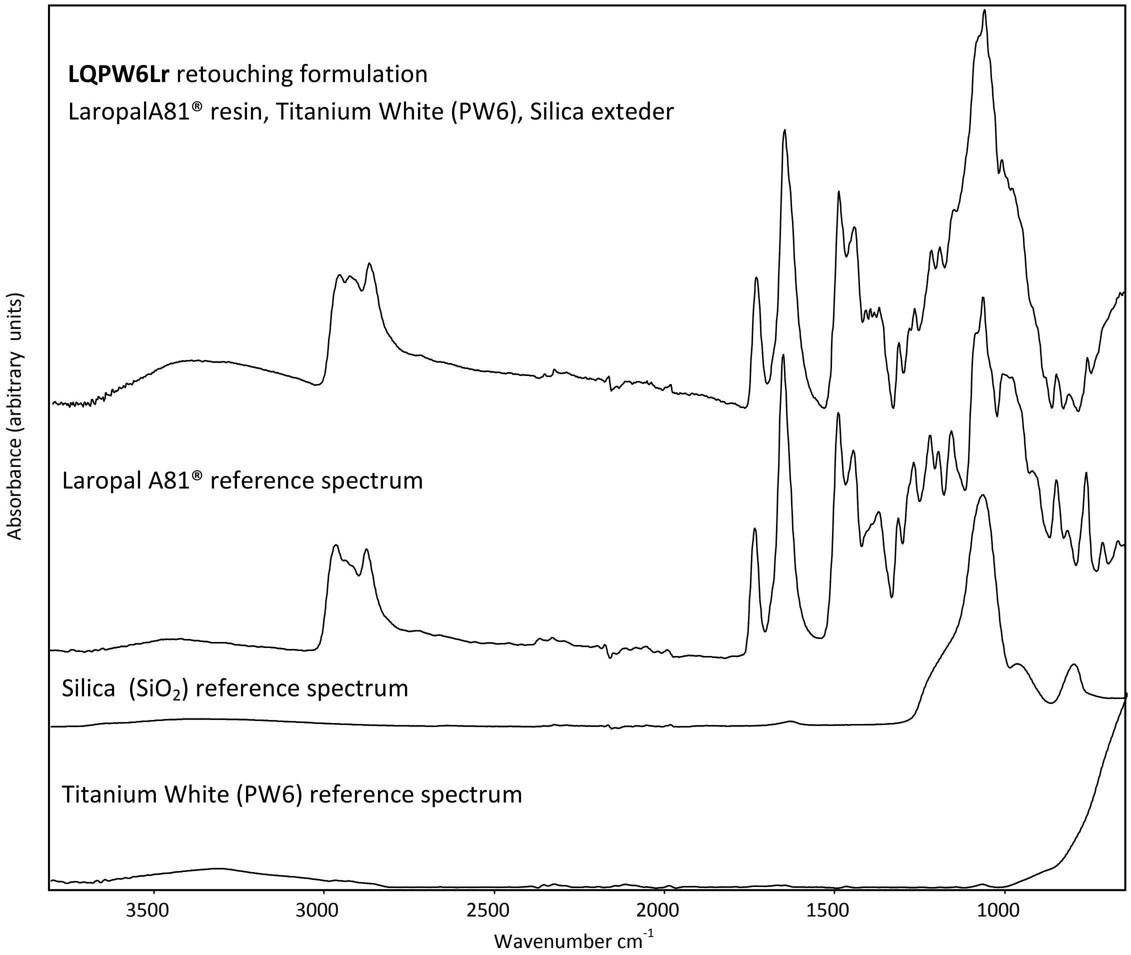

Fig.3.2-1: The FTIR spectrum of the LQPW6Lr retouching formulation, followed by the reference spectra of its components: Laropal A81® resin (binder); silica extender and Titanium White(PW6) pigment.

As shown in the figure 3.2-1, the main absorption features of the urea-aldehyde resin[69] (Laropal A81®) are: the pronounced C-H stretching absorptions from the polymer backbone at 2960 cm^{-1} and 2869 cm^{-1} (methylene asymmetric and symmetric stretching); the ester carbonyl stretching at 1728 cm^{-1}; the carbonyl stretching of the tertiary amide at 1646 cm^{-1}. The remaining absorptions in the fingerprint region are due to various ether and ester C-O-C stretching, C-C stretching and C-H bendings with the

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[69] Data are consistent with those reported by: de la Rie, *et al.* 2002.

strongest being the methylene scissor vibration at 1485 cm^{-1}. The geminal dimethyl groups lead to the doublet at 1388 and 1366 cm^{-1}, while the ether group is absorbing between 1100÷1000 cm^{-1}(with a principle peak at 1057 cm^{-1}).

An additional feature that is sometimes detected is the primary hydroxyl group absorption around 3500÷3300 cm^{-1}.

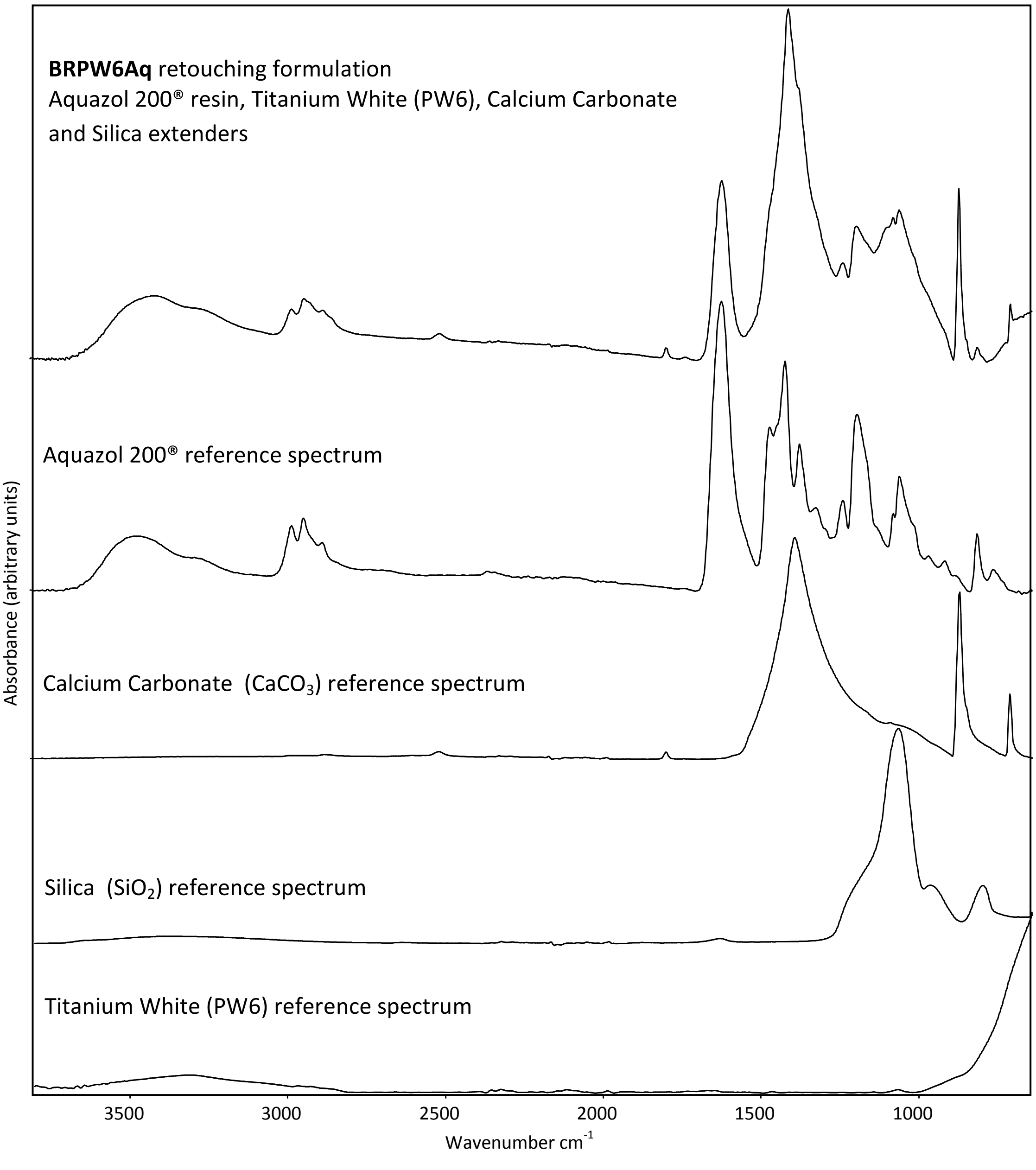

Fig.3.2-2: The FTIR spectrum of the BRPW6Aq retouching formulation, followed by the reference spectra of its components: Aquazol200® resin (binder), Calcium Carbonate and Silica extenders, Titanium White(PW6) pigment.

As shown in figure 3.2-2, the main absorptions in the spectrum of the p(2-ethyl-2-oxazoline) resin (Aquazol 200®) are those expected for a complex aliphatic tertiary amide: three bands in the C-H stretching region at about 2975 cm^{-1}, 2940 and 2880 cm^{-1}

(CH_3 asymmetric stretching, CH_2 asymmetric stretching and CH_3 symmetric stretching); the carbonyl stretching of the amide at about 1630 cm^{-1}; several bands in the fingerprint region due to C-C stretching, C-N stretching and C-H bending vibrations.[70] An additional feature is the broad absorption band between 3600 and 3100 cm^{-1}, mainly peaking at 3460 cm^{-1} and showing a shoulder around 3280 cm^{-1} (OH stretching and NH stretching region).

Some spectra of the Aquazol 200® based formulations showed a minor absorption band around 1730 cm^{-1}, tentatively ascribable to the carbonyl stretching of an early oxidation product.

The full list of the absorption features detected for each one of the retouching formulations is given in the following tables (Tab: 3.2-1, 3.2-2, 3.2-3).

Retouching paints prepared to inpaint FLASHE®-L&B- samples										
PW6 Aq	**PW6 Lr**	**PB29 Aq**	**PB29 Lr**	**PY42 Aq**	**PY42 Lr**	**PV19 Aq**	**PV19 Lr**	**PG7 Aq**	**PG7 Lr**	**Band Assignement**
-	-	3691	3688	-	-	-	-	-	-	PB29
-	-	3619	3621	-	-	-	-	-	-	PB29
3396	-	3412	-	3400	-	3407	-	3395	-	Aquazol200®
3272	-	3270	-	-	-	3270	-	3273	-	Aquazol200®
-	-	-	-	-	-	-	3264	-	-	PV19
-	-	-	-	-	-	3219	3222	-	-	PV19
-	-	-	-	-	-	3155	3155	-	-	PV19
-	-	-	-	3115	3110	-	-	-	-	PY42
-	-	-	-	-	-	-	3101	-	-	PV19
-	-	-	-	-	-	-	3062	-	-	PV19
2977	-	2978	-	2978	-	2976	-	2978	-	Aquazol200®
-	2957	-	2958	-	2955	-	2957	-	2957	LaropalA81®
2938	-	2941	-	2939	-	2937	-	2938	-	Aquazol200®
-	2927	-	2928	-	2922	-	2923	-	2925	LaropalA81®
-	-	-	-	-	-	2921	-	-	-	PV19
-	-	-	-	-	-	-	-	2920	-	PG7
2876	-	2880	-	2878	-	2877	-	2877	-	Aquazol200®
-	2870	-	2871	-	2869	-	2870	-	2871	LaropalA81®
-	-	-	-	-	-	2853	-	-	-	PV19
2511	2511	2512	2512	2511	2512	2512	2512	2511	2514	$CaCO_3$
1796	1796	1796	1796	1796	1796	1796	1796	1796	1796	$CaCO_3$
-	1730	-	1730	-	1730	-	1730	-	1730	LaropalA81®
-	1650	-	1649	-	1651	-	1648	-	1649	LaropalA81®
1629	-	1627	-	1629	-	1628	-	1631	-	Aquazol200®
-	-	-	-	-	-	-	1588	-	-	PV19
1389	1399	1405	1399	1392	1396	1393	1391	1391	1394	$CaCO_3$
-	1310sh	-	1311sh	-	1311sh	-	1309	-	1309	LaropalA81®

Table 3.2-1: FTIR absorption features (cm^{-1}) of the formulations used to inpaint Flashe®-L&B- samples. Aq=Aquazol200® based paint; Lr= LaropalA81® based paint.; PW6=Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Rose; PG7= Phathalocyanine Green; $CaCO_3$=Calcium Carbonate; SiO_2= Silica (the table continues in the following page)

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[70] Wolbers, McGinn and Duerbeck (1998), tentatively ascribed some minor bands (around 1250 cm^{-1}, 1209 cm^{-1} and 769 cm^{-1}) to an aromatic sulfonic acid or a sulfonate ester. Methyl tosylate was actually reported to be used as initiator during the polymerization process of the PEOX resins.

Retouching paints prepared to inpaint FLASHE®-L&B- samples										
PW6 Aq	**PW6 Lr**	**PB29 Aq**	**PB29 Lr**	**PY42 Aq**	**PY42 Lr**	**PV19 Aq**	**PV19 Lr**	**PG7 Aq**	**PG7 Lr**	**Band Assignement**
-	-	-	-	-	-	-	-	1307	-	PG7
-	-	-	-	-	-	-	-	1278	1278	PG7
-	1262	-	1265	-	1261	-	1263	-	1261	LaropalA81®
-	1215	-	1217	-	1216	-	1215	-	1215	LaropalA81®
-	-	-	-	-	-	-	-	1207	-	Aquazol200®/PG7
1202	-	1200	-	1198	-	1200	-	-	-	Aquazol200®
-	1191	-	1190	-	1188	-	1190	-	1188	LaropalA81®
-	1152	-	1151	-	1151	-	1151	-	1153	LaropalA81®
-	-	-	-	-	-	-	-	1152	-	PG7
-	-	-	-	-	-	-	-	1093	-	PG7
-	1087	-	1081sh	-	1081	-	1085	-	1084	LaropalA81®
1060	-	-	-	1062	-	1061	-	-	-	Aquazol200®
-	1058	-	-	-	1058	-	1060	-	1061	LaropalA81®
-	1006	-	-	-	1005	-	1006	-	1005	LaropalA81®
-	-	981	996	-	-	-	-	-	-	PB29
-	-	-	-	-	-	-	-	950	-	PG7
-	-	-	-	906	907	-	-	-	-	PY42
871	872	871	871	871	872	870	870	870	871	$CaCO_3$
-	-	-	-	-	-	850sh	846sh	-	-	PV19
-	-	-	-	-	-	817sh	812sh	-	-	PV19
-	-	-	-	797	798	-	-	-	-	PY42
-	-	-	-	-	-	-	-	769	771	PG7
-	756	-	755	-	756	-	754	-	756	LaropalA81®
-	-	-	-	-	-	749sh	-	-	-	PV19
-	-	-	-	-	-	-	-	748	-	PG7
711	711	709	710	712	712	711	711	711	710	$CaCO_3$
-	-	690	-	-	-	-	-	-	-	PB29
-	-	658	658	-	-	-	-	-	-	PB29
-	-	-	-	606	606	-	-	-	-	PY42

Table 3.2-1: FTIR absorption features (cm^{-1}) of the formulations used to inpaint Flashe®-L&B- samples. Aq=Aquazol 200® based form.; Lr= LaropalA81® based form.; PW6=Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Rose; PG7= Phathalocyanine Green; $CaCO_3$=Calcium Carbonate; SiO_2= Silica

Retouching paints prepared to inpaint H.B.- Liquitex® samples										
PW6 Aq	**PW6 Lr**	**PB29 Aq**	**PB29 Lr**	**PY42 Aq**	**PY42 Lr**	**PV19 Aq**	**PV19 Lr**	**PG7 Aq**	**PG7 Lr**	**Band Assignement**
-	-	3691	3690	-	-	-	-	-	-	PB29
-	-	-	3619	-	-	-	-	-	-	PB29
3414	-	3412	-	3377	-	3426	-	3408	-	Aquazol200®
3272	-	3274	-	-	-	-	-	3274	-	Aquazol200®
-	-	-	-	-	-	3263	3264	-	-	PV19
-	-	-	-	-	-	3222	3223	-	-	PV19
-	-	-	-	-	-	3157	3154	-	-	PV19
-	-	-	-	-	-	3108	3105	-	-	PV19
-	-	-	-	-	-	3060	3058	-	-	PV19
2977	-	2978	-	-	-	2978	-	2979	-	Aquazol200®
-	2958	-	2958	-	2953	-	2959	-	2956	LaropalA81®
2939	-	2939	-	2918	-	2939	-	2938	-	Aquazol200®
-	2927	-	2929	-	2919	-	2923	-	2925	LaropalA81®
2880	-	2881	-	2853	-	2881	-	2881	-	Aquazol200®
-	2870	-	2871	-	2871	-	2870	-	2870	LaropalA81®
2512	-	-	2515	-	-	2512	2511	-	-	$CaCO_3$
1796	-	-	1796	-	-	1796	1796	-	-	$CaCO_3$
1734	-	1735	-	-	-	1734	-	1733	-	Aquazol200®?
-	1729	-	1730	-	1727	-	1731	-	1729	LaropalA81®
-	1645	-	1648	-	1648	-	1648	-	1647	LaropalA81®
1618	-	1621	-	1629	-	1623	-	1615	-	Aquazol200®
-	-	-	-	-	-	-	1588	-	-	PV19
-	-	-	-	-	-	1556s	-	-	-	PV19
-	1486	-	1484	-	-	-	-	-	1485	LaropalA81®
-	-	1470	-	-	-	-	-	1470		Aquazol200®
-	1441	-	1434		1434		-		1439	LaropalA81®
1419	-	1421	-	-	-	-	-	1421	-	Aquazol200®
-	-	-	-	-	-	1414	-	-	-	Aquazol200®/ $CaCO_3$
-	-	-	-	-	1411	-	-	-	-	PV19
-	1399	-	1408	-	-	-	1408	-	-	$CaCO_3$
-	-	-	-		-		-	1390	1392	PG7
1377	-	1377	-	-	-	1376	-	1377	-	Aquazol200®
-	1368	-	-	-	-	-	-	-	1369	LaropalA81®
-	-	-	-	-	-	-	-	1321	-	Aquazol200®
-	-	-	-	-	-	-	1344	-	-	PV19
-	1307	-	1310	-	1310	-	1310	-	1309	LaropalA81®
-	-	-	-	-	-	-	-	1305	1305	LaropalA81®/ PG7
-	-	-	-	-	-	-	-	1276	1278	PG7
-	1267	-	1264	-	1263	-	1263	-	1264	LaropalA81®
1239	-	1236	-	-	-	1237	-	1241	-	Aquazol200®
-	1215	-	1215	-	1217	-	1215	-	1212	LaropalA81®
1196	-	1192	-	-	-	1196	-	1199	-	Aquazol200®
-	1188	-	1186	-	-	-	1190	-	1190	LaropalA81®

Table 3.2-2: FTIR absorption features (cm^{-1}) of the formulations used to inpaint Heavy Body-Liquitex® samples. Aq=Aquazol 200® based paint; Lr= Laropal A81® based paint; PW6=Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Rose; PG7= Phathalocyanine Green; $CaCO_3$=Calcium Carbonate; SiO_2= Silica. The question mark is used for uncertain attribution
(the table continues in the following page)

Retouching paints prepared to inpaint H.B.- Liquitex® samples										
PW6 Aq	**PW6 Lr**	**PB29 Aq**	**PB29 Lr**	**PY42 Aq**	**PY42 Lr**	**PV19 Aq**	**PV19 Lr**	**PG7 Aq**	**PG7 Lr**	**Band Assignement**
-	-	-	-	-	1160	-	-	-	-	PV19
-	1146	-	-	-	-	-	1151	-	1152	LaropalA81®
-	-	-	-	-	-	-	-	1153	-	PG7
-	-	-	-	-	-	-	-	1094	-	PG7
-	1074	-	-	-	-	-	1081	-	-	LaropalA81®
1080	-	-	-	-	-	1080	-	1080	-	Aquazol200®
1062	-	-	-	-	-	1061	-	1059	-	Aquazol200®
-	1058	-	-	-	1060	-	1058	-	1058	LaropalA81®
-	-	1056	-	-	-	-	-	-	-	SiO_2
-	-	-	-	-	1024	-	-	-	-	PV19
-	-	1008	-	-	-	-	-	-	-	PB29
-	1005	-	-	-	-	-	1006	-	1002	LaropalA81®
-	-	-	986	981	992	-	-	-	-	PB29
-	-	-	-	-	-	960	-	-	-	PV19
-	-	-	-	-	-	-	-	949	951	PG7
-	-	-	-	-	902	-	-	-	-	PY42
-	-	-	-	-	-	-	-	876	874	PG7
873	-	-	873	-	-	872	872	-	-	$CaCO_3$
-	845	-	-	-	-	-	847	-	847	LaropalA81®
-	-	-	-	-	-	-	815	-	-	PV19
-	-	-	-	-	-	817	-	-	-	Aquazol200®/ PV19
815	-	-	-	-	-	-	-	813	-	Aquazol200®/
-	811	-	-	-	-	-	-	-	805	LaropalA81®
-	-	798	798	-	-	-	800	-	-	SiO_2
-	-	-	-	783	796	-	-	-	-	PY42
-	-	-	-	-	777	-	-	769	769	PG7
-	754	-	756	-	755	-	753	-	755	LaropalA81®
-	-	-	-	-	-	746	-	-	-	PV19
-	-	-	-	-	-	-	-	746	-	PG7
711	-	-	710	-	-	711	711	-	-	$CaCO_3$
-	-	-	-	-	-	-	-	-	710	LaropalA81®
-	-	692	693	-	695	-	-	-	-	PB29
-	-	655	657	-	-	-	-	-	-	PB29
-	-	-	-	643	-	-	-	-	-	PG7
-	-	-	-	-	606	-	-	-	-	PY42

Table 3.2-2: FTIR absorption features (cm^{-1}) of the formulations used to inpaint the Heavy Body-Liquitex® samples. Aq=Aquazol 200® based paint; Lr= Laropal A81® based paint; PW6=Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Rose; PG7= Phathalocyanine Green; $CaCO_3$=Calcium Carbonate; SiO_2= Silica

Retouching paints prepared to inpaint BRERA- Maimeri® samples										
PW6 Aq	**PW6 Lr**	**PB29 Aq**	**PB29 Lr**	**PY42 Aq**	**PY42 Lr**	**PV19 Aq**	**PV19 Lr**	**PG7 Aq**	**PG7 Lr**	**Band Assignement**
-	-	3692	3691	-	-	-	-	-	-	PB29
-	-	-	3618	-	-	-	-	-	-	PB29
3410	-	3415	-	3406	-	3412	-	3415	-	Aquazol200®
3277	-	3274	-	3253	-	3269	-	3281	-	Aquazol200®
-	-	-	-	3112	3112	-	-	-	-	PY42
-	-	-	-	-	-	-	3264	-	-	PV19
-	-	-	-	-	-	3220	3221	-	-	PV19
-	-	-	-	-	-	3153	3155	-	-	PV19
-	-	-	-	-	-	3103	3099	-	-	PV19
-	-	-	-	-	-	3060	3059	-	-	PV19
2977	-	2977	-	2977	-	2977	-	2979	-	Aquazol200®
-	2960	-	2960	-	2959	-	2959	-	2956	LaropalA81®
2938	-	2937	-	2940	-	2939	-	2939	-	Aquazol200®
-	2928	-	2924	-	2928	-	2925	-	2923	LaropalA81®
2880	-	2879	-	2880	-	2879	-	2879	-	Aquazol200®
-	2870	-	2869	-	2869	-	2870	-	2870	LaropalA81®
2512	-	-	-	2510	2509	2511	2511	-	-	$CaCO_3$
1796	-	-	-	1796	1796	1796	1796	-	-	$CaCO_3$
-	-	1734	-	-	-	1733	-	1733	-	Aquazol200®?
-	1730	-	1730	-	1730	-	1730	-	1730	LaropalA81®
-	1646	-	1646	-	1647	-	1650	-	1648	LaropalA81®
1621	-	1621	-	1621	-	1625	-	1618	-	Aquazol200®
-	-	-	-	-	-	-	1587	-	-	PV19
-	-	-	-	-	-	1555	-	-	-	PV19
-	1487	-	1486	-	1483	-	-	-	1486	LaropalA81®
-	-	1471	-	-	-	-	-	1467	-	Aquazol200®
-	1441	-	1440	-	-	-	-	-	1437	LaropalA81®
-	-	1423	-	-	-	-	-	1420	-	Aquazol200®
1411	-	-	-	1413	-	1400	-	-	-	Aquazol200®/ $CaCO_3$
-	-	-	1408	-	1410	-	1398	-	-	$CaCO_3$
-	-	-	-	-	-	-	-	1390	1393	PG7
-	-	1377	-	1378	-	-	-	1377	-	Aquazol200®
-	1367	-	-	-	-	-	-	-	1369	LaropalA81®
-	-	-	-	-	-	-	-	1323	-	Aquazol200®
-	-	-	-	-	-	1345	1344	-	-	PV19
-	1308	-	1309	-	1310	-	1310	-	1307	LaropalA81®
-	-	-	-	-	-	-	-	1305	-	PG7
-	-	-	-	-	-	-	-	1278	1278	PG7
-	1264	-	1264	-	1262	-	1263	-	1264	LaropalA81®
1237	-	1233	-	1239	-	1238	-	1238	-	Aquazol200®
-	1215	-	1214	-	1214	-	1216	-	1210	LaropalA81®
1196	-	1196	-	1194	-	1198	-	1196	-	Aquazol200®
-	1189	-	1187	-	1190	-	1188	-	1184	LaropalA81®
-	-	-	-	-	1152	-	1151	-	1149	LaropalA81®
-	-	-	-	-	-	-	-	1152	-	PG7

Table 3.2-3: FTIR absorption features (cm^{-1}) of the formulations used to inpaint the Brera-Maimeri® samples. Aq=Aquazol 200® based paint; Lr= LaropalA81® based paint; PW6=Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Rose; PG7= Phathalocyanine Green; $CaCO_3$=Calcium Carbonate; SiO_2= Silica. The question mark is used for uncertain attributions.
(the table continues in the following page)

Retouching paints prepared to inpaint BRERA- Maimeri® samples										
PW6 Aq	**PW6 Lr**	**PB29 Aq**	**PB29 Lr**	**PY42 Aq**	**PY42 Lr**	**PV19 Aq**	**PV19 Lr**	**PG7 Aq**	**PG7 Lr**	**Band Assignement**
-	-	-	-	-	-	-	1136	-	-	PV19
-	-	-	-	-	-	-	-	1091	-	PG7
-	-	-	-	-	1081	-	1080	-	1078	LaropalA81®
1080	-	1078	-	1080	-	1080	-	1080	-	Aquazol200®
1061	-	-	-	1061	-	1062	-	1058	-	Aquazol200®
-	-	1060	-	-	-	-	-	-	-	Aquazol200®/ SiO_2
-	1059	-	1056	-	1058	-	1060	-	1057	LaropalA81®
-	-	1030	1028	-	-	-	-	-	-	PV19
-	-	1005	-	-	-	-	-	-	-	PB29
-	1004	-	-	-	1006	-	1005	-	995	LaropalA81®
-	976	-	-	-	976	-	-	-	-	LaropalA81®
-	-	-	986	981	-	-	-	-	-	PB29
-	-	-	-	-	-	962	-	-	-	PV19
-	-	-	-	-	-	-	-	948	950	PG7
-	-	-	-	902	902	-	-	-	-	PY42
-	-	-	-		-	-	-	874	875	PG7
873	-	-	-	874	871	871	871	-	-	$CaCO_3$
-	845	-	847	-	847	-	847	-	-	LaropalA81®
-	-	-	-	-	-	-	-	-	-	PV19
-	-	811	-	-	-	813	-	-	-	Aquazol200®/ PV19
815	-	-	-	-	-	-	-	812	-	Aquazol200®
-	811	-	-	-	-	-	-	-	-	LaropalA81®
-	-	800	798	-	-	-	-	-	-	SiO_2
-	-	-	-	796	797	-	-	-	-	PY42
-	-	-	-	-	777	-	-	770	769	PG7
-	755	-	755	-	755	-	753	-	756	LaropalA81®
-	-	-	-	-	-	748	-	-	-	PV19
-	-	-	-	-	-	-	-	747	-	PG7
711	-	-	-	712	711	712	713	-	-	$CaCO_3$
-	-	-	-	-	-	-	-	-	712	LaropalA81®
-	-	693	699	-	-	-	-	-	-	PB29
-	-	657	657	-	-	-	-	-	-	PB29
-	-	-	-	643	-	-	-	-	-	PG7
-	-	-	-	-	602	-	-	-	-	PY42

Table 3.2-3: FTIR absorption features (cm^{-1}) of the formulations used to inpaint Brera-Maimeri® samples. Aq=Aquazol200® based form.; Lr= LaropalA81® based form.; PW6=Titanium Dioxade; PB29= Ultramarine Blue; PY42= Mars Yellow; PV19= Quinacridone Rose; PG7= Phathalocyanine Green; $CaCO_3$=Calcium Carbonate; SiO_2= Silica

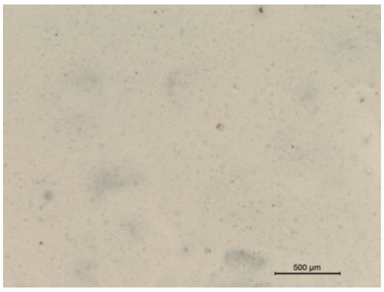
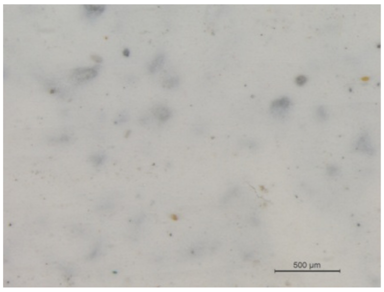
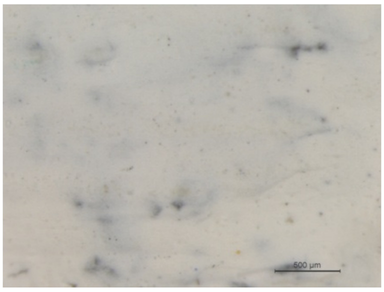
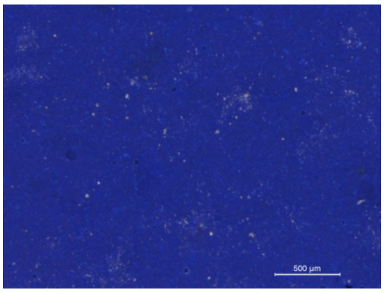
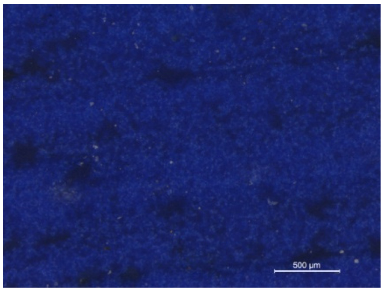
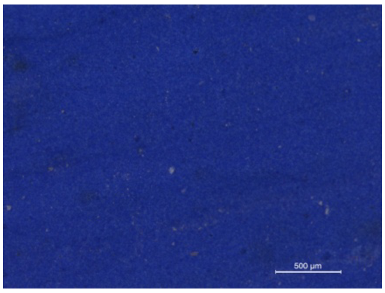
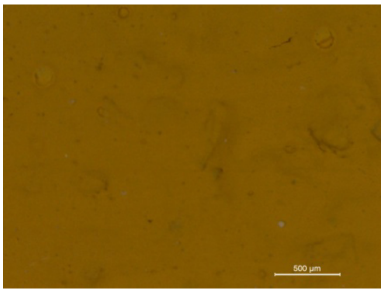
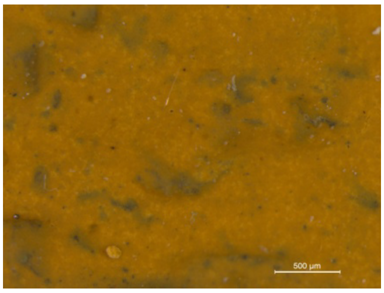
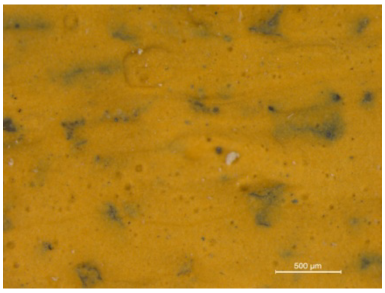
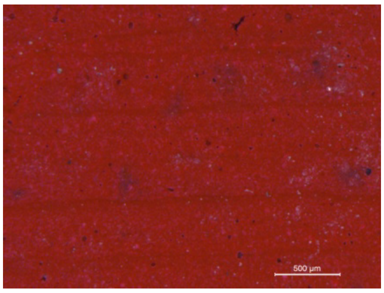
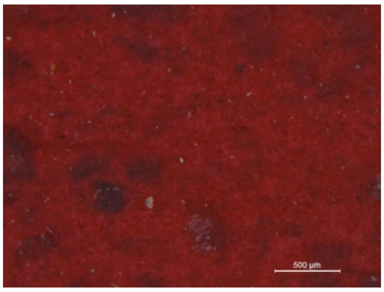
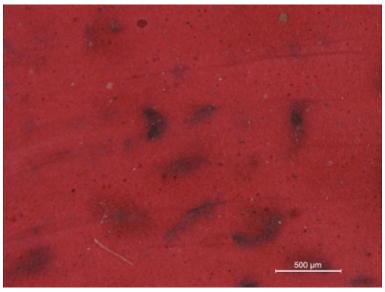
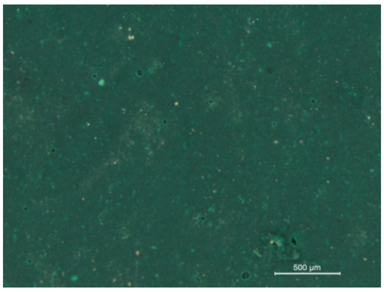
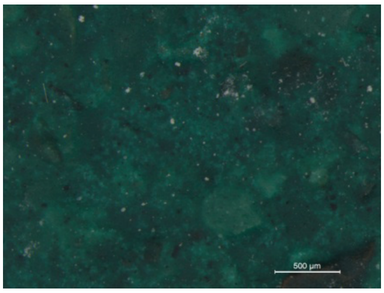
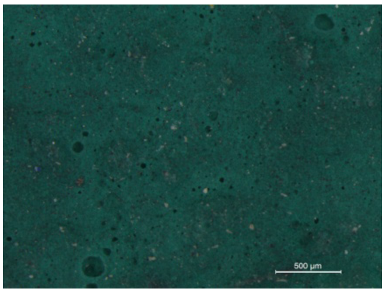
Data coming from this preliminary characterization pointed out that:

- it was difficult to detect the absorption features of those components introduced in the formulations in amounts lower than the 3-5% (e.g. the Mars Yellow PY42 pigment added as about 1% by weight in the formulations prepared to inpaint red areas; silica extender)
- the interpretation of the spectra from paints containing organic pigments was more difficult (it was not always possible to univocally discriminate between pigment and binder absorptions)
- notwithstanding the fact that little amounts of Tween 20® surfactant were included in the formulation of the retouching paints, no evidences of this compound were detected when characterizing the inpainted areas
- all the retouching formulations were brushed over a base layer of Regalrez 1094®, but the spectra did not show any features related to this resin
- since the samples were directly scraped from the surfaces of the mock-ups, contamination problems sometimes arose (e.g. the LQPY42Aq spectrum showed the typical features of calcium carbonate, since the extender was not included in the formulation, it is reasonable to suppose that these absorptions are due to the cement-lime mortar support).

Since the spectra collected from the areas inpainted with the artists’ emulsion paints mainly corresponded to the spectra shown in section *3.1.1.1 Chemical characterization*, they are not discussed here. It could be however noticed that the spectra of the ‘retouching’ artists’ emulsion paints did not show any absorption features clearly related to the surface exudation of organic additives.

3.2.1.2 Morphological and color characterization

The color and morphological properties of the paint layers resulting from the different retouching formulations were preliminary studied. In the following tables (3.2-4; 3.2-5 and 3.2-6), the Light Microscopy pictures of the reference paint areas are compared with those of the respective inpainted areas. Since those areas inpainted using the atists’ emulsion paints (P method) looked as the reference ones, they were not included in the tables.

<table>
<tr><th colspan="3">FLASHE® (LeFranc & Bourgeois)</th></tr>
<tr><td>WHITE (25X)</td><td>FLPW6Lr (25X)</td><td>FLPW6Aq (25X)</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
<tr><td>ULTRAMARINE BLUE (25X)</td><td>FLPB29Lr (25X)</td><td>FLPB29Aq (25X)</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
<tr><td>YELLOW OCHRE (25X)</td><td>FLPY42Lr(25X)</td><td>FLPY42Aq (25X)</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
<tr><td>RUBY RED (25X)</td><td>FLPV19Lr (25X)</td><td>FLPV19Aq (25X)</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
<tr><td>ARMOR GREEN (25X)</td><td>FLPG7Lr (25X)</td><td>FLPG7Aq(25X)</td></tr>
<tr><td> </td><td> </td><td> </td></tr>
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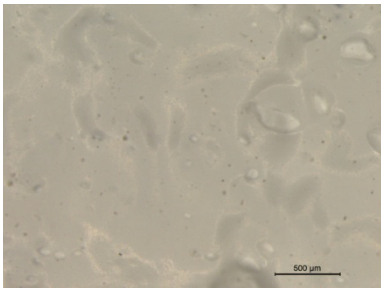
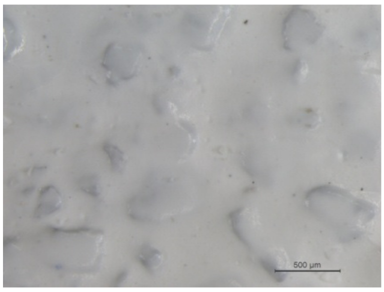
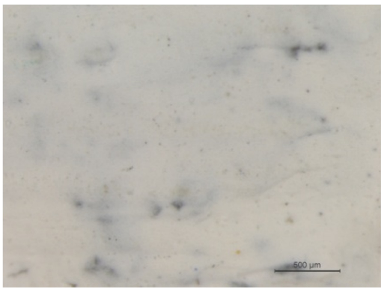
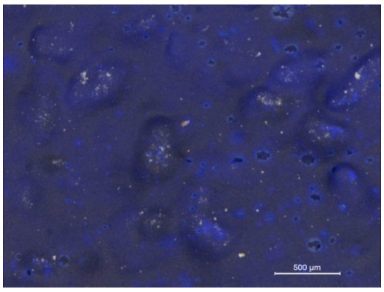
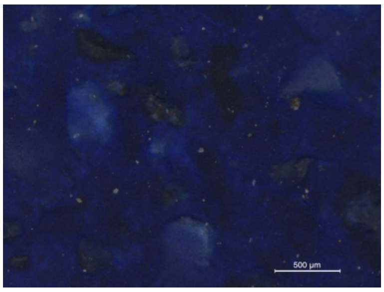
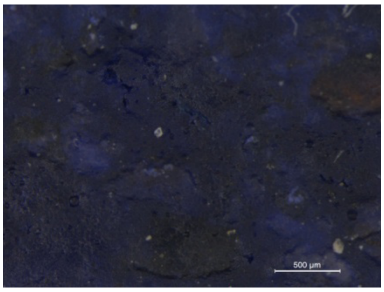
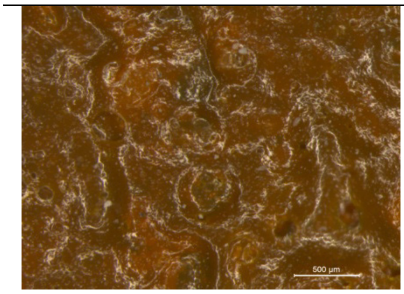
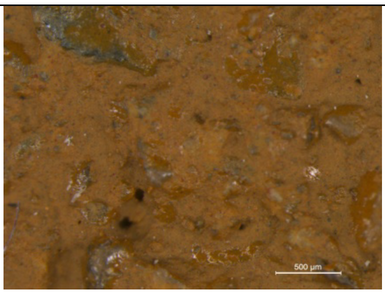
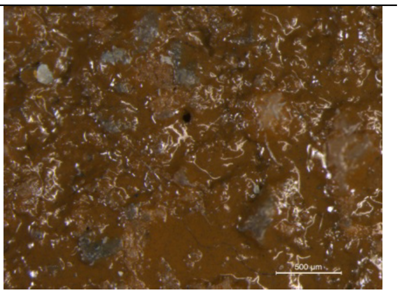
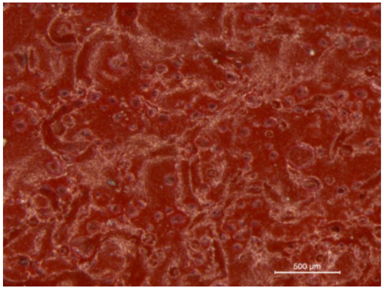
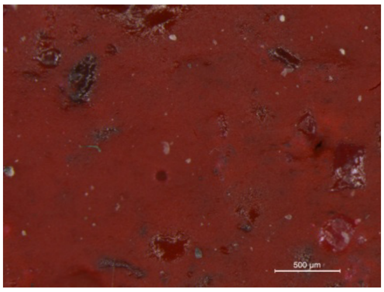
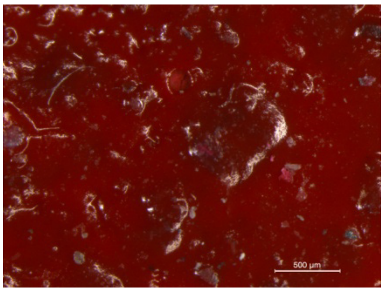
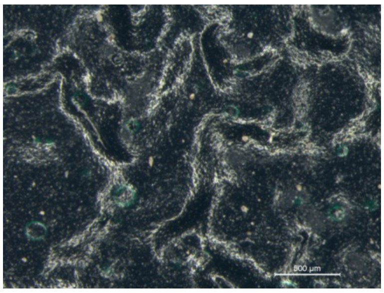
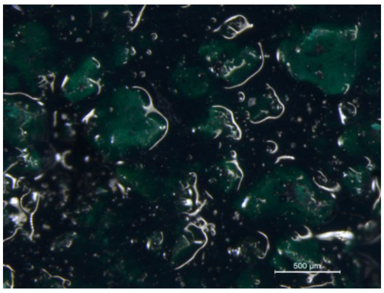
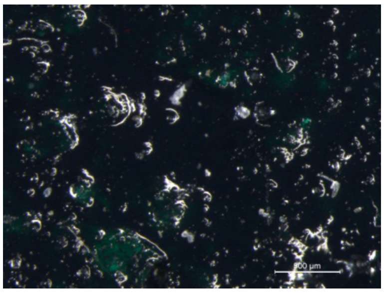
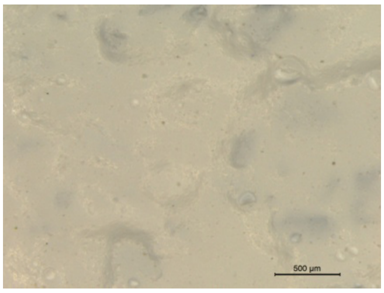
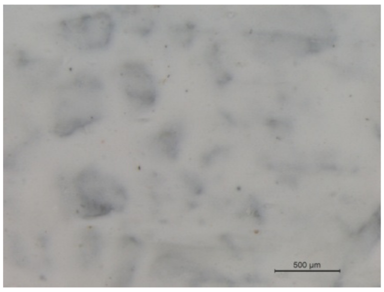
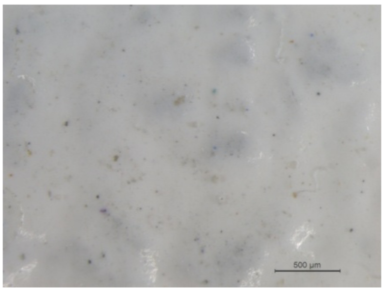
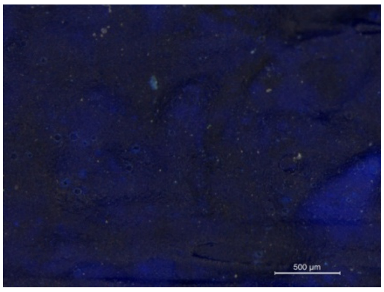
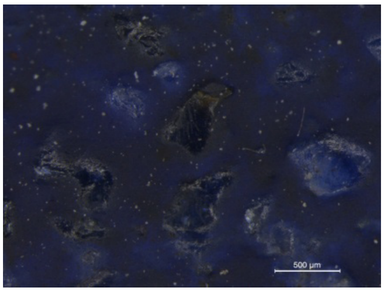
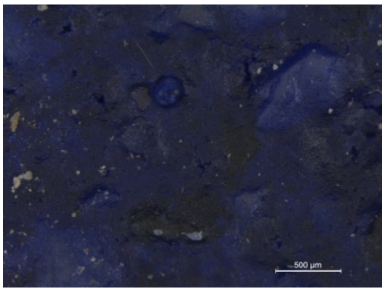
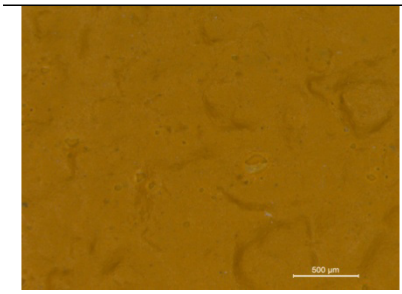
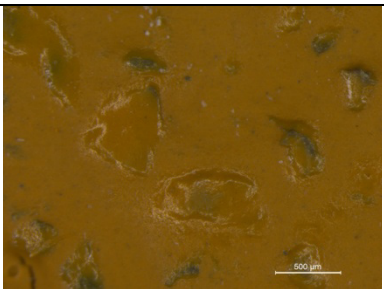
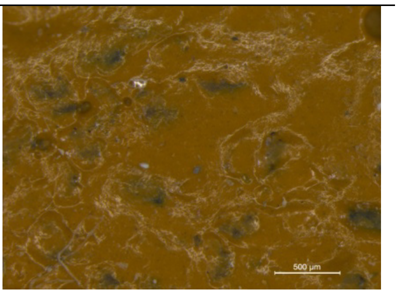
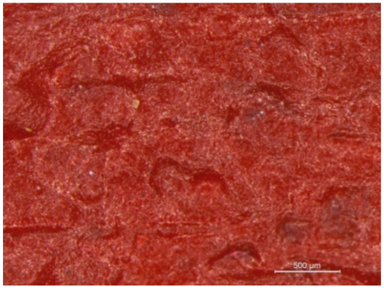
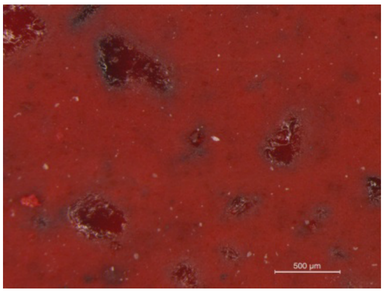
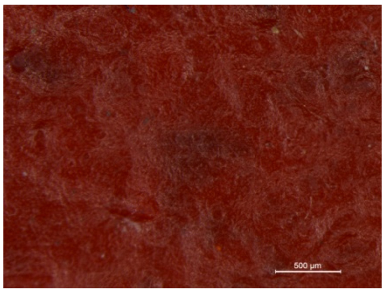
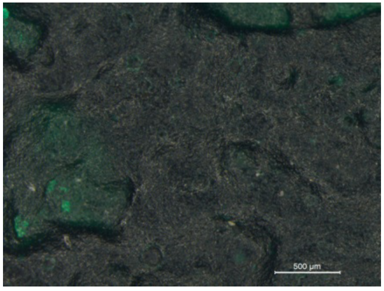
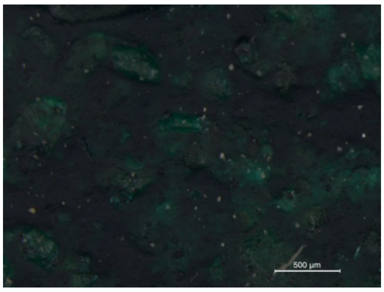
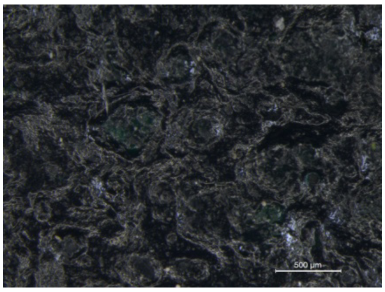
Tab.3.2-4: Retouching Flashe®(LeFranc & Bourgeois) samples: Light Microscopy (25X) pictures comparing the reference paint areas (on the left), with the areas painted using Laropal A81® formulations (in the middle) and areas painted using Aquazol200® formulations (on the right).

HEAVY BODY PAINTS (Liquitex®)

TITANIUM WHITE (25X) 	LQPW6Lr (25X) 	LQPW6Aq (25X) 
ULTRAMARINE BLU (25X) 	LQPB29Lr (25X) 	LQPB29Aq (25X) 
TRANSPARENT RAW SIENNA (25X) 	LQPY42Lr(25X) 	LQPY42Aq (25X) 
QUINACRIDONE CRIMSON (25X) 	LQPV19Lr (25X) 	LQPV19Aq (25X) 
PHTHALOCYANINE GREEN (25X) 	LQPG7Lr (25X) 	LQPG7Aq(25X) 

Tab.3.2-5: Retouching Heavy Body (Liquitex®) samples: Light Microscopy (25X) pictures comparing the reference paint areas (on the left), with the areas painted using Laropal A81® formulations (in the middle) and areas painted using Aquazol200® formulations (on the right).

BRERA PAINTS (Maimeri®)		
TITANIUM WHITE (25X) 	BRPW6Lr (25X) 	BRPW6Aq (25X) 
ULTRAMARINE (25X) 	BRPB29Lr (25X) 	BRPB29Aq (25X) 
YELLOW OCHRE (25X) 	BRPY42Lr(25X) 	BRPY42Aq (25X) 
PRIMARY RED MAGENTA(25X) 	BRPV19Lr (25X) 	BRPV19Aq (25X) 
PHTHALO GREEN (25X) 	BRPG7Lr (25X) 	BRPG7Aq(25X) 

Tab.3.2-6: Retouching Brera (Maimeri®) samples: Light Microscopy (25X) pictures comparing the reference paint areas (on the left), with the areas painted using Laropal A81® formulations (in the middle) and areas painted using Aquazol200® formulations (on the right).

In order to quantitatively evaluate the color match between the reference and inpainted areas, the colorimetric values in the CIEL*a*b*76 color space coming from the reflectance spectra were studied. The colorimetric measurements were carried out for all the retouching methods: the paint layers based on Laropal A81® resin (Lr), those based on Aquazol 200® resin (Aq) and the commercial paints (P).

Due to the relatively small dimension of the inpainted areas, the measurements were taken only in one point per each area (with data coming from set of 3 spectra). The color of these areas was compared to the color of the reference paint areas (evaluated from 3 spectra collected in one point as well), and the color difference between inpainted and reference areas was expressed as $\Delta E^*_{ab.}$

Besides the total color difference, Tab. 3.2-7, Tab. 3.2-8 and Tab.3.2-9 also show the differences of the three colorimetric values (ΔL*, Δa* and Δb*). These latter variations were calculated as differences between the values collected from the inpainted areas and those from the reference paint ones. As always, SCI and SCE data were both considered.

FLASHE® (LeFranc & Bourgeois)

Retouching Methods	SCI				SCE			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
FLPW6Lr	-6.75	-0.05	0.02	**6.75**	-6.63	-0.09	0.08	**6.64**
FLPW6Aq	-5.38	0.34	1.41	**5.58**	-5.37	0.30	1.44	**5.57**
FLPW6P	-5.24	-0.05	-2.12	**5.65**	-5.21	-0.06	-2.05	**5.60**
FLPB29Lr	1.12	-4.52	1.41	4.87	1.07	-4.46	1.44	4.80
FLPB29Aq	10.21	-10.29	-4.15	**15.08**	10.23	-10.27	-3.71	**14.96**
FLPB29P	-1.23	-1.29	2.15	2.79	1.32	-1.03	2.02	2.63
FLPB29DsP	-2.40	3.44	0.12	4.19	-2.52	3.67	-0.06	4.45
FLPY42Lr	-7.66	1.15	9.35	**12.14**	-7.48	0.98	8.64	**11.47**
FLPY42Aq	4.09	-0.91	3.71	**5.58**	4.04	-0.94	3.80	**5.63**
FLPY42P	-0.68	-0.32	2.08	2.21	-0.69	-0.31	1.96	2.10
FLPV19Lr	-5.67	-3.63	8.97	**11.22**	-5.95	-2.78	8.33	**10.61**
FLPV19Aq	5.31	-0.36	-4.92	**7.25**	5.27	-0.53	-4.25	**6.79**
FLPV19P	-0.66	1.31	7.83	**7.97**	-0.88	1.71	7.83	**8.06**
FLPG7Lr	-0.65	-15.64	5.30	**16.53**	-0.93	-16.57	5.42	**17.46**
FLPG7Aq	6.12	-13.88	4.33	**15.78**	5.85	-14.37	4.59	**16.18**
FLPG7P	-5.88	-8.86	5.84	**12.16**	-6.06	-10.53	6.11	**13.60**

Tab.3.2-7: Comparing the color of Flashe®(LeFranc& Bourgeois) samples with the color of the respective inpainted areas: the total color difference (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from the values collected both including and excluding specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to the naked-eye.

HEAVY BODY PAINTS (Liquitex®)

Retouching Methods	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔEab*	ΔL*	Δa*	Δb*	ΔEab*
LQPW6Lr	-2.71	0.07	-0.55	2.77	-2.70	0.06	-0.47	2.74
LQPW6Aq	-3.98	0.08	0.57	4.02	-5.10	0.05	0.76	**5.15**
LQPW6P	-1.38	0.10	-0.55	1.49	-1.57	0.12	-0.50	1.65
LQPB29Lr	0.49	-9.19	5.21	**10.57**	0.63	-9.42	5.26	**10.81**
LQ PB29Aq	0.62	-12.05	8.59	**14.81**	0.91	-12.56	9.18	**15.58**
LQ PB29P	1.59	0.15	-2.54	3.00	1.67	-0.45	-2.19	2.78
LQPB29DsP	0.38	-7.86	4.29	**8.96**	0.33	-7.64	4.22	**8.73**
LQPY42Lr	-2.16	-4-65	1.75	**5.42**	-1.87	-4.91	1.32	**5.42**
LQ PY42Aq	-2.80	-5.01	-8.96	**10.64**	-2.70	-5.00	-8.25	**10.02**
LQ PY42P	1.02	-1.30	2.60	3.08	0.51	-1.02	4.29	4.44
LQPV19Lr	-3.34	-5.70	-4.20	**7.83**	-3.31	-5.35	-4.13	**7.52**
LQPV19Aq	-0.09	-4.15	-5.59	**6.96**	-0.91	-3-44	-2.54	4.37
LQ PV19P	-1.10	-0.72	1.73	2.17	-1.26	-0.56	2.33	2.70
LQPG7Lr	-0.69	1.14	4.71	4.89	-0.47	0.62	4.75	4.82
LQPG7Aq	-2.91	8.75	3.88	**10.00**	-3.14	9.11	4.34	**10.56**
LQPG7P	1.27	-5.86	4.41	**7.44**	1.36	-6.26	4.75	**7.97**

Tab.3.2-8: Comparing the color of Heavy Body (Liquitex®) samples with the color of the respective inpainted areas: the total color difference (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from the values acquired both including and excluding the specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination

BRERA PAINTS (Maimeri®)

Retouching Methods	SCI				SCE			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
BRPW6Lr	-3.34	0.08	-1.46	3.65	-3.30	0.06	-1.40	3.59
BRPW6Aq	-4.16	0.10	0.77	4.23	-4.34	0.08	0.84	4.42
BRPW6P	-3.52	-0.18	-1.67	3.90	-3.38	-0.20	-1.60	3.75
BRPB29Lr	0.06	-15.58	10.61	**18.85**	0.33	-15.65	10.67	**18.94**
BRPB29Aq	-1.09	-11.05	9.17	**14.40**	-1.00	-10.64	9.01	**13.98**
BRPB29P	6.79	-7.30	-4.12	**10.78**	7.04	-8.50	-3.41	**11.55**
BRPB29DsP	1.29	-4.34	0.96	4.63	1.18	-4.12	0.98	4.39
BRPY42Lr	-1.36	-0.80	4.65	4.91	-1.50	-0.73	5.18	**5.44**
BRPY42Aq	-2.39	-1.88	1.33	3.32	-2.86	-1.69	3.33	4.70
BRPY42P	-0.73	0.17	2.87	2.96	-0.71	0.15	2.72	2.81
BRPV19Lr	-4.79	0.01	4.44	**6.53**	-4.73	0.80	3.18	**5.75**
BRPV19Aq	-0.39	0.83	7.54	**7.59**	-1.10	1.89	8.57	**8.84**
BRPV19P	-0.77	1.37	2.05	2.59	-0.47	1.12	1.35	1.82
BRPG7Lr	-4.50	7.44	8.02	**11.83**	-4.95	6.78	8.12	**11.68**
BRPG7Aq	-3.27	5.72	6.38	**9.17**	-3.76	5.85	6.33	**9.41**
BRPG7P	-0.77	-3.35	4.17	**5.41**	-1.04	-4.33	4.07	**6.03**

Tab.3.2-9: Comparing the color of Brera (Maimeri®) samples with the color of the respective inpainted areas: the total color difference (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from the values acquired both including and excluding the specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination

The high ΔE_{ab}* values suggested that the differences between the color of the reference paint surfaces and the color of the corresponding inpainted areas were quite high. Even though none of the retouching formulations allowed a perfect color match, if considering a ΔE_{ab}* threshold value of 5, an acceptable match was achieved for: FLPB29Lr (ΔE_{ab}* about 5); LQPW6Lr (ΔE_{ab}* about 3), LQPW6Aq (ΔE_{ab}* about 4), LQPG7Lr(ΔE_{ab}* about 5), BRPW6Lr (ΔE_{ab}* about 4), BRPW6Aq (ΔE_{ab}* about 4), BRPY42Lr (ΔE_{ab}* about 5), BRPY42Aq (ΔE_{ab}* about 3).

Apparently there is no connection between the quality of the match and the synthetic resin used as binding medium, nor between the quality of the match and the color of the area to inpaint. The only general consideration that could be drawn is that the best matches were those achieved for the white samples.

In most of the cases the values coming from the colorimetric measurements, expressed color differences that were already detectable to the naked-eye. For instance, the measurements suggested that the color of FLPY42Lr area was darker (decrements of L) and more yellowish (increment of b) than the color of the reference one and this information was confirmed when looking at the surfaces (table 3.2-4).

Sometimes instead, high ΔE_{ab}* values did not correspond to relevant color differences (as in the case of the FLPG7Aq sample, Tab. 3.2-4 and Tab. 3.2-7).

The color difference between the reference paints and those areas inpainted using the same emulsion paints (methods labeled as P) were expected to be very low. On the contrary, the calculated ΔE_{ab}* were sometimes considerable, as in the case of samples FLPW6P (ΔE_{ab}*of about 6), FLPV19P (ΔE_{ab}*of about 8), FLPG7P(ΔE_{ab}*of about 12), LQPG7P (ΔE_{ab}*of about 7) and BRPB29P (ΔE_{ab}*of about 11).
This suggests that the colorimetric measurements could be affected by some errors: since the dimensions of the sampled areas were small, they could not be representative of the color of the whole surface.
This is a sound remark even when considering those areas painted with the retouching formulations. As pointed out by the LM pictures of the previous tables (Tab. 3.2-4, Tab. 3.2-5 and Tab. 3.2-6), due to the poor dispersion of the pigments, the resulting surfaces were sometimes uneven.
For all these reasons, if evaluating the quality of the color match between original and inpainted areas through colorimetric measurements, the ΔE_{ab}* threshold value for identifying an acceptable result could be raised to a value higher than 5.
Moreover, even if collected considering both SCI and SCE, the results of the colorimetric measurements did not allow a clear evaluation of the gloss properties of the paint surfaces.

Finally, the most effective (and easiest) system to evaluate the color match between original and inpainted areas remains the careful naked-eye examination.

Considering the results coming from the comparison of the blue discolored areas (D) and areas labeled as DsP (emulsion paints diluted or added with some extenders), it turned out that it is possible to satisfactory match the color and texture of aged paint layers even when using a commercial paint: the ΔE_{ab}^* calculated for FLPB29DsP and BRPB29DSP samples are both about 4, while that calculated for LQPB29DsP sample is about 9.

3.2.1.3 Evaluation of the discernibility

As already described in Chapter 1 (*1.3 Inpainting contemporary murals*) it is supposed that, when examining the surface of a painting under UV light, areas painted with different binders will look different.

In the attempt of evaluating the actual discernibility of the inpainted areas, the first step was to assess the possibility of setting apart treated and original aged areas (400h UVA-light exposure) under the light of a Wood’s lamp (λ 365 nm).
The discernibility may actually come from slight differences in the age of the paint layers (the original aged areas in comparison with the retouchings based on the same emulsion unaged paints) or from differences in the chemical composition of the binders (the original acrylic, styrene-acrylic and vinyl paints in comparison with the retouching based on Aquazol 200® or Laropal A81® resins).

After applying the retouching paints, all the samples were carefully examined under Visible and UV light. A selection of the pictures taken using both light sources are presented in figure 3.2-3, 3.2-4 and 3.2-5: no relevant differences in the UV fluorescence of original and inpainted areas were detected, if it was possible to perceive some difference this was due to a poor color match (detectable also under Vis light).

For this reason a strategy to enhance the difference perceived when comparing original and treated areas under UV light was studied, and the Europium(III) complex was added to the retouching formulations. As already described in chapter 1 (*1.3.1 Luminescent lanthanide complexes*), when exposed to the light of a Wood’s lamp (λ 365 nm) this complex is characterized by a strong red luminescence (with the main emission at 612 nm).
Notwithstanding the fact that all the formulations were added with the same amount of complex (2% by weight), different paint layers showed different luminescence properties, in term of both color and intensity.
The luminescence achieved adding the complex to the commercial paints was weaker than that achieved adding the complex to the retouching formulations based on the other resins. Even though this aspect should be further investigated, it could be due to the presence of higher pigments amounts in the commercial paints.
Apparently, those areas inpainted with the Laropal A81® based formulations showed the strongest luminescence.

Considering areas characterized by the same binder, the luminescence of the layers containing the Quinacridone Rose pigment (PV19) turned out to be very strong (figure 3.2-3), while the luminescence of the layers containing the Phthalo Green pigment (PG7) was particularly dull (figure 3.2-4). This latter aspect could relate to a partial absorption of the 'red light' by the green pigment.

Unlike the majority of the areas, which showed a red fluorescence, those areas containing the Titanium White pigment (PW6) showed a pink fluorescence (figure 3.2-5).

Fig.3.2-3: BRPV19 sample examined under Vis and UV light. A= reference paint, D= reference aged paint (400h of UV light exposure), B= reference inpainted areas, C= inpainted areas to age, P= artists' emulsion paint, Lr= Laropal A81® formulation, Aq= Aquazol 200® formulation, Eu= formulation added with 2% by weight of the Europium (III) complex.

Fig.3.2-4: BRPG7 sample examined under Vis and UV light. A= reference paint, D= reference aged paint (400h of UV light exposure), B= reference inpainted areas, C= inpainted areas to age, P= artists' emulsion paint, Lr= Laropal A81® formulation, Aq= Aquazol 200® formulation, Eu= formulation added with 2% by weight of the Europium (III) complex.

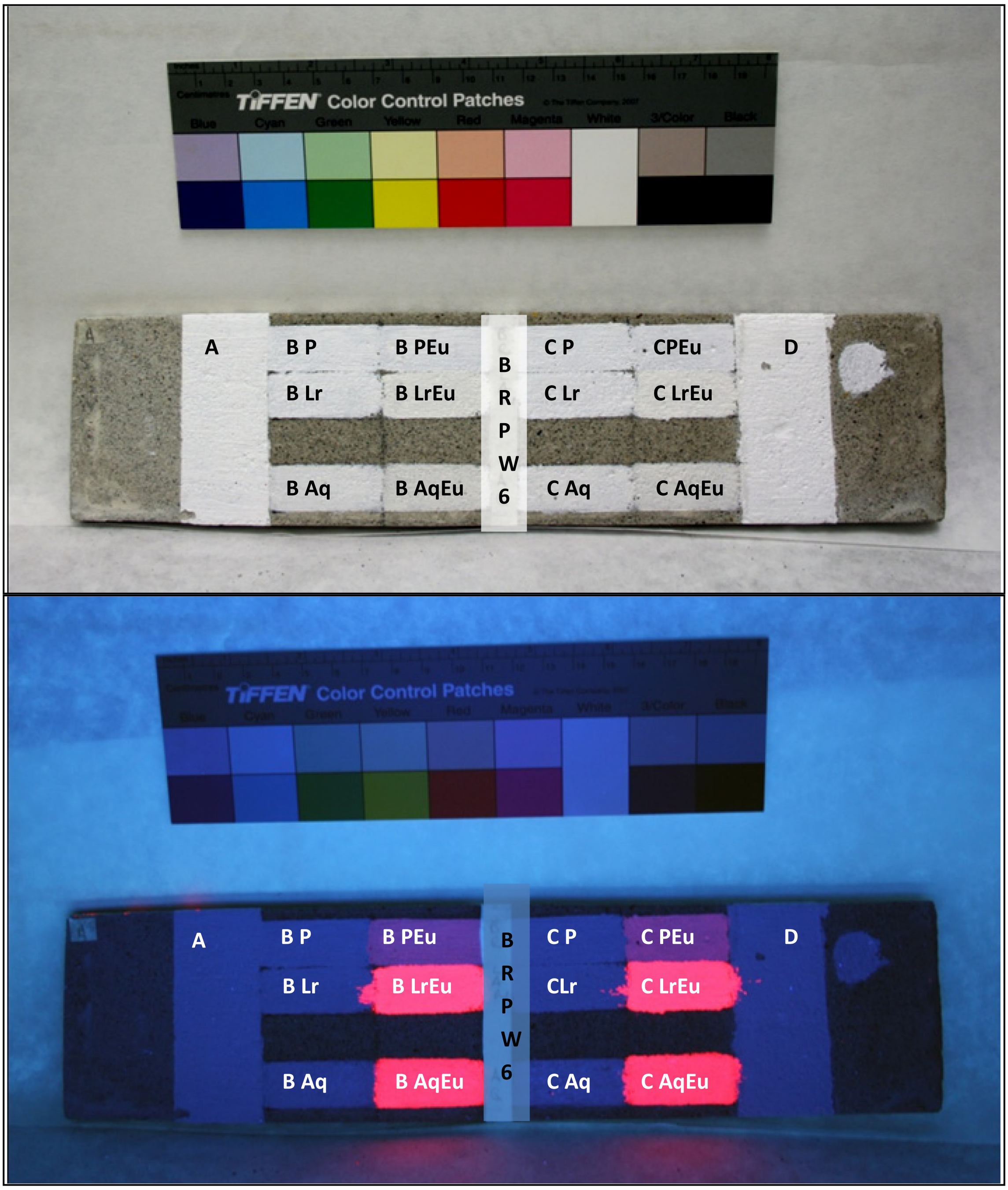


Fig.3.2-5: BRPW6 sample examined under Vis and UV light. A= reference paint, D= reference aged paint (400h of UV light exposure), B= reference inpainted areas, C= inpainted areas to age, P= artists' emulsion paint, Lr= Laropal A81® formulation, Aq= Aquazol 200® formulation, Eu= formulation added with 2% by weight of the Europium (III) complex.

3.2.1.4 Chemical characterization of the formulations added with the Europium (III) complex

The retouching formulations added with the Europium(III) complex (2% by weight), were preliminary characterized through FTIR spectroscopy analysis.

By way of example, the spectra collected for the LQPB29Aq and LQPB29AqEu areas are shown in figure 3.2-6, together with the reference spectrum of the Europium (III) complex. In the LQPB29AqEu spectrum the absorptions falling at 1551 cm^{-1}, 1522 cm^{-1}, 1454 cm^{-1}, 724 cm^{-1} and 608 cm^{-1} are related to the luminescent compound.

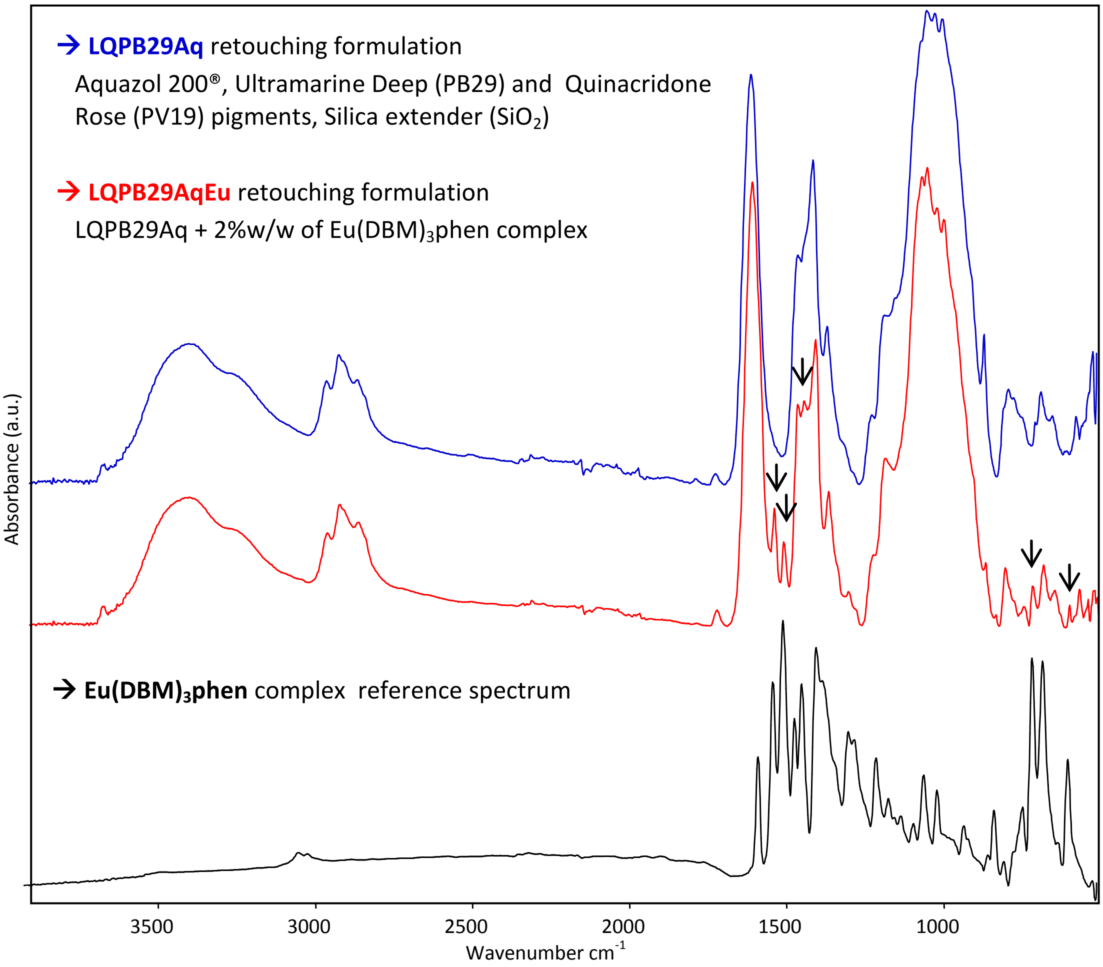


Fig.3.2-6: The FTIR spectra of the LQPB29Aq (blue) and LQPB29Eu (red) retouching formulations. Arrows point out those features related to the Europium (III) complex (whose reference spectrum is also displayed, back).

As shown in the Table 3.2-10, when studying the spectra of the paints/formulations added with the Europium (III) complex, it was not always possible to detect the absorptions features due to this component (2% by weight).

This was especially true for those formulations containing significant amounts of the calcium carbonate extender ($CaCO_3$), as in the case of some Flashe® paints, or of some retouching paints formulated to simulate the Flashe® paints.

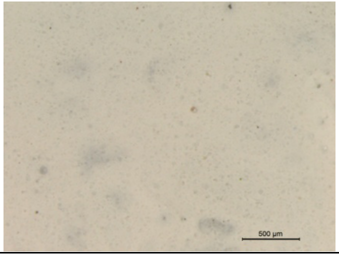
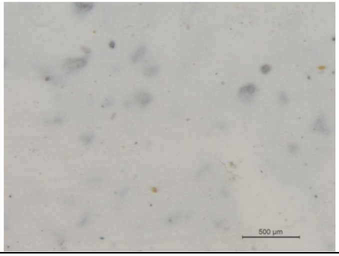
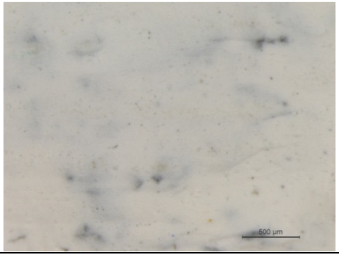
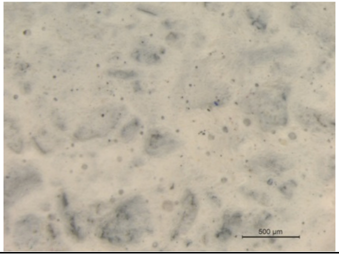
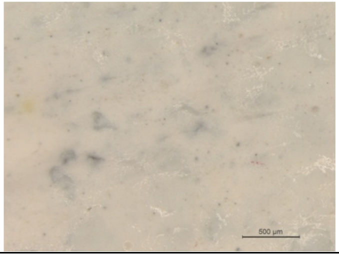
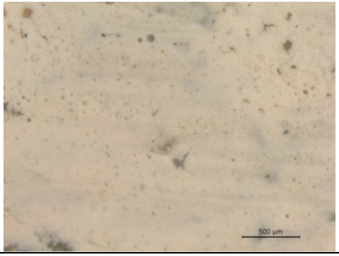
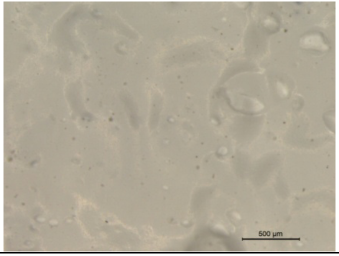
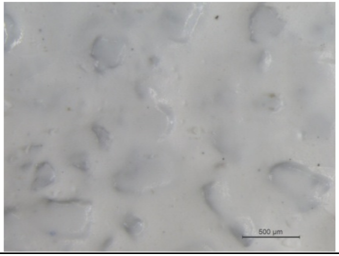
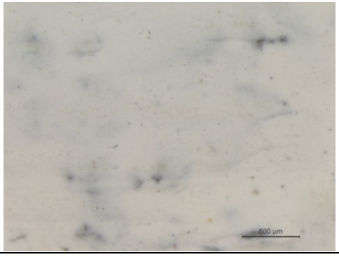
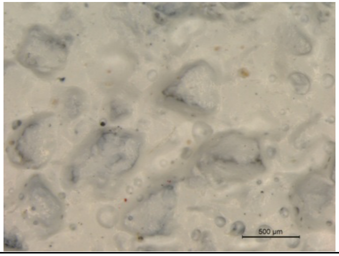
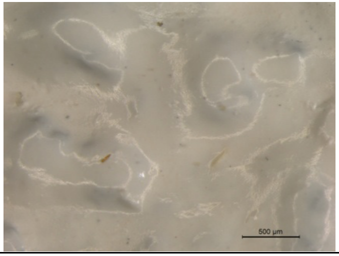
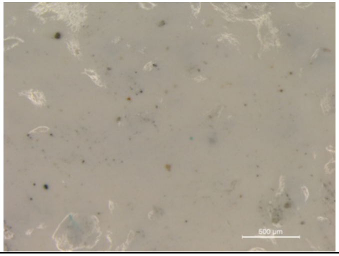
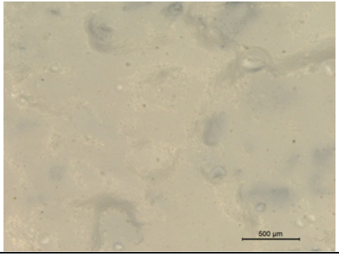
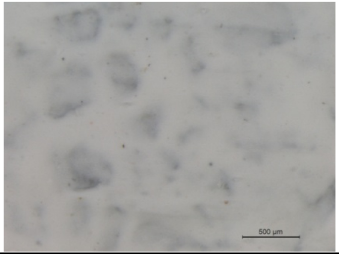
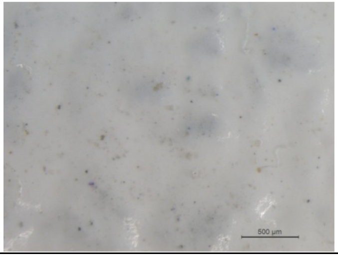
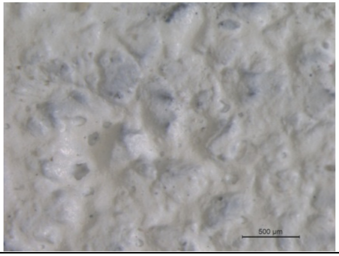
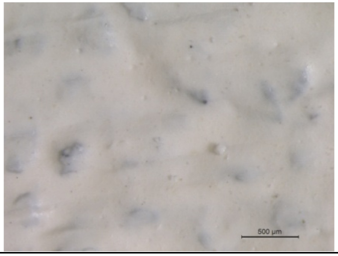
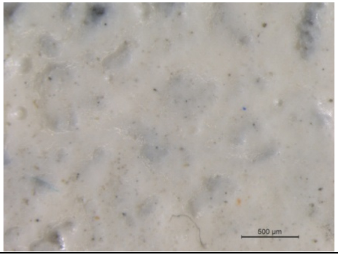
FLASHE INPAINITNGS		**LIQUITEX INPAINITNGS**		**BRERA INPAINITNGS**	
Retouching Formualtions	**Eu-compl. related features (cm^{-1})**	**Retouching Formualtions**	**Eu-compl. related features (cm^{-1})**	**Retouching Formualtions**	**Eu-compl. related features (cm^{-1})**
FLPW6PEu	1593	LQPW6PEu	1597, 1547, 1512	BRPW6PEu	-
FLPW6AqEu	-	LQPW6AqEu	1550 1517	BRPW6AqEu	-
FLPW6LrEu	-	LQPW6LrEu	1549	BRPW6LrEu	1550
FLPB29PEu	1596	LQPB29PEu	1593, 1551, 1515, 842?	BRPB29PEu	1550, 1515, 1415
FLPB29AqEu	-	LQPB29AqEu	1551, 1522, 1454, 724, 608	BRPB29AqEu	1550,1519,1454 725,606
FLPB29LrEu	1593	LQPB29LrEu	1599?	BRPB29LrEu	1551,1059,1033
FLPY42PEu	1599, 1547, 1512	LQPY42PEu	1593, 1550, 1517, 1451, 1024, 721?	BRPY42PEu	-
FLPY42AqEu	-	LQPY42AqEu	1544	BRPY42AqEu	1550
FLPY42LrEu	1594	LQPY42LrEu	1550, 1474?	BRPY42LrEu	-
FLPV19PEu	-	LQPV19PEu	1555, 1515, 1409, 691,	BRPV19PEu	1515?
FLPV19AqEu	-	LQPV19AqEu	1552, 1518, 727	BRPV19AqEu	1550, 1518 sh
FLPV19LrEu	-	LQPV19LrEu	-	BRPV19LrEu	-
FLPG7PEu	-	LQPG7PEu	1596, 1551, 1512	BRPG7PEu	1602? 1547? 1515?
FLPG7AqEu	-	LQPG7AqEu	1519	BRPG7AqEu	1550,1519
FLPG7LrEu	1596	LQPG7LrEu	1552	BRPG7LrEu	1550

Tab.3.2-10: Absorption features of Eu(DBM)$_3$phen, in the spectra of the retouching formulations added with this complex. The question mark (?) is used in case of uncertain attribution. – is used when it was not possible to detect any absorption features clearly related to the complex.

3.2.1.5 Evaluation of the pros and cons of using the Europium (III) complex

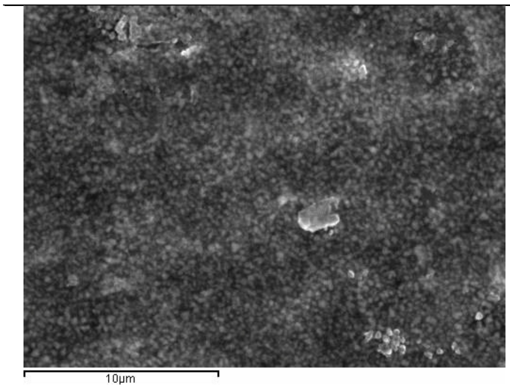
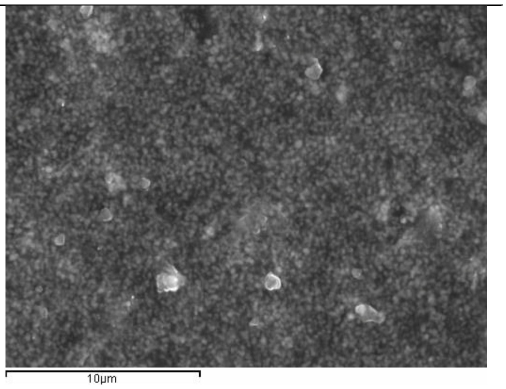
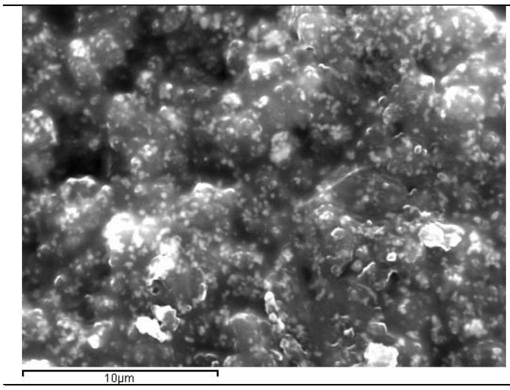
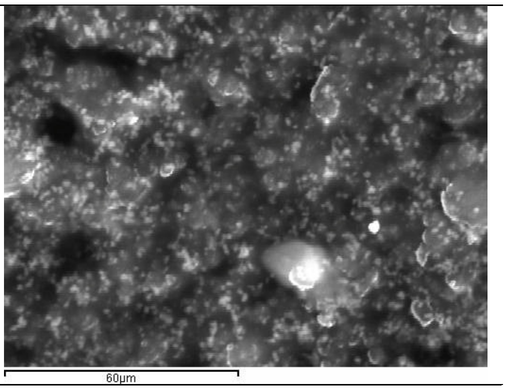
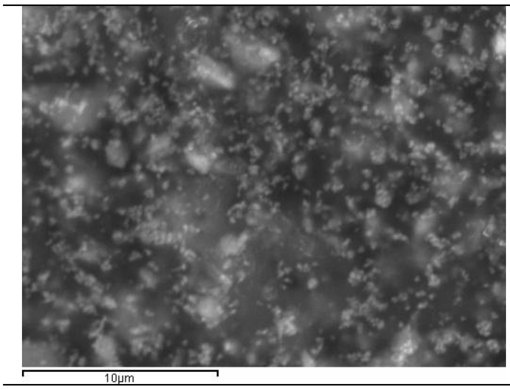
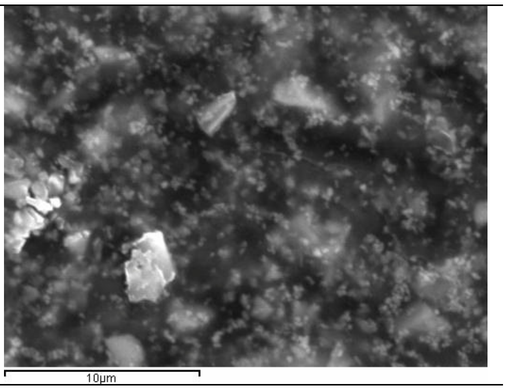
The first step to evaluate the suitability of the Europium (III) complex for conservation purposes, was to assess its influence on the properties of the materials it was added to. As already pointed out, the aesthetic properties of a retouching paint layer are very important. For this reason, the color and morphological properties of the paint layers resulting from the formulations added with the complex were investigated.

When comparing the appearance of the inpainted areas containing or not the Europium (III) complex, no relevant differences were detected: the presence of the complex did not generally affect the macroscopic properties of the paint layers.
However, as shown in table 3.2-11, the inclusion of the complex in the white formulations may induce slight color variations (discernible to the naked-eye). The color of white paint layers containing the Europium (III) complex was actually warmer than that of the pure paints. This slight yellowing is reasonably related to the color of the complex itself which, under Vis light, looks pale yellow.

<table>
<tr><th colspan="3">FLASHE ® (LeFranc&Bourgeois) WHITE sample</th></tr>
<tr><td>FLPW6P(25X)
 </td><td>FLPW6Lr (25X)
 </td><td>FLPW6Aq(25X)
 </td></tr>
<tr><td>FLPW6PEu (25X)
 </td><td>FLPW6LrEu (25X)
 </td><td>FLPW6AqEu(25X)
 </td></tr>
<tr><th colspan="3">HEAVY BODY (Liquitex®) TITANIUM WHITE sample</th></tr>
<tr><td>LQPW6P(25X)
 </td><td>LQPW6Lr(25X)
 </td><td>LQPW6Aq(25X)
 </td></tr>
<tr><td>LQPW6PEu(25X)
 </td><td>LQPW6LrEu(25X)
 </td><td>LQPW6AqEu(25X)
 </td></tr>
<tr><th colspan="3">BRERA (Maimeri®) TITANIUM WHITE sample</th></tr>
<tr><td>BRPW6P(25X)
 </td><td>BRPW6Lr (25X)
 </td><td>BRPW6Aq(25X)
 </td></tr>
<tr><td>BRPW6PEu(25X)
 </td><td>BRPW6LrEu (25X)
 </td><td>BRPW6AqEu(25X)
 </td></tr>
</table>

Tab.3.2-11: Comparing the paint surfaces coming from different white retouching formulations: the inclusion of the Eu(DBM)$_3$phen complex could results in a slight yellowing (discernible to the naked eye).

Due to these slight differences in the appearance of the white paints, the morphology of the paint layers characterized by the Europium (III) complex where studied at higher magnifications, using Scanning Electron Microscopy. Some of the pictures taken using Secondary Electrons (SE) are shown in table 3.2-12: no significant morphological differences were detected comparing the paint layers cast with formulations containing or not the Europium (III) complex.

BRERA (Maimeri) – TITANIUM WHITE SAMPLE -	
BRPW6P (5000X)	BRPW6PEu (5000X)
	
BRPW6Lr (5000X)	BRPW6LrEu (5000X)
	
BRPW6Aq (5000X)	BRPW6AqEu (5000X)
	

Tab.3.2-12: The paint layers coming from the retouching paints formulated to inpaint the Titanium White-Brera sample (PW6) are compared to those achieved using the same paints, added with the Europium (III) complex (on the right). No relevant differences were detected (SEM images, Secondary Electrons, 5000X).

The color variations induced by the inclusion of the Europium (III) complex were evaluated in a quantitative way, by colorimetric measurements.[71] The results are shown in the following tables (3.2-13, 3.2-14, 3.2-15).

The color variations detected when comparing the surfaces of the white retouching paint, corresponded to slight ΔEab* values (ranging from 2.01 for the BRPW6P sample, to 5.71 for the BRPW6Lr sample). These color variations are generally related to increments of a* and b* chromaticity coordinates, suggesting that the paint layers characterized by the complex are more reddish and more yellowish than the others. These results were completely consistent with the slight color differences discernible to the naked eye.

FLASHE® PAINTS (LeFranc&Bourgeois)

Retouching Methods compared	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔEab*	ΔL*	Δa*	Δb*	ΔEab*
FLPW6Lr -FLPW6LrEu	-1.90	1.86	2.34	3.54	-2.02	1.81	2.31	3.57
FLPW6Aq- FLPW6AqEu	0.67	1.48	1.89	2.49	0.66	1.45	1.86	2.45
FLPW6P- FLPW6PEu	0.49	0.44	1.94	2.05	0.45	0.42	1.92	2.01
FLPB29Lr- FLPB29LrEu	0.02	-3.06	2.32	3.84	0.11	-3.13	2.41	3.95
FLPB29Aq- FLPB29AqEu	2.37	-4.52	3.04	**5.94**	2.60	-4.26	3.38	**6.03**
FLPB29P- FLPB29PEu	2.64	-2.23	-2.07	4.03	2.58	-2.19	-2.00	3.93
FLPY42Lr- FLPY42LrEu	2.49	0.97	1.22	2.94	2.47	0.99	1.36	2.99
FLPY42Aq- FLPY42AqEu	2.88	0.43	-0.26	2.92	2.81	0.44	-0.14	2.85
FLPY42P- FLPY42PEu	-0.30	-0.01	-0.11	0.32	-0.29	-0.02	-0.11	0.31
FLPV19Lr-FLPV19LrEu	-1.35	-2.32	2.42	3.62	-1.32	-2.33	2.31	3.54
FLPV19Aq- FLPV19AqEu	1.81	1.46	0.77	2.45	1.78	1.44	0.75	2.41
FLPV19P- FLPV19PEu	0.74	0.84	1.61	1.96	0.76	0.88	1.38	1.81
FLPG7Lr- FLPG7LrEu	-1.62	2.37	-0.62	2.94	-1.58	2.35	-0.63	2.90
FLPG7Aq- FLPG7AqEu	-4.02	-1.24	0.85	4.30	-4.01	-1.27	0.86	4.29
FLPG7P- FLPG7PEu	3.00	4.17	0.26	**5.14**	2.94	-3.44	0.30	4.53

Tab.3.2-13: Evaluating the color variations due to the inclusion of the Europium (III) complex in the formulations used for inpainting Flashe® (LeFranc&Bourgeois) samples. The total color difference (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL*) and of the chromaticity coordinates (Δa* and Δb*). Data were calculated from values acquired both including and excluding the specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination.

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[71] Even in this case only one point was considered for each area, repeating the measurement three times. The variations of the three colorimetric values were calculated as differences between the values collected for the areas containing the Europium (III) complex and the other ones. The total color variation was expressed as $\Delta E^*_{ab.}$ As always, SCI and SCE data were both considered.

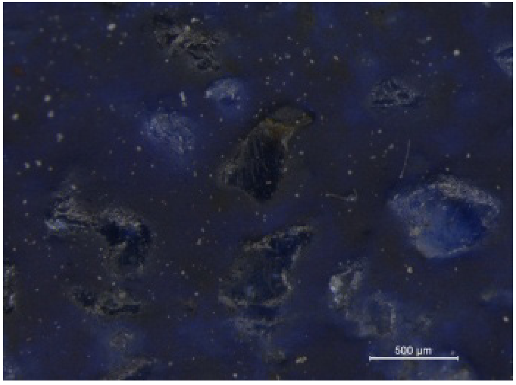
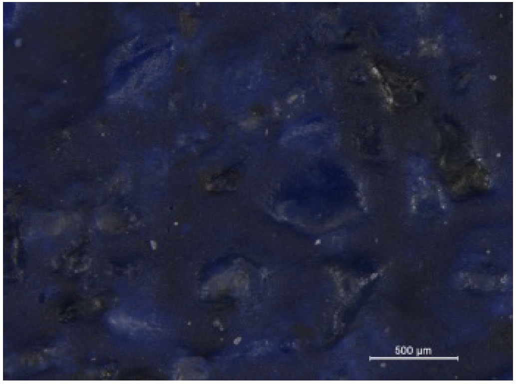
HEAVY BODY PAINTS (Liquitex®)								
Retouching Methods compared	**SCI**				**SCE**			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
LQPW6Lr -LQPW6LrEu	-0.32	0.59	4.19	4.24	-0.22	0.55	4.14	4.18
LQPW6Aq- LQPW6AqEu	1.52	0.50	3.38	2.49	1.93	0.51	3.74	3.90
LQPW6P- LQPW6PEu	-3.59	-0.32	0.27	3.61	-3.54	-0.34	0.28	3.57
LQPB29Lr- LQPB29LrEu	-0.99	-2.66	2.92	4.07	-1.03	-2.45	2.80	3.86
LQPB29Aq- LQPB29AqEu	3.59	4.27	0.50	**5.60**	4.09	2.93	1.97	**5.40**
LQPB29P- LQPB29PEu	0.65	0.56	-1.42	1.66	0.66	0.27	-1.23	1.42
LQPY42Lr- LQPY42LrEu	1.67	-0.46	1.47	2.27	1.60	-0.38	1.57	2.27
LQPY42Aq- LQPY42AqEu	1.44	1.45	1.44	2.50	1.46	1.40	1.39	2.46
LQPY42P- LQPY42PEu	0.72	0.19	-0.76	1.07	1.38	-0.14	-3.10	3.40
LQPV19Lr-LQPV19LrEu	1.40	-2.32	-4.16	4.84	1.97	1.20	-3.82	4.46
LQPV19Aq- LQPV19AqEu	2.56	3.42	2.77	**5.09**	2.08	3.72	4.48	**6.18**
LQPV19P- LQPV19PEu	-0.08	-0.97	-1.79	2.04	0.18	-1.04	-2.43	2.65
LQPG7Lr- LQPG7LrEu	1.14	-3.69	-0.95	3.97	0.87	-3.25	-0.66	3.43
LQPG7Aq- LQPG7AqEu	0.56	-0.61	-1.81	1.99	-1.07	2.82	0.57	3.07
LQPG7P- LQPG7PEu	0.13	-0.05	-0.32	0.35	0.34	-0.42	-0.46	0.71

Tab.3.2-14: Evaluating the color variations due to the inclusion of the Europium (III) complex in the formulations used to inpaint Heavy Body (Liquitex®) samples. The total color difference (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL^*) and of the chromaticity coordinates (Δa^* and Δb^*). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination. SCI= specular component included. SCE= specular component excluded

BRERA PAINTS (Maimeri®)								
Retouching Methods compared	**SCI**				**SCE**			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
BRPW6Lr -BRPW6LrEu	1.02	0.78	5.56	**5.71**	1.09	0.76	5.50	**5.66**
BRPW6Aq- BRPW6AqEu	-0.30	0.55	3.58	3.63	-0.33	0.53	3.56	3.61
BRPW6P- BRPW6PEu	-1.96	0.16	-0.41	2.01	-1.95	0.16	-0.42	2.00
BRPB29Lr- BRPB29LrEu	5.66	-2.45	5.06	**7.98**	6.42	-3.23	6.74	**9.85**
BRPB29Aq- BRPB29AqEu	1.33	3.03	-1.20	3.52	1.31	2.66	-0.49	3.01
BRPB29P- BRPB29PEu	0.91	-1.70	-0.33	1.96	0.81	-1.60	-0.30	1.82
BRPY42Lr- BRPY42LrEu	-0.78	-0.01	0.65	1.01	-0.65	-0.10	0.16	0.67
BRPY42Aq- BRPY42AqEu	0.05	1.73	4.59	4.90	0.20	1.61	3.22	3.61
BRPY42P- BRPY42PEu	-1.59	-0.50	0.93	1.90	-1.55	-0.54	0.83	1.84
BRPV19Lr-RPV19LrEu	1.16	0.23	-0.89	1.48	1.13	0.11	-0.60	1.28
BRPV19Aq- BRPV19AqEu	0.62	2.13	1.63	2.75	0.79	1.81	1.03	2.23
BR PV19P- BR PV19PEu	-1.37	-2.88	-2.28	3.92	-1.31	-2.81	-2.39	3.91
BRPG7Lr- BRPG7LrEu	-0.36	1.30	-0.04	1.35	-0.40	1.41	-0.08	1.46
BRPG7Aq- BRPG7AqEu	1.20	-4.70	1.55	**5.09**	1.35	-5.19	1.71	**5.62**
BRPG7P- BRPG7PEu	0.31	-1.98	1.61	2.57	0.29	-2.14	1.75	2.78

Tab.3.2-15: Evaluating the color variations due to the inclusion of the Europium (III) complex in the formulations used to inpaint Brera (Maimeri®) samples. The total color difference (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL^*) and of the chromaticity coordinates (Δa^* and Δb^*). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination. SCI= specular component included. SCE= specular component excluded

As far as the other paints, the color variations due to the inclusion of the Europium (III) complex into the retouching formulations were minor. In the majority of the cases (38 out of 45) the calculated ΔEab* values were actually lower than 5 (the threshold value that is usually considered for defining appreciable color variations). In addition, leaving out the white samples, it could be said that even when dealing with ΔEab* higher than 5, the color variations were barely discernible to the naked eye examination (eg. BRPB29Lr and BRPB29LrEu samples, compared in table 3.2-16).

Color variations due to the Europium (III) complex	
BRPB29Lr before ageing (25X-LM)	BRPB29LrEu before ageing (25X-LM)
	

Tab.3.2-16: Two paint layers consisting of the same Laropal A81® formulation (BRPB29Lr): that on the left does not contain the Europium (III) complex, that on the right do contain it. Even though the measured color difference was quite high (ΔE_{ab}*~8), the surfaces look very similar.

It is finally to remember that the color variations could be influenced by many factors, such as an uneven distribution of the pigments in the binder matrix (when considering Aquazol 200® and Laropal A81® formulations) or the influence of the mortar support.

3.2.2 Artificial ageing: UV-light stability testing

As already described in Chapter 2 (*2.3.2 UV-light stability testing*), the stability of the retouching paints was tested by exposing the inpainted areas to 400h of UV-light (UVA-340 lamps, temperature 45°C).

While carrying out the ageing, the occurrence of any chemical or physical variations was assessed through different analytical techniques: FTIR spectra were collected every 100h;[72] colorimetric measurements were carried out every 200h; while the morphology of the paint layers was examined, before and after ageing, through Light and Scanning Electron Microscopy.[73]

Since it is not possible to fully discussed all the collected data (a total of 96 different formulations were cast), only a selection of the results is presented here.

The intention is to stress those aspects which are more relevant within the conservation field, such as:

- the actual stability of the different binding media;
- the connection between the chemical stability of the resins and the variation of their solubility (and so the actual reversibility of the treatments);
- the influence of the Europium (III) complex in affecting the stability of the formulations;
- the stability of the Europium (III) complex itself (*discernibility* long-term properties).

3.2.2.1 Chemical, morphological and color variations

LAROPAL A81® FORMULATIONS

As pointed out in specialized literature,[74] it is possible to successfully follow the ageing processes of the Laropal A81® resin through FTIR spectroscopy.

As the ageing of this urea-aldehyde resin is extended, different species containing polar functional groups (as hydroxyl, ketones and carboxylic acids) may develop. The occurrence of photooxidative processes can be studied monitoring the absorptions in the hydroxyl region (3200÷3100 cm^{-1}), the carbonyl band of the ester functionality (at about 1730 cm^{-1}) and the carbonyl band of the tertiary amide (at about 1640 cm^{-1}). The first absorption feature is actually expected to broaden and increase in intensity, while

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[72] Using the Vertex 70 FTIR (Bruker Optik GmbH), equipped with ATR accessory. The processing, carried out using OPUS 5.0 software, included: ATR→ABS conversion, automatic base line correction (Rubberbend, 64 baseline points), automatic smoothing and scale normalization.

[73] Using respecively: the Leica DMR Light Micrsocope and the Jeol JSM 6300 Scanning Electron Microscope.

[74] de la Rie, *et al.* (2002), assessed the stability of different urea-aldehyde resins. The study was carried out considering un-pigments films of an experimental formulation, LaropalA81® and Laropal A101® resins. The films were cast on glass plates and aged for a total of 2996 hours, under conditions simulating daylight passing through window glass, including the UV component.

the other two are expected to merge. No significant changes are instead expected, as far as the fingerprint region absorptions.

The results were totally consistent with the pieces of information reported in literature: as suggested by the occurrence of the spectral changes described above, after 400h of UVA-light exposure, the paints containing the Laropal A81® binder underwent some photooxidative processes. Even though some evidences of this degradation process were detected for all the formulations, those containing the Mars Yellow (PY42) pigment turned out to be more stable than the other ones (see the spectra in Fig.3.2-7). The degradation process was instead particularly pronounced for formulations containing the Ultramarine Deep (PB29) pigment (Fig.3.2-8).

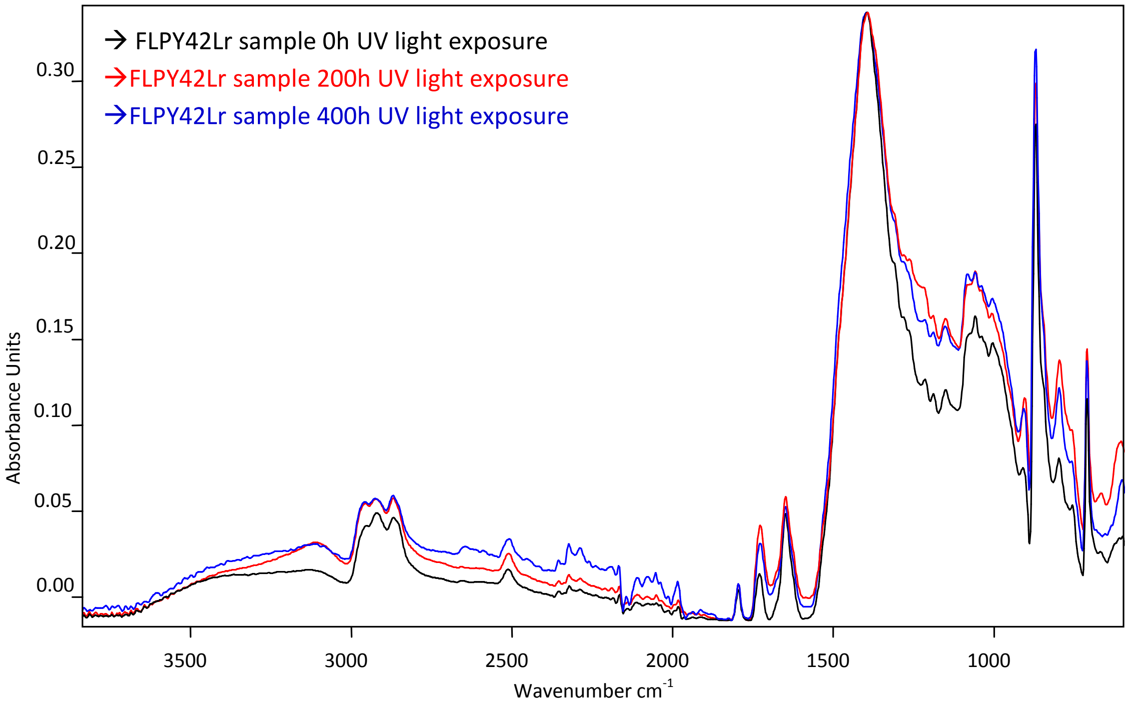


Fig. 3.2-7: Comparing the FTIR spectra from FLPY42Lr, sample at different steps of the UV-light ageing. The retouching formulation contains: Laropal A81® resin, Mars Yellow pigment (PY42) and calcium carbonate extender($CaCO_3$). In black the spectrum collected before ageing, in red and blue those collected after 200h and 400h of exposure respectively. The slight variations in the intensity of the absorption features show that the formulation is pretty stable.

As the ageing was carried on and the photooxidative processes continued to develop, the paint layers became harder and more brittle. Nevertheless, when examining the surfaces through Light Microscopy, only some minor changes in the morphology of the paint layers were detected. The only layers being affected by some cracks were those based on the formulations containing the Titanium White (PW6) pigment. As displayed in table 3.2-17, the occurrence of microscopic cracking was also confirmed by Scanning Electron Microscopy examinations (carried out only for the BRPW6Lr sample).

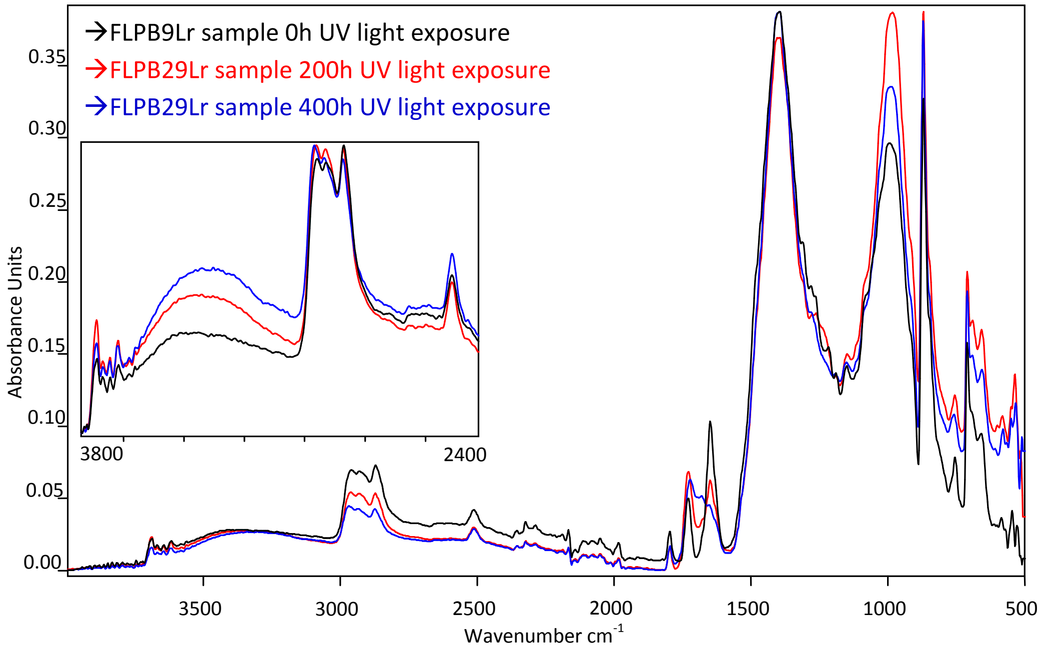
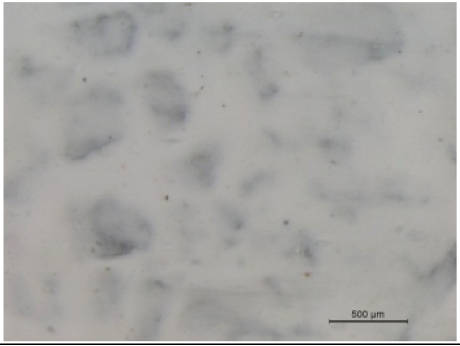
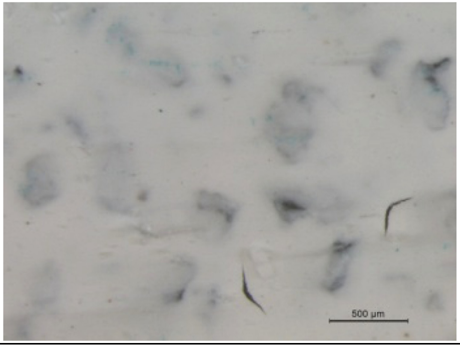
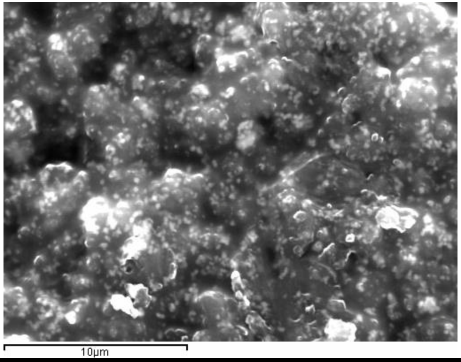
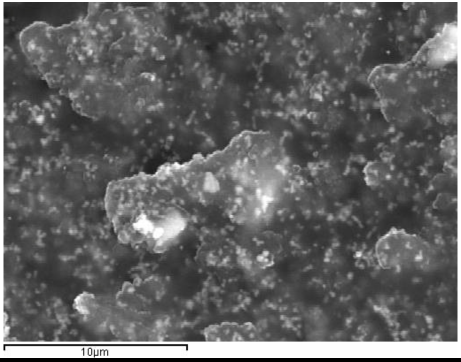


Fig. 3.2-8:Comparing the FTIR spectra from FLPB29Lr sample at different steps of the UV-light ageing. The retouching formulation contains: Laropal A81® resin, Ultramarine Deep pigment (PB29) and calcium carbonate extender($CaCO_3$). In black the spectrum collected before ageing, in red and blue those collected after 200h and 400h of exposure respectively. The merging of the two carbonyl bands and the increment in the absorption in the OH stretching region (enlarged detail) suggest that the resin is undergoing some photooxidative processes.

BRPW6Lr sample: MORPHOLOGICAL VARIATIONS	
Before Ageing (25X-LM)	After 400h of UV-light exposure (25X-LM)
	
Before Ageing (5000X-SEI)	After 400h of UV-light exposure (5000X-SEI)
	

Tab.3.2-17: The morphological variations detected for one of the retouching formulations based on the Laropal A81® resin binder (BRPW6Lr). The pictures taken after 400h of UV-light exposure (on the right) show the occurrence of some cracks.

The photooxidative degradation of the binder did not result in significant color changes. As shown in table 3.2-18, for the majority of the samples, the ΔE_{ab}* calculatedd at the end of the ageing were minor (between 3 and 5) or negligible (lower than 3). The color variation detected for one of the samples containing the Phthalo Green pigment was slightly higher (LQPG7Lr, final ΔE_{ab}* of 6.21).

FLASHE®- L&B- LAROPAL A81® retouching methods

Sample ID	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔEab*	ΔL*	Δa*	Δb*	ΔEab*
FLPW6Lr200	1.70	0.07	0.62	1.81	1.68	0.08	0.59	1.78
FLPW6Lr400	0.94	0.12	0.22	0.97	0.96	0.11	0.17	0.98
FLPB29Lr200	4.17	-5.77	-1.02	**7.19**	4.23	-5.85	-0.90	**7.28**
FLPB29Lr400	6.09	-9.28	-0.48	**11.11**	6.28	-9.47	-0.28	**11.37**
FLPY42Lr200	0.86	0.21	2.45	2.61	0.90	0.22	2.41	2.58
FLPY42Lr400	0.65	0.02	1.77	1.89	0.73	0.00	1.65	1.80
FLPV19Lr200	2.29	1.35	-9.38	**9.75**	2.39	1.16	-8.88	**9.27**
FLPV19Lr400	3.15	1.84	-10.66	**11.26**	3.25	1.56	-10.16	**10.78**
FLPG7Lr200	0.64	-1.30	0.18	1.46	0.62	-1.35	0.19	1.50
FLPG7Lr400	2.15	0.77	-0.75	2.43	2.21	0.74	-0.79	2.46

HEAVY BODY- Liquitex®- LAROPAL A81® retouching methods

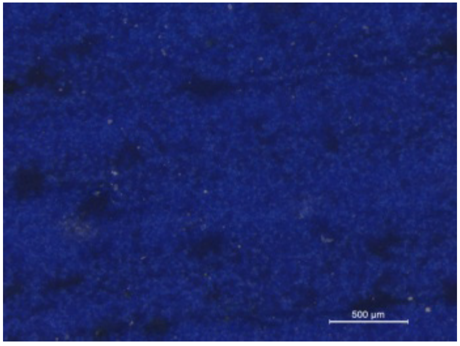
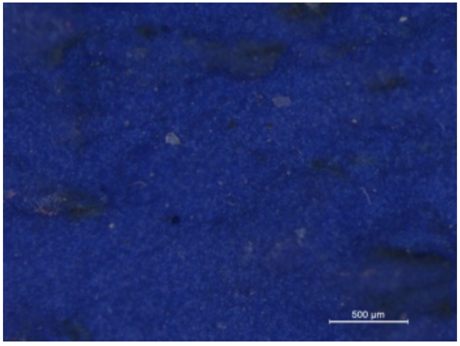
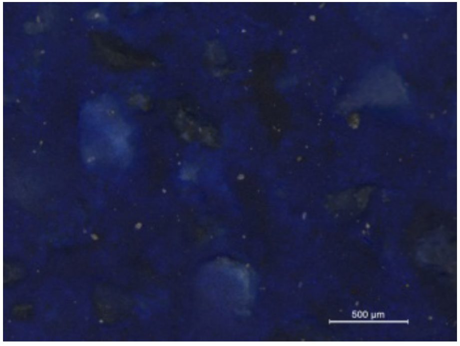
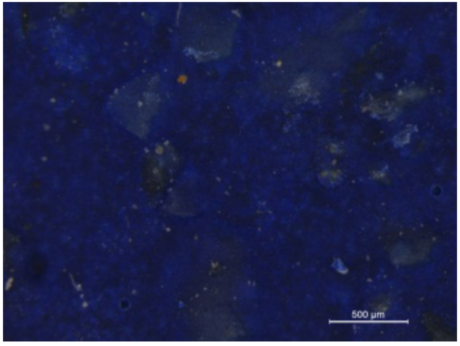
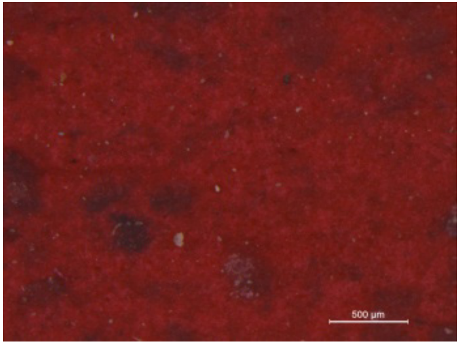
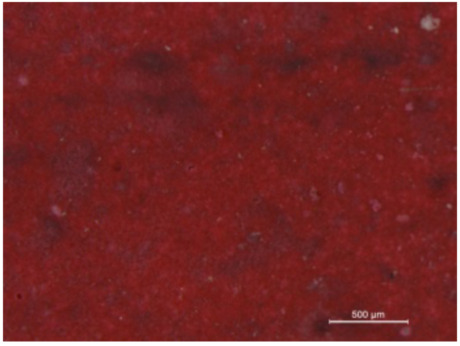
Sample ID	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔEab*	ΔL*	Δa*	Δb*	ΔEab*
LQPW6Lr200	-0.35	-0.08	-0.14	0.38	-0.29	-0.08	-0.16	0.34
LQPW6Lr400	-1.44	-0.05	-0.26	1.46	-1.31	-0.07	-0.29	1.34
LQPB29Lr200	1.33	2.74	-3.67	4.76	1.42	2.14	-3.36	4.23
LQPB29Lr400	1.11	7.01	-6.09	**9.36**	1.14	6.62	-5.90	**8.94**
LQPY42Lr200	0.63	0.25	0.92	1.14	0.62	0.25	0.90	1.12
LQPY42Lr400	0.23	0.41	0.73	0.87	0.27	0.39	0.66	0.81
LQPV19Lr200	-0.74	-0.96	0.50	1.32	-0.72	-0.92	0.68	1.35
LQPV19Lr400	-1.05	-1.23	2.37	2.87	-1.02	-1.15	2.61	3.03
LQPG7Lr200	-0.30	0.01	1.62	1.65	-0.89	1.19	2.05	2.53
LQPG7Lr400	-1.94	5.83	-0.88	**6.21**	-2.03	5.95	-1.19	**6.40**

BRERA- Maimeri®- LAROPAL A81® retouching methods

Sample ID	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔEab*	ΔL*	Δa*	Δb*	ΔEab*
BRPW6Lr200	1.04	0.00	0.56	1.18	1.12	-0.01	0.52	1.24
BRPW6Lr400	-0.98	-0.10	-0.02	0.98	-0.82	-0.12	-0.06	0.83
BRPB29Lr200	-0.96	4.33	-2.02	4.88	-1.15	4.72	-2.31	**5.38**
BRPB29Lr400	-0.82	4.11	-2.01	4.65	-0.97	4.52	-2.33	**5.17**
BRPY42Lr200	-0.33	-0.04	-0.17	0.38	-0.24	-0.10	-0.50	0.56
BRPY42Lr400	-0.08	-0.15	-0.41	0.44	-0.09	-0.14	-0.35	0.39
BRPV19Lr200	1.33	1.50	-0.56	2.08	1.33	1.50	-0.54	2.08
BRPV19Lr400	-0.39	-0.54	3.24	3.31	-0.37	-0.47	3.00	3.06
BRPG7Lr200	-1.70	6.02	0.46	**6.27**	-1.91	6.49	0.63	**6.79**
BRPG7Lr400	1.12	-4.27	1.88	4.80	1.40	-5.06	2.21	**5.69**

Tab. 3.2-18: The color variations induced by the UV-light ageing of the retouching formulations based on the Laropal A81®resin. The total color variation (ΔE^*_{ab}) is shown, together with the variation of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from values collected including and excluding the specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination.

Two of the blue samples (containing the Ultramarine Deep pigment, PB29) and one of the red samples (containing the Quinacridone Rose pigment, PV19) underwent more significant color variations (final ΔE_{ab}* of 11.11 for the FLPB29Lr sample, of 9.36 for the LQPB29Lr one and of 11.26 for FLPV19Lr). Despite leading to ΔE_{ab}* higher than 5, the color variations were barely discernible to naked eye examination (as displayed in Tab. 3.2-19). It is possible that the ΔE_{ab}* values were slightly influenced by an uneven distribution of the pigments in the binding medium.

<table>
<tr><th colspan="2">DISCERNIBLE COLOR VARIATIONS</th></tr>
<tr><td>FLPB29Lr before ageing (25X-LM)

 </td><td>FLPB29Lr after 400h of UV-light ex. (25X-LM)

 </td></tr>
<tr><td>LQPB29Lr before ageing (25X-LM)

 </td><td>LQPB29Lr after 400h of UV-light ex. (25X-LM)

 </td></tr>
<tr><td>FLPV19Lr before ageing (25X-LM)

 </td><td>FLPV19Lr after 400h of UV-light ex. (25X-LM)

 </td></tr>
</table>

Tab.3.2-19: Comparing the appearance of Laropal A81® based samples before and after ageing. Even though the measured total variations are quite high (FLPB29Lr ΔE_{ab}*~11; LQPB29Lr ΔE_{ab}*~9; FLPV19Lr ΔE_{ab}*~11), the color changes are barely discernible to the naked eye.

AQUAZOL 200® FORMULATIONS

As reported in specialized literature,[75] it is possible to follow the ageing processes of Aquazol 200® resin through FTIR spectroscopy. The appearance of additional bands, such as a carbonyl absorption around 1740 cm^{-1}, may suggest the growth of oxidation products in the polymer. Moreover, polymer chain scission reactions may result in a secondary amide and a terminal double bond,[76] revealed by an increment in the intensity of the bands around 3290 cm^{-1} (N-H stretching) and 1540 cm^{-1} (II amide band of a secondary amide) and its respective overtone at 3085 cm^{-1}.

Before starting the ageing, the spectra from some of the Aquazol 200® based formulations were already characterized by an absorption around 1730 cm^{-1}. This feature, possibly related to a carbonyl stretching, suggested the occurrence of some early oxidation processes.

By exposing the samples to UVA-light an additional absorption band were detected at 1730 cm^{-1} for those retouching formulations which initially did not show any degradation feature and, for those formulations which already showed some oxidation evidences, the carbonyl stretching band shifted to lower wavelengths (from 1730 to 1725 cm^{-1}) and increased in intensity. These spectral variations usually came with: the enhancement of the absorption in the 3100 cm^{-1} region and some variations in the intensities of the absorptions in the C-H stretching region (with an enhancement of the ν_{as} CH_3 at 2975 cm^{-1} and a slight decrement of the band at 2880 cm^{-1}).

As shown in figures 3.2-9 and 3.2-10, these features were barely detectable for the samples consisting of organic pigments (such as Quinacridone Rose, PV19) but were particularly pronounced for the formulations containing the Ultramarine Deep (PB29) pigment. Upon ageing, all the blue samples showed a slight decrement and broadening of the I amide bands (falling between 1630 cm^{-1} and 1620 cm^{-1}) and the occurrence of an additional absorption feature around 1550 cm^{-1} (possibly related to the II amide band of a secondary amide).

These results suggested that, when applied on a cement-lime mortar support and exposed to UVA-light, Aquazol 200® resin is likely to undergo two concurrent degradation processes: photooxidative reactions resulting in new functionalities (as carbonyl and hydroxyl groups); polymer chain scission reactions, leading to the formation of a secondary amide and, possibly, terminal double bonds. The formation of this latter features (absorbing in the 1640÷1630 cm^{-1} region) could not be clearly

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[75] Wolbers, McGinn and Duerbeck (1998), tested the stability of Aquazol 50® and Aquazol 500® un-pigmented films, by exposing them to alternate light and dark ageing conditions (72h of light, 72h of dark, 72light), resulting in a total radiant exposure comparable to 24 years of natural ageing in museum conditions.

[76] This degradation pathway was proposed by Appolonia, *et al.* (2009) who compared the stability of different resins which may be used for consolidation purposes.

appreciated because of the presence of the tertiary amide I band in the same spectral region.

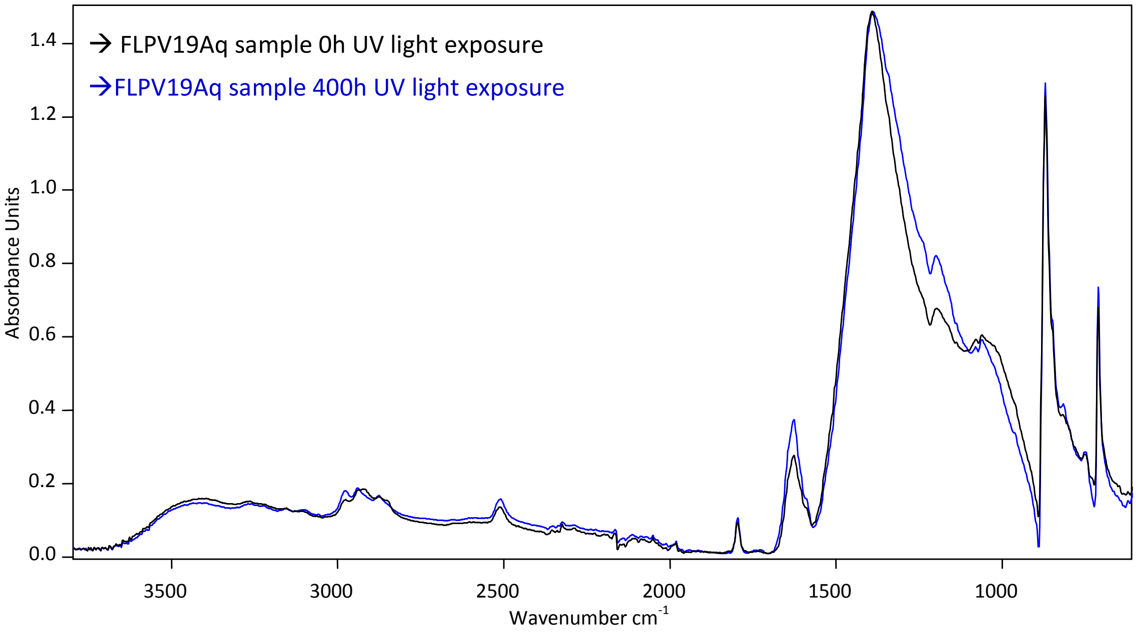


Fig. 3.2-9:Comparing the FTIR spectra from the FLPV19Aq sample at different steps of the UV-light ageing. The retouching formulation contains: Aquazol 200®, Quinacridone Rose (PV19) and Mars Yellow (PY42) pigments, calcium carbonate extender (CaCO$_3$). In black and blue the spectra collected before ageing and after 400h of UVA-light exposure respectively: the slight variations in the intensity of the absorption features show that the formulation is quite stable.

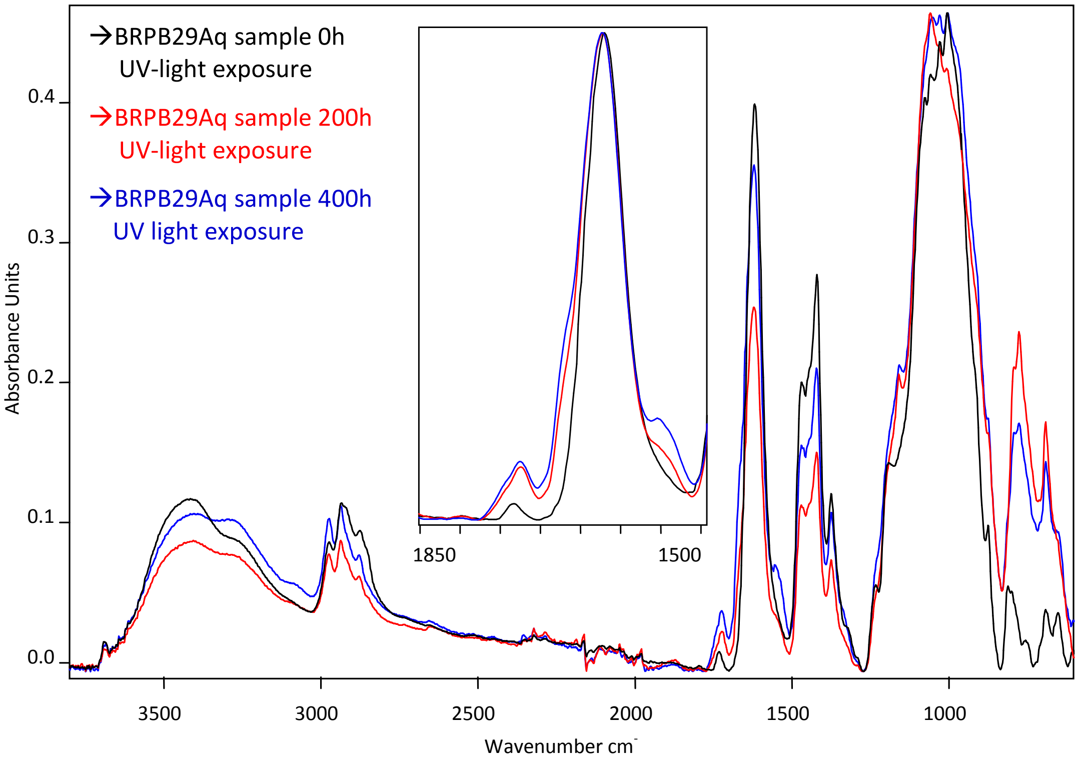
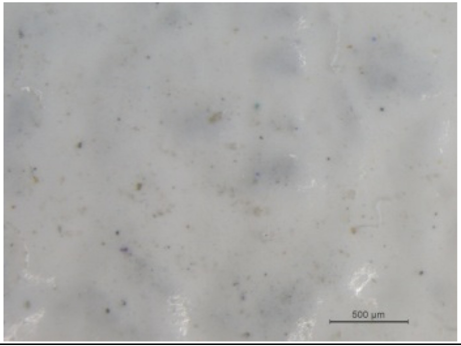
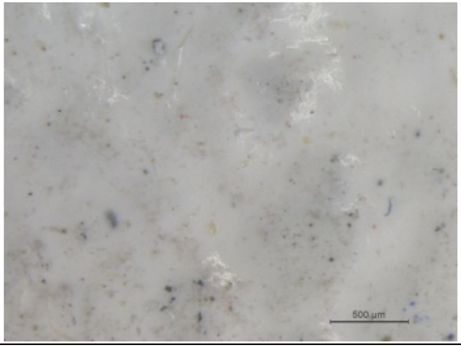
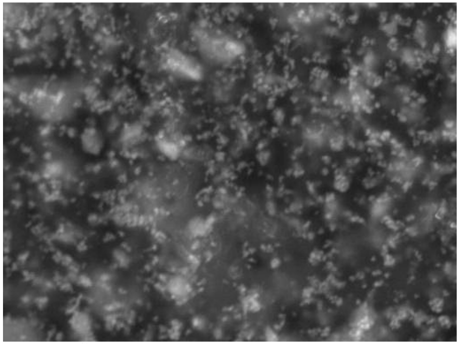
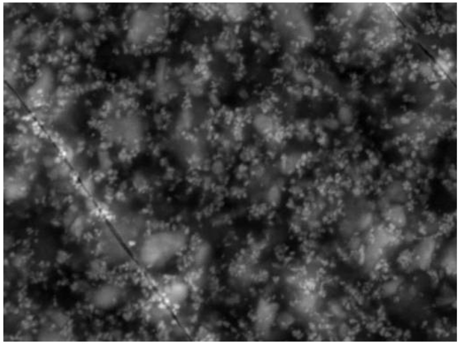


Fig. 3.2-10:Comparing the FTIR spectra collected from the BRPB29Aq sample at different steps of the UV-light ageing. The retouching formulation contains: the Aquazol 200® resin, Ultramarine Deep (PB29) and Quinacridone Rose (PV19) pigments, and silica extender(SiO$_2$). In black the spectrum collected before ageing, in red and blue those collected after 200h and 400h of UVA-light exposure respectively. In the enlarged detail the main variations due to photooxidation and chain-scission processes are shown.

Despite being affected by photooxidative processes, the slightly aged Aquazol 200® paint layers did not harden, nor become more brittle. On the contrary, the paint layers remained quite sticky and prone to dirt pick up.[77] This was especially true for those samples characterized by low pigment volume concentrations (e.g. LQPG7Aq).
Upon ageing, no morphological changes were detected through Light Microscopy examinations. On the contrary, Scanning Electron Microscopy examinations pointed out the occurrence of some fine cracks (see table 3.2-20), which could be consistently due to the supposed chain-scission degradation process (leading to a weakening of binder mechanical properties).

BRPW6Aq sample: MORPHOLOGICAL VARIATIONS

Before Ageing (25X-LM)	After 400h of UV-light exposure (25X-LM)
	
Before Ageing (5000X-SEI)	After 400h of UV-light exposure (5000X-SEI)
	

Tab.3.2-20: The morphological variations detected for one of the retouching formulations based on the Aquazol 200® resin binder (BRPW6Aq). The SEM picture taken after 400h of UV-light exposure (on the right) shows the occurrence of some thin cracks.

Upon ageing, the retouching paints formulated using the Aquazol 200® resin did not show significant discoloration. As shown in table 3.2-21, for the majority of the samples, the $\Delta E_{ab}*$ values measured after 400h of UV-light exposure were minor (between 3 and 5) or negligible (lower than 3). Higher color variations were detected for: the FLPB29Aq sample (containing the Ultramarine Deep pigment; final $\Delta E_{ab}*$ of 8.65), the LQPV19Aq sample (containing the Quinacridone Rose pigment; final $\Delta E_{ab}*$ of 5.58) and the FLPG7Aq sample (containing the Phthalo Green pigment, final $\Delta E_{ab}*$ of 8.34).

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[77] This is actually consistent with the pieces of information reported in specialized literature, were the hygroscopic nature of all Aquazol resins is often remarked.

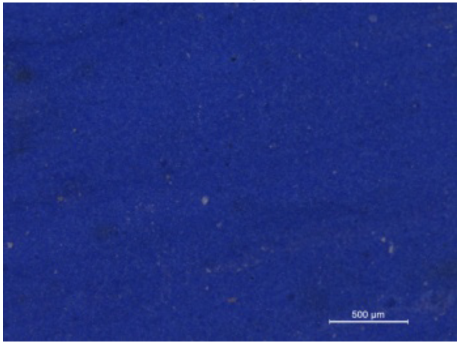
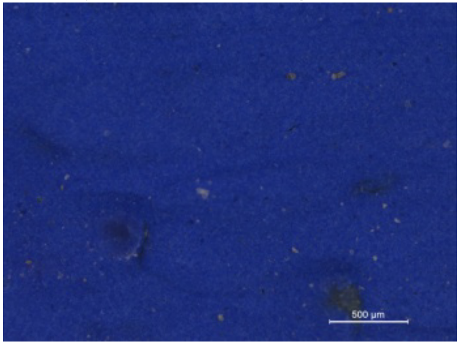
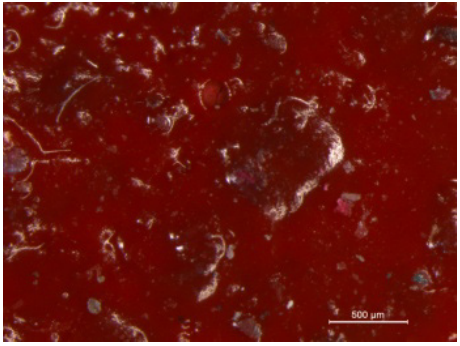
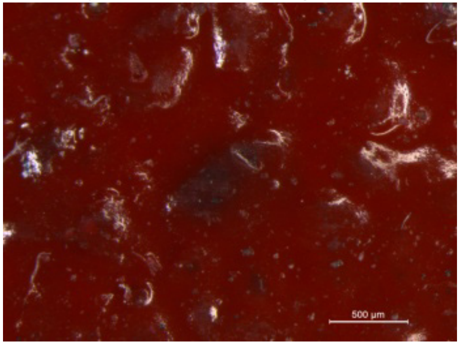
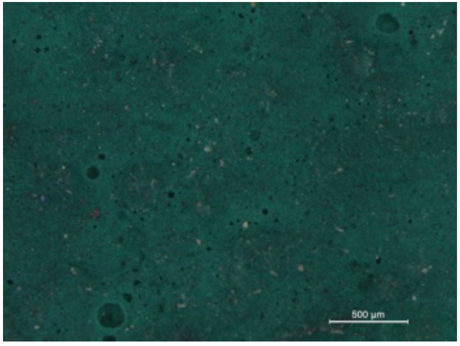
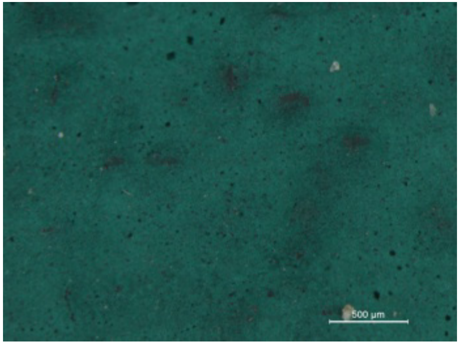
As displayed in Table 3.2-22 these variations were barely discernible to naked eye examination.

FLASHE®- L&B- AQUAZOL 200® retouching methods								
Sample ID	**SCI**				**SCE**			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
FLPW6Aq200	-0.13	-0.16	-0.55	0.59	-0.06	-0.16	-0.56	0.59
FLPW6Aq400	-0.86	-0.16	-0.58	1.05	-0.78	-0.16	-0.60	0.99
FLPB29Aq200	3.68	-6.72	4.04	**8.66**	3.95	-6.46	4.47	**8.79**
FLPB29Aq400	4.29	-6.56	3.66	**8.65**	4.65	-6.30	4.11	**8.84**
FLPY42Aq200	0.89	-0.53	-1.72	2.00	0.89	-0.51	-1.60	1.91
FLPY42Aq400	0.85	-0.71	-2.06	2.34	0.92	-0.69	-1.96	2.27
FLPV19Aq200	0.69	-2.43	-1.28	2.83	0.71	-2.48	-1.17	2.83
FLPV19Aq400	0.23	-2.86	-1.20	3.11	0.31	-2.96	-1.18	3.20
FLPG7Aq200	5.62	4.31	-1.12	**7.17**	5.61	4.43	-1.12	**7.23**
FLPG7Aq400	6.70	4.78	-1.37	**8.34**	6.72	4.93	-1.36	**8.45**

HEAVY BODY- Liquitex®- AQUAZOL 200® retouching methods								
Sample ID	**SCI**				**SCE**			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
LQPW6Aq200	-0.47	0.03	-0.10	0.48	-0.05	0.03	-0.12	0.13
LQPW6Aq400	-3.47	0.12	0.89	3.58	-2.95	0.10	0.84	3.07
LQPB29Aq200	-0.89	-0.05	0.29	0.93	-0.97	0.26	-0.26	1.03
LQPB29Aq400	-1.37	0.08	0.88	1.63	-1.52	0.81	-0.09	1.72
LQPY42Aq200	-0.64	0.13	0.60	0.89	-0.44	-0.04	0.33	0.55
LQPY42Aq400	1.06	0.45	0.46	1.24	1.08	0.43	0.41	1.23
LQPV19Aq200	-0.73	-3.05	-2.82	4.22	-0.54	-3.35	-3.31	4.74
LQPV19Aq400	-2.31	-4.16	-2.92	**5.58**	-2.20	-4.26	-3.32	**5.83**
LQPG7Aq200	1.33	-0.95	-2.36	2.87	-0.04	0.38	-0.08	0.39
LQPG7Aq400	0.51	1.85	-4.00	4.44	-1.50	4.70	0.01	4.93

BRERA- Maimeri®- AQUAZOL 200® retouching methods								
Sample ID	**SCI**				**SCE**			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
BRPW6Aq200	0.45	0.03	0.05	0.46	0.42	0.02	0.04	0.42
BRPW6Aq400	-1.47	0.10	0.37	1.52	-1.28	0.08	0.33	1.33
BRPB29Aq200	1.06	2.04	-2.97	3.76	1.14	1.55	-2.80	3.39
BRPB29Aq400	0.44	3.45	-3.15	4.69	0.44	3.33	-3.21	4.64
BRPY42Aq200	0.23	-0.16	-0.41	0.50	0.13	-0.10	0.35	0.39
BRPY42Aq400	-0.36	-0.10	-0.03	0.37	-0.33	-0.07	0.27	0.43
BRPV19Aq200	-0.64	-1.22	-0.93	1.66	-0.84	-0.90	-0.49	1.32
BRPV19Aq400	-1.99	-1.79	-1.41	3.02	-1.77	-2.08	-1.86	3.31
BRPG7Aq200	-0.43	2.62	-1.77	3.19	-0.58	3.18	-1.92	3.76
BRPG7Aq400	0.12	-0.23	-0.59	0.64	0.35	-0.86	-0.85	1.26

Tab. 3.2-21: The color variations induced by the UV-light ageing of the retouching formulations containing the Aquazol 200®resin binder. The total color variation (ΔE^*_{ab}) is shown, together with the variations of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from values acquired including and excluding the specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination.

DISCERNIBLE COLOR VARIATIONS	
FLPB29Aq before ageing (25X-LM)  	FLPB29Aq after 400h of UV-light ex. (25X-LM) 
LQPV19Aq before ageing (25X-LM)  	LQPV19Aq after 400h of UV-light ex. (25X-LM) 
FLPG7Aq before ageing (25X-LM)  	FLPG7Aq after 400h of UV-light ex. (25X-LM) 

Tab.3.2-22: Comparing the appearance of Aquazol 200® based samples before and after ageing: even though the measured color variations are quite high (FLPB29Aq ΔE_{ab}*~9; LQPV19Aq ΔE_{ab}*~6; FLPG7Aq ΔE_{ab}*~8), the color changes are barely discernible to the naked eye.

3.2.2.2 Evaluation of the drawbacks of using the Europium (III) complex

The suitability of the Europium (III) complex as UV-discernible pigment to use within the conservation field should satisfy a number of different criteria.

First of all it should not affect the stability properties of the materials it is added to.

For this reason the ageing processes of the paint layers cast with the retouching formulations containing the Europium (III) complex were followed through FTIR spectroscopy analysis, colorimetric measurements, Light and Scanning Electron Microscopy examinations. These data were compared to those gathered studying the stability of the pure retouching formulations.

FTIR SPECTROSCOPY ANALYSIS

Upon 400 hours of UVA-light exposure, the spectra collected from the majority of the artists' grade emulsion paints containing the Europium(III) complex did not significantly differ from those collected from the respective pure paints.

This was especially true for the Heavy-Body (Liquitex®) and Brera (Maimeri®) samples. By way of example the spectra from the Transparent Raw Sienna (PY42) Heavy-Body (Liquitex®) paint are shown in figure 3.2-11. Since the position and intensity of the absorption features of the spectra are very similar, the Europium complex (III) is supposed not to influence the ageing process of the paint.

When considering Flashe® (Lefranc&Bourgeois) vinyl paints instead, slight differences in the intensity of the carbonyl stretching band were sometimes detected. As displayed in figure 3.2-12, the intensity of the band at 1738 cm^{-1} is slightly lower when considering the aged paint added with the Europium (III) complex. Even though these differences are minor, the influence of the complex in enhancing the degradation of vinyl binders should be better investigated.[78]

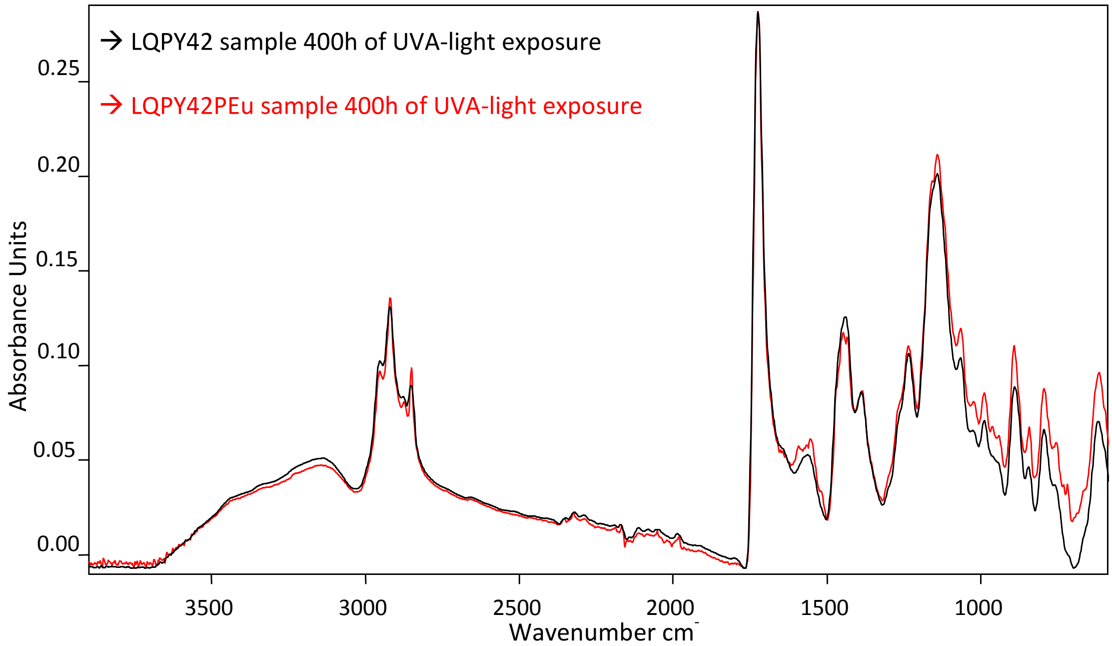


Fig.3.2-11:Studying the influence of the Europium (III) complex on the stability of acrylic paints: spectra from the Transparent Raw Sienna (PY42) Heavy Body-Liquitex® paint, added (red) or not (black) with the complex, after 400h of UVA-light exposure.

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[78] It is to notice that, when studying the ageing of mural paintings, the FTIR spectra could be affected by some support contamination. If further research is carried out in order to assess the role played by the complex in affecting resins' degradation, it will be preferable to test free-film samples.

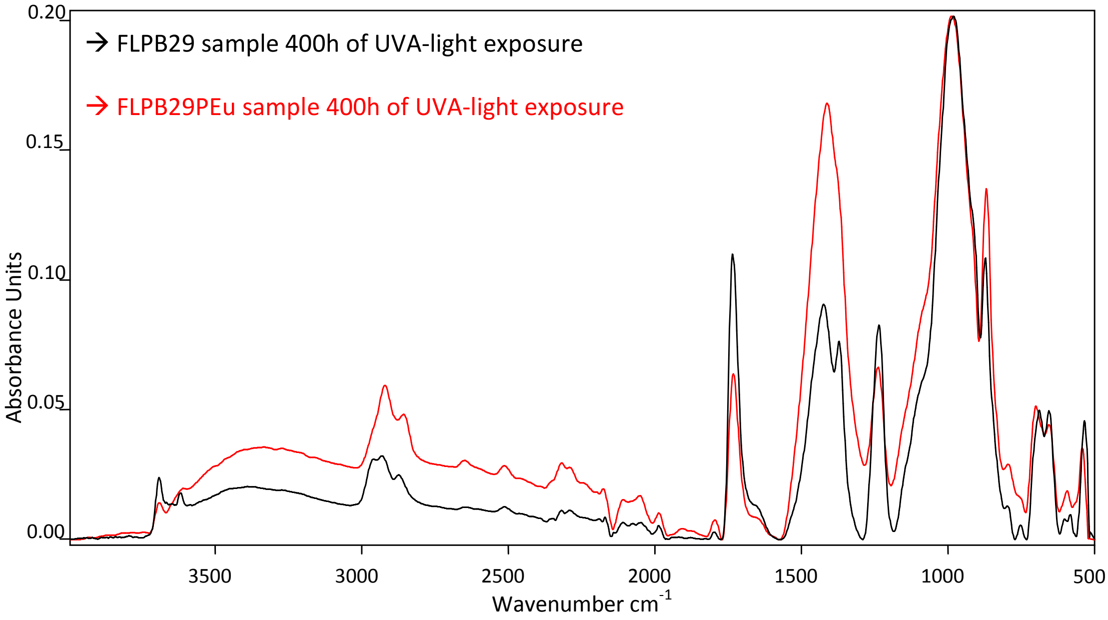

Fig.3.2-12:Studying the influence of the Europium (III) complex on the stability of vinyl paints: the spectra from the Ultramarine Blue (PB29) Flashe®- L&B paint, added (red) or not (black) with the complex, after 400h of UVA-light exposure.

After 400 hours of UVA-light exposure, the spectra of the Laropal A81® formulations containing the Europium (III) complex looked very similar to those collected for the respective pure formulations (figures 3.2-13 and 3.2-14). Even though some differences were at times detected in the intensity of the bands related to the development of photooxidation products (1800 ÷ 1600 cm^{-1} area), the role played by the complex in worsening the degradation process of the resin seemed to be negligible.

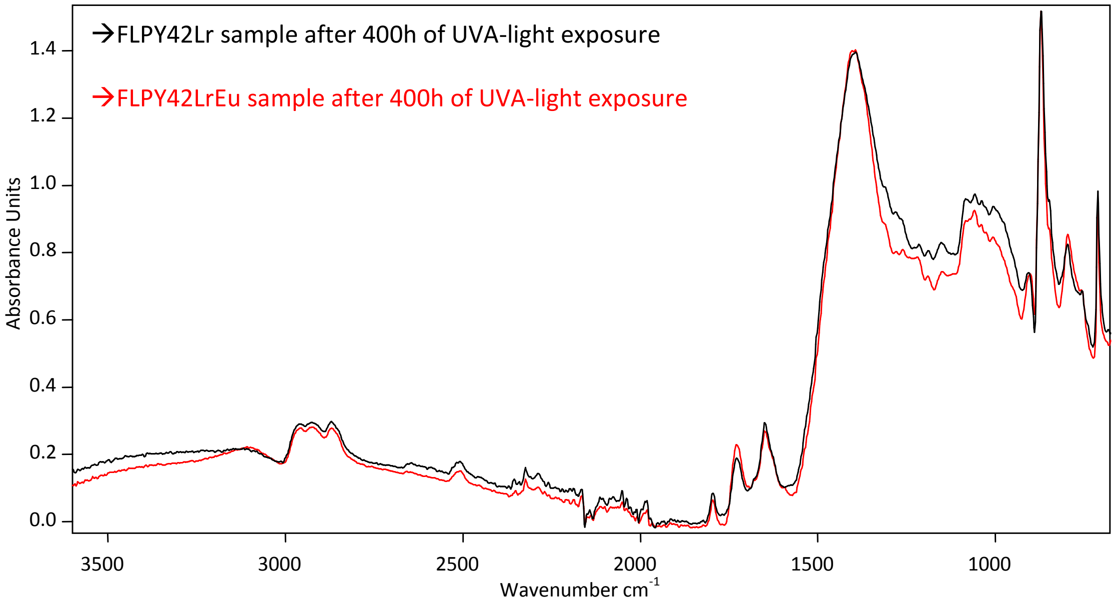

Fig.3.2-13:Studying the influence of the Europium (III) complex on the stability of Laropal A81® formulations: the spectra from FLPY42Lr (black) and FLPY42LrEu (red) formulations after 400 hours of UVA-light exposure.

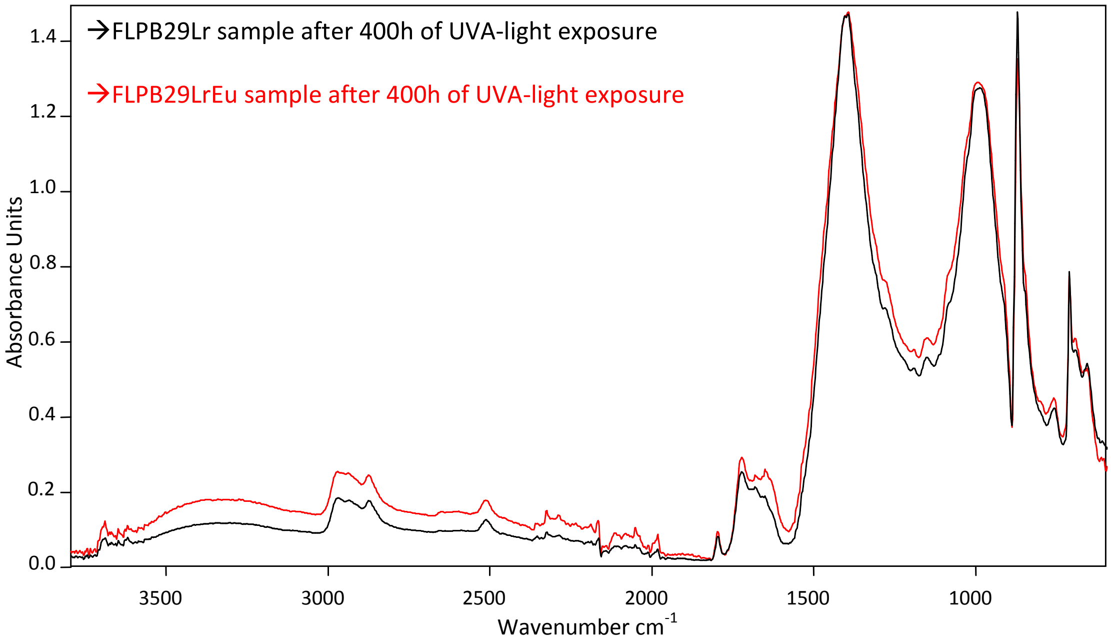

Fig.3.2-14: Studying the influence of the Europium (III) complex on the stability of Laropal A81® formulations: the spectra from FLPB29Lr (black) and FLPB29LrEu (red) formulations after 400 hours of UVA-light exposure.

In the majority of the cases, the spectra of the slightly aged Aquazol 200® formulations containing the Europium (III) complex, were very similar to those of the respective pure formulations (see figure 3.2-15).

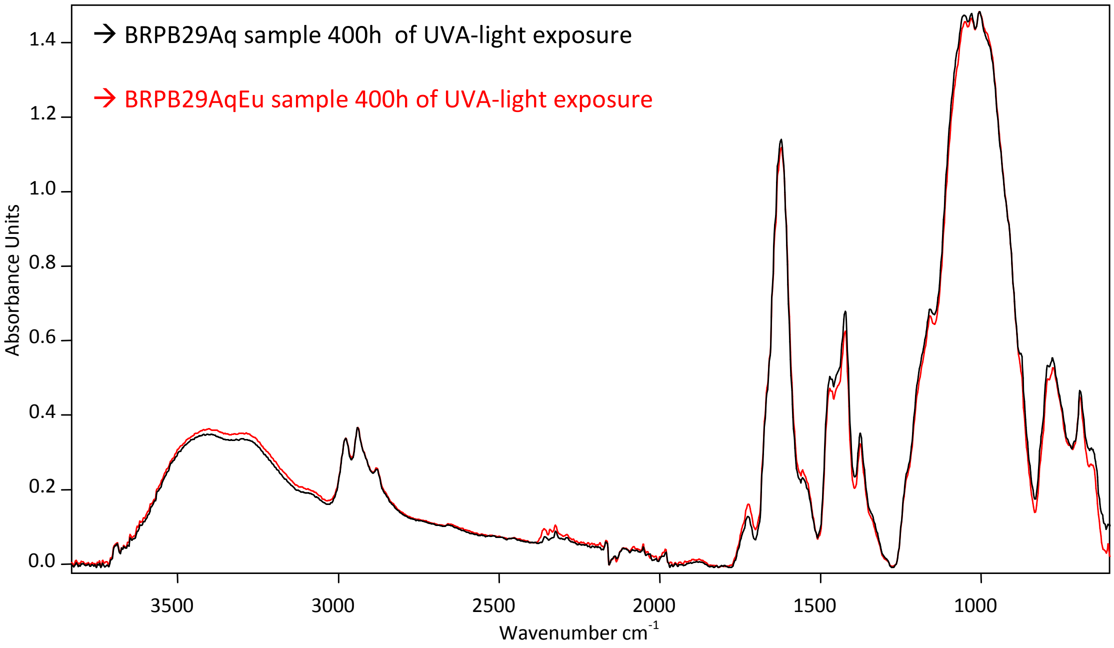

Fig.3.2-15:Studying the influence of the Europium (III) complex on the ageing process of Aquazol 200® formulations: the spectra from BRPB29Aq (black) and BRPB29AqEu (red) formulations after 400 hours of UVA-light exposure.

As shown in figure 3.2-16, in comparison with the spectra of the pure aged paints, the spectra of the formulations containing the complex could present: an increment in the intensity of the band between 1730÷1725 cm^{-1} (related to the development of photooxidative reaction products) and a decrement of the band around 1630 cm^{-1} (stretching of the polymer tertiary amide).

Even though these differences were minor, the influence of the complex in enhancing the degradation processes of the p(2-ethyl-2-oxazoline) resin should be better investigate.

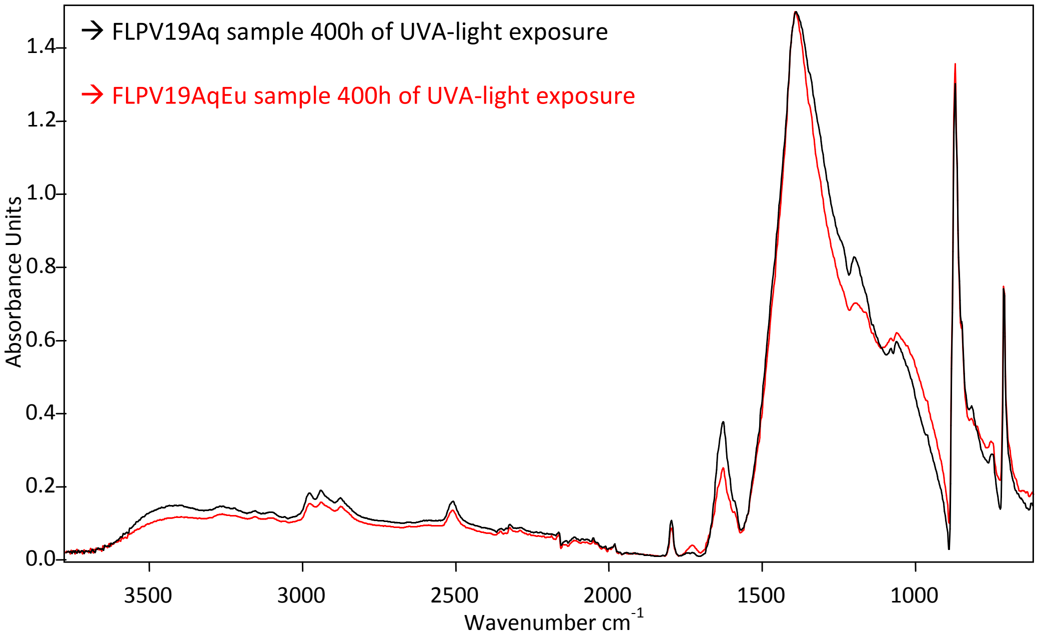

Fig.3.2-16: Studying the influence of the Europium (III) complex on the stability of Aquazol 200® formulations: the spectra from FLPV19Aq (black) and FLPV19AqEu (red) formulations after 400 hours of UVA-light exposure.

MORPHOLOGICAL CHARACTERIZATION

In order to fully evaluate the potential influence of the Europium (III) complex in affecting the stability of the retouching formulations, the painted surfaces were carefully studied through LM and, in some cases, SEM examinations.[79]

In the attempt of focusing the attention on the most relevant results, only some of the pictures taken at SEM are displayed in Table 3.2-23.

Upon 400 hours of UVA-light exposure, no relevant differences were detected between the morphological properties of the paint layers cast with the pure retouching formulations and those cast with the same formulations added with the Europium (III) complex.

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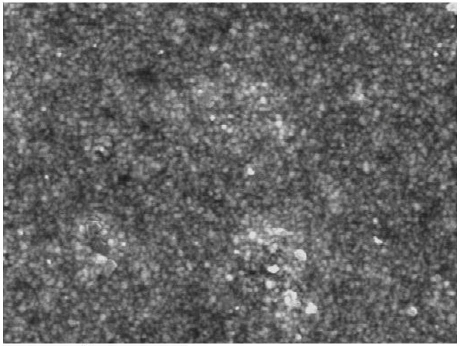
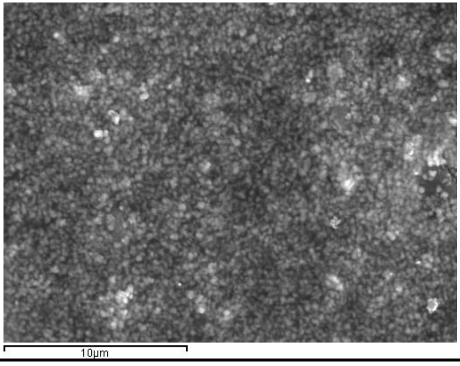
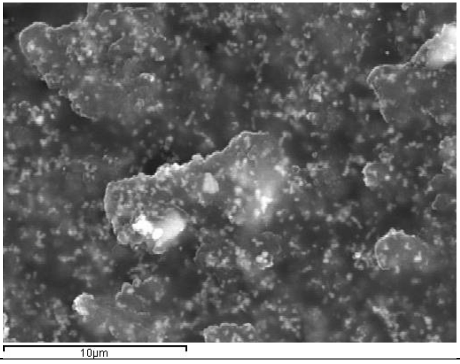
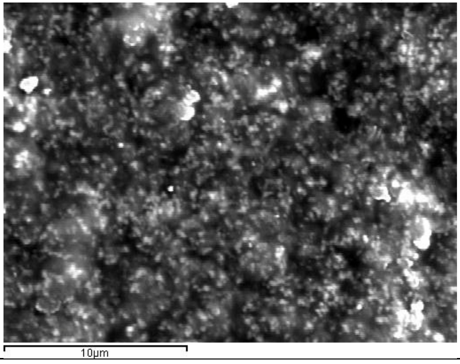
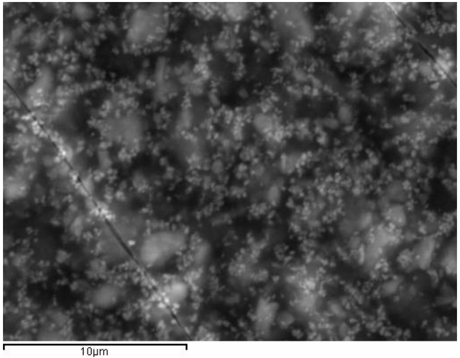
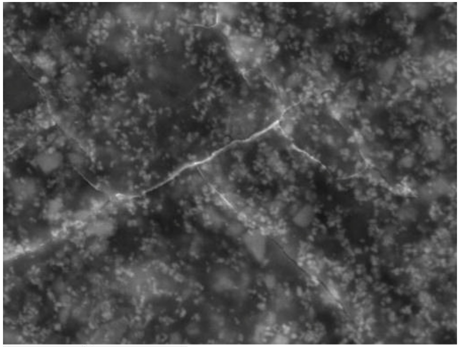
[79] Due to time reasons, Scanning Electron Microscopy examinations were carried out only for the following samples:BRPW6PEu, BRPB29PEu, BRPY42PEu, BRPV19PEu, BRPG7PEu, BRPW6Lr, BRPW6LrEu, BRPW6Aq and BRPW6AqEu.

Even though it is desirable to extend SEM examinations to all the samples, these first results seemed to confirm that the addition of the complex to the retouching paints did not significantly affect their stability properties.

<table>
<tr><th colspan="2">Comparing the morphology of the formulations used to inpaint the BRPW6 sample</th></tr>
<tr><td>BRPW6P 400h (5000X-SEI)
 </td><td>BRPW6PEu 400h (5000X-SEI)
 </td></tr>
<tr><td>BRPW6Lr 400h (5000X-SEI)
 </td><td>BRPW6LrEu 400h (5000X-SEI)
 </td></tr>
<tr><td>BRPW6Aq400h (5000X-SEI)
 </td><td>BRPW6LrAq 400h (5000X-SEI)
 </td></tr>
</table>

Tab. 3.2-23: SEM examinations of the paint layers cast using the retouching paints prepared to inpaint the BRPW6 sample. Pictures taken after 400 hours of UV-light exposure: the pure retouching formulations (on the lefts) are compared to those added with the Europium (III) complex (on the right). Layers based on the same medium, present the same morphological features (e.g. fine cracks for Aquazol200®layers).

COLORIMETRIC MEASUREMENTS

The potential influence of the Europium (III) complex in affecting the color variation rates of the retouching formulations, was assessed through colorimetric measurements.

The color variations detected while ageing the retouching paints added with the complex are shown in tables 3.2-24 (artists' emulsion paints), 3.2-25 (Laropal A81® formulations) and 3.2-26 (Aquazol 200® formulations). In order to better evaluate the influence of the complex, the values displayed in these tables should be compared to those detected for the pure retouching formulations: table 3.2-18 (UV-light ageing of Laropal A81® formulations), table 3.2-21 (UV-light ageing of Aquazol 200® formulations), table 3.1-35 (UV-light ageing of Flashe®-L&B- paints), table 3.1-38 (UV-light ageing of Heavy Body-Liquitex® paints), table 3.1-41 (UV-light ageing of Brera-Maimeri® paints).

As shown in table 3.2-24, the addition of the Europium (III) complex to the emulsion paints did not worsen their discoloration rates. The total color variations detected at the end of the 400 hours of UV-light exposure are generally minor (ΔEab* between 3 and 5) or negligible (ΔEab*<3). The only color variations appreciable to naked eye examinations were those detected for the Flashe® Ultramarine Blue (final ΔEab* about 9) and the Heavy Body-Liquitex® Ultramarine Blue samples (final Eab* about 7). These color variations were anyway lower than those detected for the samples cast with the respective pure emulsion paints (ΔEab* about 12 for the Flashe® one, ΔEab* about 21 for the Heavy Body-Liquitex® one). The ΔEab* values detected for the paints added with the Europium (III) complex are very close to (if not minor than) those detected for the pure paints.

As shown in table 3.2-25, upon ageing the majority of the Laropal A81® retouching formulations added with the Europium (III) complex showed minor (between 3 and 5) or negligible (lower than 3) color variations. Higher color variations were detected for: FLPB29LrEu and BRPB29LrEu samples containing the Ultramarine Deep pigment (final ΔE_{ab}* of 9.15 and 7.73 respectively); the BRPV19LrEu sample containing the Quinacridone Rose pigment (final ΔE_{ab}* of 5.09) and the LQPG7LrEu sample, containing the Phthalo Green pigment (final ΔE_{ab}* of 7.05).

The addition of the Europium (III) complex to the Laropal A81® retouching formulations did not seem to affect their discoloration rates significantly: the majority of the ΔEab* values were very close or lower than those detected when studying the discoloration process of the pure resins. When the color variations were higher than those detected for the pure resins (LQPW6LrEu, BRPW6LrEu, BRPB29LrEu, LQPV19LrEu, BRPV19LrEu and LQPG7LrEu) it was not possible to clearly define the role played by the complex in worsening the discoloration process, with data being possibly affected by other factors (such as uneven pigment dispersion) .

FLASHE® -L&B- added with the Europium (III) complex

Sample ID	SCI				SCE			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
FLPW6PEu200	0.41	0.17	0.81	0.92	0.41	0.18	0.79	0.90
FLPW6PEu400	0.28	0.22	0.67	0.76	0.37	0.21	0.63	0.76
FLPB29PEu200	3.15	-4.67	-0.48	**5.65**	3.20	-4.77	-0.39	**5.76**
FLPB29PEu400	4.50	-7.85	0.28	**9.05**	4.59	-8.05	0.48	**9.28**
FLPY42PEu200	0.19	0.07	0.17	0.27	0.22	0.06	0.18	0.29
FLPY42PEu400	0.12	-0.05	0.23	0.26	0.18	-0.05	0.19	0.26
FLPV19PEu200	-0.38	-0.56	-2.30	2.40	-0.36	-0.59	-2.20	2.30
FLPV19PEu400	-0.41	-0.70	-2.65	2.78	-0.35	-0.71	-2.62	2.73
FLPG7PEu200	1.85	-0.59	0.35	1.98	1.86	-0.51	0.34	1.96
FLPG7PEu400	3.25	1.05	-0.53	3.46	3.26	1.19	-0.58	3.52

HEAVY BODY- Liquitex®- added with the Europium (III) complex

Sample ID	SCI				SCE			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
LQPW6PEu200	0.36	-0.05	0.63	0.73	0.49	-0.05	0.61	0.78
LQPW6PEu400	-0.46	0.16	0.40	0.63	-0.30	0.15	0.36	0.50
LQPB29PEu200	1.68	4.19	-4.77	**6.57**	1.77	3.79	-4.59	**6.21**
LQPB29PEu400	3.09	3.05	-5.80	**7.25**	3.30	2.28	5.49	**6.80**
LQPY42PEu200	0.89	-0.21	-1.37	1.65	0.73	-0.13	-0.65	0.99
LQPY42PEu400	0.81	-0.39	-0.60	1.08	0.79	-0.35	-0.29	0.92
LQPV19PEu200	-1.13	-1.30	1.14	2.06	-1.15	-1.22	1.52	2.27
LQPV19PEu400	-1.56	-1.89	0.89	2.61	-1.60	-1.82	1.33	2.76
LQPG7PEu200	1.21	-2.90	-0.42	3.17	1.28	-2.63	-0.41	2.95
LQPG7PEu400	0.64	-0.43	-1.81	1.97	0.71	-0.11	-1.87	2.00

BRERA- Maimeri®- added with the Europium (III) complex

Sample ID	SCI				SCE			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
BRPW6PEu200	0.16	-0.15	0.30	0.38	0.20	-0.15	0.29	0.38
BRPW6PEu400	-0.38	-0.32	0.11	0.51	-0.28	-0.33	0.07	0.44
BRPB29PEu200	0.96	-3.70	1.62	4.15	1.04	-3.81	1.71	4.31
BRPB29PEu400	1.26	-3.83	1.33	4.25	1.38	-3.95	1.40	4.41
BRPY42PEu200	1.23	-0.13	-1.46	1.91	1.27	-0.11	-1.44	1.92
BRPY42PEu400	0.74	-0.16	-0.78	1.09	0.82	-0.16	-0.83	1.18
BRPV19PEu200	-1.22	-1.82	-0.41	2.23	-1.22	-1.77	-0.38	2.19
BRPV19PEu400	-0.82	-0.16	1.90	2.08	-0.83	0.00	1.71	1.90
BRPG7PEu200	0.21	-0.24	-0.42	0.52	0.15	0.10	-0.43	0.46
BRPG7PEu400	-0.25	1.34	-0.82	1.60	-0.27	1.49	-0.93	1.78

Tab. 3.2-24: The color variations induced by the UV-light ageing for the artists' emulsion paints added with the Europium (III) complex. The total color variation (ΔE^*_{ab}) is shown, together with the variations of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from values acquired including and excluding the specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination.

FLASHE®- L&B- LAROPAL A81® retouching methods – Eu(III) compl.

Sample ID	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔEab*	ΔL*	Δa*	Δb*	ΔEab*
FLPW6LrEu200	-0.62	-0.93	-0.01	1.12	-0.52	-0.90	-0.01	1.04
FLPW6LrEu400	-0.49	-0.94	0.16	1.07	-0.33	-0.93	0.13	0.99
FLPB29LrEu200	3.65	-3.62	-2.25	**5.61**	3.63	-3.58	-2.25	**5.58**
FLPB29LrEu400	6.10	-6.19	-2.86	**9.15**	5.21	-6.87	-1.50	**8.76**
FLPY42LrEu200	-0.13	-0.59	1.19	1.33	-0.08	-0.60	1.10	1.25
FLPY42LrEu400	-0.91	-1.15	1.13	1.85	-0.82	-1.15	0.96	1.71
FLPV19EuLr200	-1.06	-1.17	-0.25	1.60	-1.03	-1.12	-0.30	1.55
FLPV19EuLr400	-0.99	-0.98	0.71	1.56	-0.94	-0.89	0.49	1.39
FLPG7EuLr200	-0.58	-1.39	0.96	1.79	-0.59	-1.47	1.00	1.88
FLPG7EuLr400	-0.07	-1.16	0.98	1.53	-0.06	-1.19	1.00	1.56

HEAVY BODY- Liquitex®- LAROPAL A81® retouching methods - Eu(III) compl.

Sample ID	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔEab*	ΔL*	Δa*	Δb*	ΔEab*
LQPW6LrEu200	-1.93	-0.32	0.38	1.99	-2.01	-0.31	0.42	2.07
LQPW6LrEu400	-3.27	-0.14	0.67	3.34	-3.24	-0.14	0.67	3.31
LQPB29LrEu200	-0.67	-0.60	1.48	1.73	-0.76	0.00	1.17	1.39
LQPB29LrEu400	0.06	1.79	-1.18	2.15	0.07	2.02	-1.34	2.42
LQPY42LrEu200	0.38	0.53	3.39	3.45	0.43	0.47	3.11	3.18
LQPY42LrEu400	0.33	-0.42	0.00	0.54	0.37	-0.40	-0.01	0.55
LQPV19LrEu200	-2.66	-2.60	2.65	4.57	-2.59	-2.41	2.19	4.16
LQPV19LrEu400	-2.85	-3.09	1.09	4.34	-2.70	-2.86	0.42	3.95
LQPG7LrEu200	1.97	-6.10	2.55	**6.90**	2.53	-6.83	2.08	**7.58**
LQPG7LrEu400	2.61	-6.40	1.38	**7.05**	3.28	-6.86	0.75	**7.64**

BRERA- Maimeri®- LAROPAL A81® retouching methods- Eu(III) compl.

Sample ID	SCI				SCE			
	ΔL*	Δa*	Δb*	ΔEab*	ΔL*	Δa*	Δb*	ΔEab*
BRPW6LrEu200	-2.39	-0.16	-0.76	2.51	-2.38	-0.16	-0.75	2.50
BRPW6LrEu400	-2.85	0.14	-0.64	2.92	-2.79	0.12	-0.65	2.86
BRPB29LrEu200	-1.92	-2.19	-5.18	**5.94**	-2.28	-2.55	-5.93	**6.85**
BRPB29LrEu400	-7.28	1.12	-2.37	**7.73**	-8.19	2.71	-4.76	**9.85**
BRPY42LrEu200	-0.29	-0.21	-0.11	0.38	-0.23	-0.23	-0.32	0.46
BRPY42LrEu400	0.20	0.22	0.22	0.37	0.29	0.20	0.06	0.36
BRPV19LrEu200	-2.36	-2.39	4.52	**5.63**	-2.32	-2.24	4.16	**5.27**
BRPV19LrEu400	-2.93	-3.40	2.40	**5.09**	-2.82	-3.23	1.92	4.70
BRPG7LrEu200	-0.54	1.95	0.07	2.02	-0.56	1.98	0.09	2.06
BRPG7LrEu400	-0.74	2.78	-0.32	2.90	-0.72	2.71	-0.36	2.83

Tab. 3.2-25: The color variations induced by the UV-light ageing of the LaropalA81®retouching formulations containing the Europium (III) complex. The total color variation (ΔE^*_{ab}) is shown, together with the variations of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from values acquired including and excluding the specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination.

FLASHE® - L&B- AQUAZOL 200® retouching methods - Eu(III) compl.

Sample ID	SCI				SCE			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
FLPW6AqEu200	-0.02	-0.43	-0.33	0.54	0.04	-0.41	-0.34	0.54
FLPW6AqEu400	-0.35	-0.38	-0.15	0.54	-0.21	-0.36	-0.15	0.46
FLPB29AqEu200	4.80	-6.92	4.50	**9.54**	4.85	-6.59	4.63	**9.40**
FLPB29AqEu400	7.01	-8.42	5.67	**12.34**	7.05	-8.00	5.68	**12.08**
FLPY42AqEu200	0.44	-1.20	-3.29	3.53	0.48	-1.18	-3.16	3.41
FLPY42AqEu400	0.84	-0.99	-3.95	4.16	0.91	-0.99	-3.76	3.99
FLPV19AqEu200	1.36	-3.18	-2.75	4.42	1.38	-3.12	-2.58	4.28
FLPV19AqEu400	1.66	-4.14	-3.45	5.63	1.64	-4.10	-3.26	5.49
FLPG7AqEu200	4.94	3.09	-0.93	**5.90**	4.93	3.11	-0.95	**5.91**
FLPG7AqEu400	7.05	4.05	-1.47	**8.26**	7.07	4.13	-1.53	**8.33**

HEAVY BODY- Liquitex®- AQUAZOL 200® retouching methods - Eu(III) compl.

Sample ID	SCI				SCE			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
LQPW6AqEu200	-2.18	-0.41	-0.85	2.38	-1.71	-0.40	-0.94	1.99
LQPW6AqEu400	-2.08	-0.23	-0.90	2.28	-1.78	-0.23	-0.96	2.04
LQPB29AqEu200	-4.75	-4.83	0.40	**6.78**	-5.39	-2.89	-1.89	**6.40**
LQPB29AqEu400	-4.86	-4.20	0.10	**6.43**	-5.52	-2.11	-2.33	**6.35**
LQPY42AqEu200	0.06	-1.03	-1.84	2.11	0.08	-0.98	-1.81	2.06
LQPY42AqEu400	-0.24	-1.42	-1.36	1.98	-0.29	-1.35	-1.30	1.89
LQPV19AqEu200	-2.42	-3.47	-2.24	4.78	-2.59	-3.07	-1.62	4.33
LQPV19AqEu400	-2.63	-4.98	-3.48	**6.62**	-2.53	-4.56	-4.24	**6.73**
LQPG7AqEu200	0.21	0.16	-0.59	0.64	0.58	-1.56	-0.35	1.70
LQPG7AqEu400	0.45	-0.24	-1.32	1.42	1.14	-2.55	-1.46	3.15

BRERA- Maimeri®- AQUAZOL 200® retouching methods - Eu(III) compl.

Sample ID	SCI				SCE			
	ΔL*	**Δa***	**Δb***	**ΔEab***	**ΔL***	**Δa***	**Δb***	**ΔEab***
BRPW6AqEu200	-0.64	-0.54	0.65	1.06	-0.50	-0.53	0.62	0.95
BRPW6AqEu400	-3.06	-0.63	-0.74	3.21	-2.97	-0.63	-0.72	3.12
BRPB29AqEu200	-2.69	-7.06	5.60	**9.40**	-2.87	-5.92	4.22	**7.81**
BRPB29AqEu400	-2.52	-5.81	4.44	**7.73**	-2.66	-4.66	3.08	**6.19**
BRPY42AqEu200	-0.41	-0.43	-2.45	2.52	-0.37	-0.43	-2.37	2.44
BRPY42AqEu400	-0.25	-0.62	-3.13	3.20	-0.45	-0.49	-1.49	1.63
BRPV19AqEu200	-2.51	-4.04	-2.20	**5.24**	-2.20	-4.28	-2.86	**5.60**
BRPV19LrEu400	-2.34	-3.75	-2.08	4.88	-1.97	-4.05	-2.89	**5.35**
BRPG7AqEu200	-0.71	1.81	0.62	2.04	-0.64	1.38	0.63	1.65
BRPG7AqEu400	-0.98	2.99	-0.32	3.17	-0.89	2.55	-0.45	2.74

Tab. 3.2-26: The color variations induced by the UV light ageing of Aquazol200® retouching formulations containing the Europium (III) complex. The total color variation (ΔE^*_{ab}) is shown, together with the variations of lightness (ΔL*) and chromaticity coordinates (Δa* and Δb*). Data were calculated from values acquired including and excluding the specular reflectance (SCI and SCE methods). The bold font is used for those variations that, being higher than 5, are supposed to be discernible to naked eye examination.

As shown in table 3.2-26, upon ageing many of the Aquazol 200® formulations added with the Europium (III) complex underwent minor ($3 < \Delta E_{ab}^* < 5$) or negligible ($\Delta E_{ab}^* < 3$) color variations. Higher changes were detected for: the three formulations containing the Ultramarine Deep pigment (FLPB29AqEu, final ΔE_{ab}^* of 12.34; LQPB29AqEu final ΔE_{ab}^* of 6.43; BRPB29AqEu, final ΔE_{ab}^* of 7.73); two formulations containing the Quinacridone Rose pigment (FLPV19AqEu, final ΔE_{ab}^* of 5.63, LQPV19AqEu, final ΔE_{ab}^* of 6.62); the FLPG7AqEu formulation (final ΔE_{ab}^* of 8.26).
In the majority of the cases, the ΔEab* values detected for the formulations added with the complex were higher than those detected for the pure retouching paints. As already seen for the Laropal A81® formulations, it was however not possible to clearly define the role played by the complex in worsening these variations, with data being likely affected by other factors (such as uneven pigment dispersion).

3.2.2.3 Discernibility issues: the stability of the Europium (III) complex

The suitability of the Europium (III) complex as pigment to use for enhancing the discernibility of the inpainted areas, is finally related to its durability.[80]

At different steps of the ageing, the surfaces of the mock-ups were examined under UV light (using a Wood's lamp, λ 365 nm) in order to qualitatively assess the lasting properties of the luminescence phenomenon.

As shown in figure 3.2-17, after 100 hours of exposure, an early drop in the intensity of the naked-eye discernible luminescence was detected. Extending the ageing, the luminescence tended to further decrease and, after 400 hours of exposure, the discernibility of some areas added with the Europium (III) complex was almost lost. This was the case of the formulations containing the Phthalo Green (PG7) pigment that, from the beginning, were characterized by lower luminescence intensities.

The degradation process of the Europium (III) complex was tentatively followed through FTIR spectroscopy analysis.

As already pointed out, it was not always possible to detect the absorptions related to Europium (III) complex in the FTIR spectra of the unaged samples (section *3.2.1.4 Chemical characterization of the formulations added with the Europium (III) complex*, tab. 3.2-10). In the majority of the cases, the absorption bands falling around 1595 cm^{-1}, 1550 cm^{-1} and 1515 cm^{-1} can be however chosen as FTIR spectroscopy marker of the $Eu(DBM)_3phen$ compound. Monitoring the variations in the intensity of these bands, the chemical stability of the complex was tentatively evaluated. The results are reported in Table 3.2-27.

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[80] It is always preferable to use durable materials which allow log-term treatments, limiting the risks and costs of frequent re-treatments.

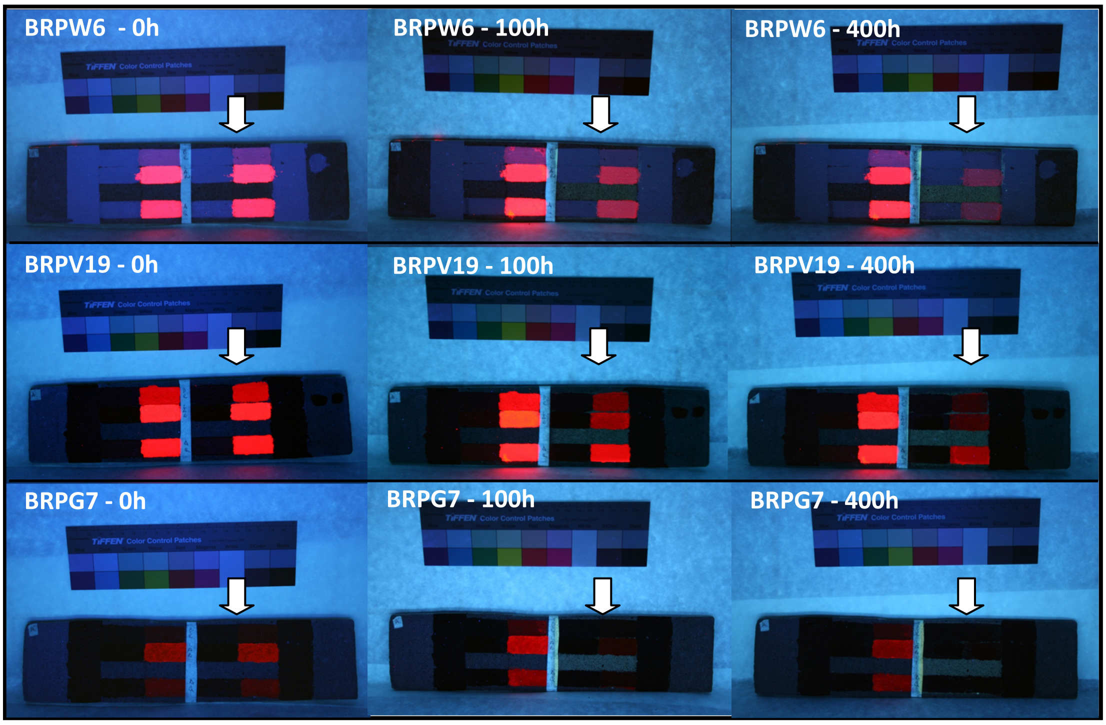

Fig. 3.2-17: Three Brera (Maimeri®) samples inpainted with various retouching media, added or not with the Europium (III) complex. The picture were taken under the light of a Wood's lamp (365 nm) at different steps of the ageing. After 400h of exposure, the intensity of the naked-eye discernible luminescence of the retouching paints containing the Phthalo Green pigment (PG7) is almost lost (BRPG7-400h picture). Arrows point out those areas exposed to the ageing conditions.

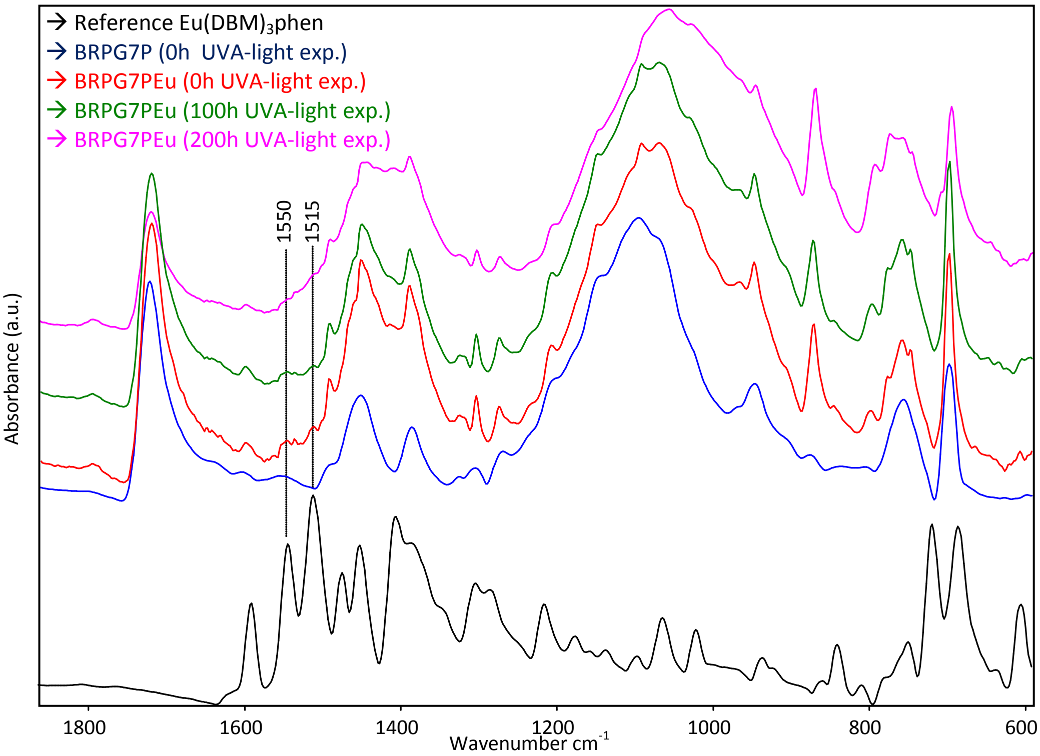

Fig. 3.2-18: Monitoring the absorption features of the Europium (III) complex at different steps of the ageing: BRPG7PEu retouching paint. After 200 hours of UVA-light exposure the bands ascribable to the luminescent compound are not detected anymore.

FLASHE INPAINITNGS		**LIQUITEX INPAINITNGS**		**BRERA INPAINITNGS**	
Retouching Formualtions	**Eu-compl. features (cm^{-1})**	**Retouching Formualtions**	**Eu-compl. features (cm^{-1})**	**Retouching Formualtions**	**Eu-compl. features (cm^{-1})**
FLPW6PEu	until 400h 1595	LQPW6PEu	until 100h 1595	BRPW6PEu	-
FLPW6AqEu	-	LQPW6AqEu	until 200h 1555 and 1515	BRPW6AqEu	-
FLPW6LrEu	-	LQPW6LrEu	until 200h 1555	BRPW6LrEu	until 100h 1550sh
FLPB29PEu	until 200h 1596	LQPB29PEu	until 100h 1595 and 1515	BRPB29PEu	n.d. after 100h
FLPB29AqEu	-	LQPB29AqEu	n.d. after 100h	BRPB29AqEu	n.d. after 100h
FLPB29LrEu	n.d. after 100h	LQPB29LrEu	n.d. after 100h	BRPB29LrEu	until 100h 1550sh
FLPY42PEu	until 200h 1596	LQPY42PEu	until 400h 1595sh, 1550, 1518sh	BRPY42PEu	-
FLPY42AqEu	-	LQPY42AqEu	until 100h 1550	BRPY42AqEu	until 400h 1550sh
FLPY42LrEu	until 400h 1595	LQPY42LrEu	until 100h 1550	BRPY42LrEu	-
FLPV19PEu	-	LQPV19PEu	until 400h 1555?, until 200h 1518	BRPV19PEu	until 200h 1555?, 1518sh
FLPV19AqEu	-	LQPV19AqEu	until 400h 1555?, until 200h 1518	BRPV19AqEu	until 400h 1555sh?
FLPV19LrEu	-	LQPV19LrEu	-	BRPV19LrEu	-
FLPG7PEu	-	LQPG7PEu	until 100h 1595sh	BRPG7PEu	until 100h 1550, 1518
FLPG7AqEu	-	LQPG7AqEu	until 100h 1518	BRPG7AqEu	until 400h 1518?
FLPG7LrEu	n.d. after 100h	LQPG7LrEu	n.d. after 100h	BRPG7LrEu	until 100h 1550sh?

Tab 3.2-27: Monitoring the absorption features related to Eu(DBM)$_3$phen at different steps of the ageing. The question mark (?) is used in case of uncertain attribution. The hyphen (–) is used when it was not possible to detect the features related to the complex in the spectra of the unaged samples. n.d. = not detected

For 8 samples out of 30, it was not possible to detected the absorption features related to the complex after only 100 hours of exposure. These samples mainly contained the Ultramarine Deep (PB29) or the Phathlo Green (PG7) pigments (figure 3.2-18).

The absorption features related to the complex were detectable until 100 hours of exposure for 9 samples, until 200 hours for 7 samples.

Only for 3 samples out of 30, it was still possible to detected the features related to the complex at the end of the ageing.[81] These three samples all contained the Mars Yellow pigment (PY42, figure 3.2-19).

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[81] For the remaining two samples (BRPV19AqEu, and BRPG7AqEu) the detection of the complex related features at the end f the ageing was uncertain (due to the pigment absorptions which partially overlap those of the complex).

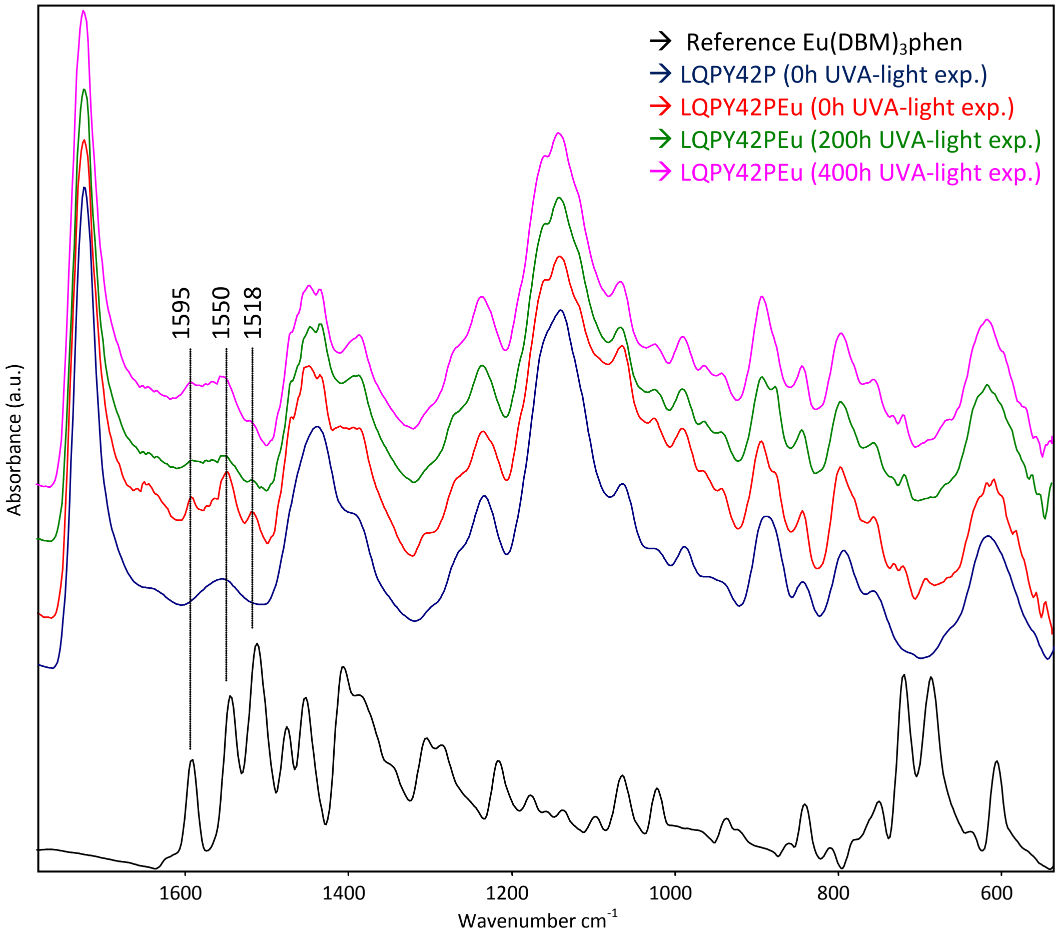


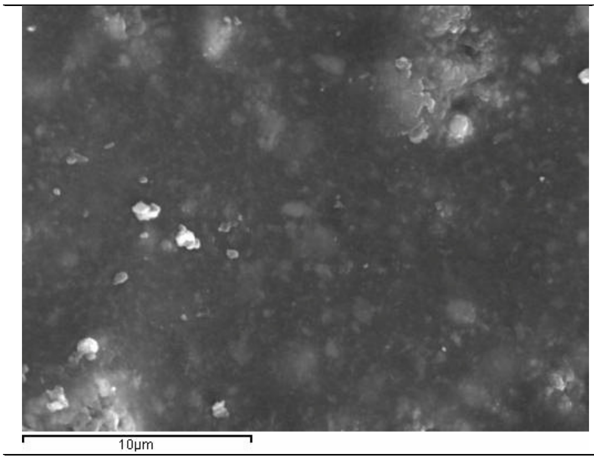
Fig. 3.2-19: Monitoring the absorption features of the Europium (III) complex at different steps of the ageing: LQPY42PEu retouching paint. After 400 hours of UVA-light exposure the bands ascribable to the luminescent compound are barely but still detectable.

At the end of the ageing, some of the samples (BRPW6PEu; BRPB29PEu; BRPY42PEu; BRPV19PEu; BRPG7PEu; BRPW6AqEu and BRPW6LrEu) were investigated using Scanning Electron Microscopy. Energy Dispersive X-ray (EDX) analysis were also carried out, considering areas and local points, in order to verify the chemical composition of the aged paint layers. It was pointed out that, all the samples were still characterized by the presence of the Europium element.

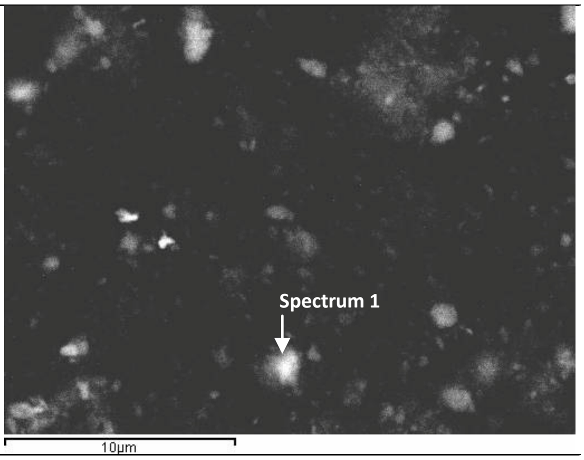
By way of example, the results gathered from the aged BRPG7PEu sample are presented in table 3.2-28. The images taken at 5000X using Secondary and Backscattered electrons are shown, together with the EDX spectrum collected from a point (which looked bright in the BSE image): even if, after 400h of UVA-light ageing the red luminescence was not discernible to the naked-eye (Fig. 3.2-17), the EDX analysis confirmed the presence of the Europium in the paint layer.

BRERA Phthalo Green paint added with the Europium (III) complex (BRPG7PEu)- after 400h of ageing

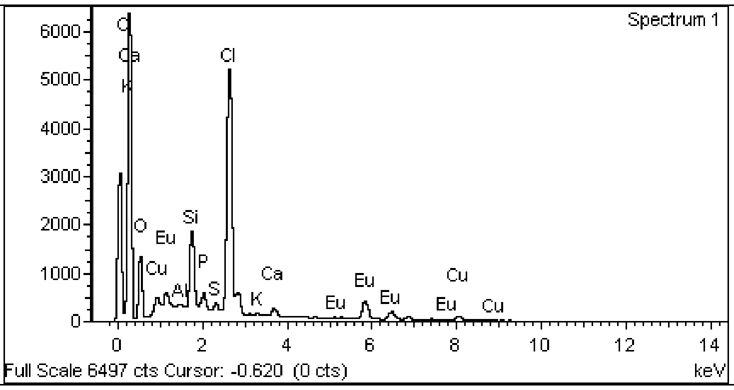
Secondary Electrons Image (5000X)



Back Scattered Electrons Image (5000X)



EDX Spectrum - 5000X - local analysis-



Tab. 3.2-28: The table shows the main results gained studying the surface of the BRPG7PEu retouching paint after 400 hours of UVA-light exposure. Two images, taken using SEI and BSE at the same magnifications (5000X) are presented, together with an EDX spectrum collected for a point.
The EDX analysis confirms the presence of the Europium.

Considering the results coming from both, FTIR spectroscopy and SEM-EDX analysis, it is therefore reasonable to suppose that, the luminescence drop was caused by degradation processes involving the coordination ligands of the complex.

As better explain in Chapter 1 (*1.3.1 Luminescent lanthanide complexes*), only a limited amount of radiation is absorbed by direct excitation in the 4f levels of the Europium (III) ion. On the contrary, much more light can be absorbed by the organic ligands of the complex. The excitation energy is then transfered from the ligands to the Europium (III), causing the strong red luminescence (typical of the lanthanide ion itself).
If the structure of the complex is affected, the so called *antenna effect* played by the ligands is lost and only a weak luminescence is seen.

3.2.2.4 Reversibility issues

A suitable retouching material is expected to present a low potential for damaging the original paint layers during both, application and removal. This means that it should be, and remain, soluble in solvents which do not affect the surrounding original paint layers.

The reversibility of the unaged and differently aged (200 hours and 400 hours of UVA-light exposure) retouching paints, was therefore tested by carrying out some solubility tests. For this purpose, the 30 samples listed in Table 2.2-5 (Chapter 2, section *2.2.2.3 Reversibility issues*) were used.

Each retouching medium was swabbed with the solvent in which it was initially soluble: deionised water for Aquazol 200® resin and the ShelsollD40-ShelsollA mixture for Laropal A81® resin.
In the attempt of removing the artists' emulsion paints, Shellsol D40 was instead used. This solvent was actually expected to partially dissolve the Regalrez 1094® interface layer. Each sample was swabbed for 30 seconds.
The ease of removal and the potential damage caused to the original paint layers were evaluated subjectively, by checking the surface appearance of the cotton swabs.

At first, the response of the reference paint layers to the solvents was tested: they were not affected by Shellsol D40 solvent, their sensitivity to deionised water was actually negligible,[82] while they were slightly affected by the ShellsolD40-ShellsolA mixture.
This means that, Regalrez 1094 ® and Aquazol 200® resins do not show any potential of damaging the original paint layers during the application, the use of LaropalA81® needs instead more care.

The results of the reversibility tests carried out for Aquazol 200® and Laropal A81® formulations are fully listed in the tables 3.2-29 and 3.2-30.
To allow a better comparison of the results, a sort of 'score' system was tentatively used: ++ indicating an optimal result (total removal of the treatment, no significant paint residues on the surface of the mortar); + indicating a positive result which could be further improved by going on with the swabbing (removal of the treatment, some paint residues on the surface of the mortar); + - indicating those cases where the paint layers were actually removed, but leaving irreversible residues; - indicating those cases were the removal was not achieved but low solubility was detected; -- indicating those cases were the removal was not achieved and no solubility was detected.

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[82] These results are consistent with the information reported in the specialized literature as far as the results of cleaning trials carried out on acrylic and vinyl paint layers, already referenced in the introduction.

TESTING the SOLUBILITY of AQUAZOL 200® based paint layers in DEIONIZED WATER						
Sample ID	0h	200h	400h	0h (Eu)	200h (Eu)	400h (Eu)
FLPW6_R1	+	+	+	+	+	+
FLPB29_R1	+	+	+	+	+	+
FLPY42_R1	+	+	+	+	+	+
FLPV19_R1	+ -	+ -	+ -	+ -	+ -	+ -
FLPG7_R1	+ -	+ -	+ -	+ -	+ -	+ -
LQPW6_R1	++	++	++	++	++	++
LQPB29_R1	++	++	++	++	++	++
LQPY42_R1	++	++	++	++	++	++
LQPV19_R1	+ -	+ -	+ -	+ -	+ -	+ -
LQPG7_R1	+ -	+ -	+ -	+ -	+ -	+ -
BRPW6_R1	++	++	++	++	++	++
BRPB29_R1	++	++	++	++	++	++
BRPY42_R1	++	++	++	++	++	++
BRPV19_R1	+	+	+	+	+	+
BRPG7_R1	+ -	+ -	+ -	+ -	+ -	+ -

Tab. 3.2-29: The results of the reversibility tests carried out for unaged and slightly aged Aquazol 200® retouching paints. The formulations containing the Europium (III) complex were tested as well.
++ optimal reversibility, + good reversibility (improvable prolonging the swabbing), + - good reversibility but residues which cannot be removed, - no reversibility but some solubility, - - no reversibility and no solubility

TESTING the SOLUBILITY of LAROPAL A81® based paint layers in SHELLSOL D40-SHELLSOLA						
Sample ID	0h	200h	400h	0h (Eu)	200h (Eu)	400h (Eu)
FLPW6_R2	+	-	- -	+	-	- -
FLPB29_R2	++	-	- -	++	-	- -
FLPY42_R2	++	+	-	++	+	-
FLPV19_R2	+	-	- -	+	-	- -
FLPG7_R2	+-	-	- -	+-	-	- -
LQPW6_R2	++	-	- -	++	-	- -
LQPB29_R2	+	- -	- -	+	- -	- -
LQPY42_R2	++	+	-	++	+	- -
LQPV19_R2	++	- -	- -	++	- -	- -
LQPG7_R2	+-	-	- -	+-	-	- -
BRPW6_R2	+	-	- -	+	-	- -
BRPB29_R2	+	-	- -	+	-	- -
BRPY42_R2	++	+	-	++	+	- -
BRPV19_R2	+	- -	- -	+	- -	- -
BRPG7_R2	+-	-	- -	+-	-	- -

Tab. 3.2-30: The results of the reversibility tests carried out for unaged and slightly aged Laropal A81® retouching paints. The formulations containing the Europium (III) complex were tested as well.
++ optimal reversibility, + good reversibility (improvable prolonging the swabbing), + - good reversibility but residues which cannot be removed, - no reversibility but some solubility, - - no reversibility and no solubility

Aquazol 200® and Laropal A81® showed no or low potential of damaging the original paint layers during application. The unaged retouching paint layers could be actually removed by swabbing their surfaces with the solvents in which they were initially soluble. The removal of the formulations containing the Phthalo Green pigment (PG7) was generally more problematic, since the pigment seemed to irreversibly stain the mortar.

Upon ageing, the paint layers based on Aquazol 200® were still water-soluble.
Those based on Laropal A81® instead, could not be removed using the Shellsol D40-Shellsol A mixture anymore. In most of the cases, this shift in the polarity of the Laropal A81® resin occurred after only 200 hours of ageing.

The inpainting treatments based on the artists' emulsion paints could not be removed by swabbing with Shellsol D40 solvent. In this case, the presence of the Regalrez 1094® interface layer did not allow the reversibility of either unaged or slightly aged inpainted areas. Since the negative results gathered for all the tested areas, it was not of interest to display them in a table.

In none of the cases the presence of the Europium (III) complex affected the solubility properties of the paint layers.

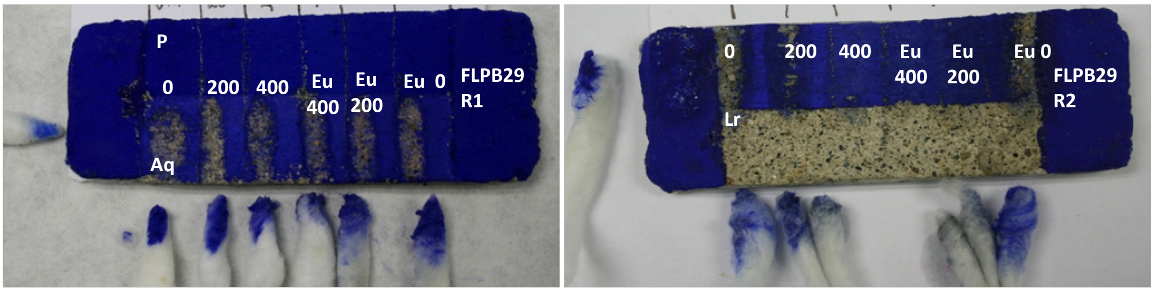

Fig. 3.2-20: The results of the solubility tests carried out to qualitatively evaluate the reversibility of the materials used for inpainting the Ultramarine Blue (PB29) Flashe® samples. The retouching media were: the same Flashe® paint (P); an Aquazol 200® based formulation (Aq); a Laropal A81®based formulation (Lr). The Eu abbreviation is used where the Europium (III) complex was added (2%w/w). The solubility of the materials was assessed after different time of UV-light exposure (0h, 200h, 400h). Pictures refer to tests carried out using deionised water (FLPB29_R1, on the left) and the ShellsolD40-ShellsolA mixture (FLPB29_R2, on the right) respectively.

3.2.3 Discussing Results

The second part of this thesis was undertaken with the aim of exploring the visual, handling and ageing properties of different paints to use for retouching acrylic/vinyl mural paintings.
At first, Aquazol 200® and Laropal A81® synthetic resins were selected as possible media to test.

A suitable retouching paint should satisfy a number of criteria related to its ability to properly match the colour and texture of the area to inpaint, and its use in practice.
As expected when comparing solvent based and water based products, Laropal A81® and Aquazol 200® resins showed different handling properties.
Being characterized by a lower molecular weight, the Laropal A81® resin tended to be absorbed in the support to a greater extent. The handling properties of Aquazol 200® resin were instead closer to those of acrylic emulsion paints and, thanks to a higher viscosity, it was successfully used for creating texture and bodied brushstrokes without adding significant amounts of additives or extenders.
When adding the resins with the same amount of pigments, the paint layers coming from the Aquazol200® formulations were glossier than those coming from the Laropal A81® ones. Thus, attempting to simulate the same texture properties the two media required different pigment loads (lower for Laropal A81®).

Despite these differences, both resins turned out to be quite versatile and to allow satisfactory aesthetic results even when inpainting areas characterized by different textures (ranging from the matt light surfaces of Flashe® paints to the gloss or semi-gloss surfaces of Heavy Body-Liquitex® and Brera-Maimeri® paints).[83]

However, these preliminary practical trials pointed out that, preparing the retouching formulations from pure synthetic resins and powder pigments could be quite problematic.
First of all, it could be difficult to homogeneously disperse the pigments in the binder.
This depends on both, the chemical nature of the components,[84] and the pigment volume concentration. It turned actually out that, the higher was the amount of pigments included in the formulations, the worse was their dispersion in the media. Even if adding a surfactant (as Tween 20®), the quality of the dispersion did not significantly improve, leading to uneven dry paint layers.

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[83] The quality of the result clearly depends on conservator's personal skills. If inadequate matches were achieved during the experimentation, it was mainly due to a lack of operator's experience.

[84] As reported also by Koneczny, 2010. Moreover, as reported in *Appendix 1*, the slightly polar character of Laropal A81® resin should allow excellent pigment wetting (this is one of the reason why it has become the binding media of *Gamblin's retouching colours*). As better explained in Chapter 1 (section *1.2.1.4 Paint additives*), the dispersion of organic pigments (such as Quinacridone Rose -PV19- or the Phthalo Green -PG7-) is more difficult when dealing with aqueous vehicles (e.g. Aquazol 200® resin, dissolved in water).

Moreover, even if carefully paying attention to the relative amount of the components used to formulate the paints, it was very difficult to work in a reproducible way.[85]
For these reasons, the artists' grade emulsion paints were included in the study, and their properties as retouching media were evaluated as well.
If properly used ('modified' formulations), these paints allowed satisfactory aesthetic results, even when treating discolored areas.

But, besides having adequate *visual and handling properties*, a suitable retouching medium should satisfy a number of further technical criteria, related to its *compatibility* with the original materials and its *stability* to exposure weathering conditions.

Being dissolved in solvents which do not substantially affect the original paint layers, the application of Aquazol 200® and Laropal A81® resins does not show any relevant potential damage.[86]

After moderate accelerate ageing (400 hours of UVA-light exposure, λ 340 nm), the quality of the match gained with both resins did not vary significantly (as pointed out by naked-eye and LM examinations and by the low color variations detected through colorimetric measurements). Aquazol 200® and Laropal A81® resins are likely to allow long-term treatments.

Anyway, both resins turned out to undergo some early degradation processes upon ageing.

The Laropal A81® resin was actually prone to photooxidative reactions. Although being consistent with the pieces of information reported in the specialized literature, this degradation process developed quite fast in the weathering conditions used.[87]
This could be due to an active role played both by the mortar support (surface pH about 8) and the pigments in speeding the process. As far as this latter aspect, the retouching formulations containing the Ultramarine Blue (PB29) pigment turned out to be particularly affected by the photooxidative processes.
As the result of photooxidative reactions, the paint layers became harder and more brittle. The development of new species containing polar functional groups (such as hydroxyl, ketones and carboxylic acids) led to a shift in the solubility of the resin which, starting from 200 hours of exposure, could not be dissolved in hydrocarbon solvents anymore. If retouching outdoor mural paintings with Laropal A81® formulations the

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[85] By the usual means of a restoration laboratory, it will be almost impossible to gain the same hue of color for two consecutive times.

[86] Testing the response of the original paint layers to the Shellsol D40-Shellsol A mixture (Laropal A81®solvent), some solubility was detected. The use of the Laropal A81® resins needs more care. It is however to notice that the swabbing time used for carrying out the trials was quite long (30 seconds).

[87] For most of the studied samples, the 2 carbonyl peaks started to merge after only 400 hours of exposure. When exposed to a radiation source simulating daylight through a window glass, unstabilized films of Laropal A81® resins are known to undergo moderate photooxidative processes, starting from 1432 hours of exposure (de la Rie, *et al.*, 2002).

paint layers are expected to undergo cracking and the reversibility of the treatment could be questionable.

The Aquazol 200® resin was likely to undergo concurrent photooxidative and chain-scissions processes. The development of these degradation reactions needs to be further studied. As already pointed out for the Laropal A81® resin, it could be interesting to evaluate the role played by the mortar support and the pigments in affecting the process. Again, the formulations containing the Ultramarine Blue (PB29) pigment were the most affected ones.

The degradation processes detected for the Aquazol 200® resin did not substantially influence the solubility of the paint layers but led to a weakening of their mechanical properties (fine cracks detected through SEM examinations). This medium satisfies the reversibility requirement, but could result in paint layers with scarce long-lasting qualities.

In the context of murals paintings, the original paint surfaces are often matt (high pigment volume concentrations) and the losses could be quite large (need of preparing high amounts of retouching paints or of re-preparing the same formulation more than once).

As already pointed out, to prepare a retouching formulation by adding a pure resin with powder pigments is often inconvenient, very time-consuming and could lead to poor results. For these reasons, the option of using commercial emulsion paints could sometimes be considered. In fact, the similarities between the properties of commercial products and the original acrylic/vinyl paints allow good quality matches, high compatibility and good durability of the treatments (because of the similar ageing response of original and inpainted areas).

However, if turning to commercial paints, the reversibility would be questionable, and further research should be carried out in the attempt of improving this aspect. These preliminary results actually pointed out that, when dealing with acrylic/vinyl emulsion retouching paints, the presence of the Regalrez 1094® interface layer did not allow a satisfactory removal of the inpainted areas.

The *discernibility* between the original and inpainted areas was investigated by carefully comparing the fluorescence of the different surfaces under UV light (λ 365 nm, Wood's lamp).

The better was the match between the inpainted area and the surrounding paint surface, the lower was its discernibility under UV light. The differences in the chemical composition of the original paint binders (slightly aged acrylic, vinyl and styrene-acrylic emulsion resins) and the retouching formulations binders (the same un-aged emulsion resins, a poly(2-ethyl-2-oxazoline) and an urea-aldheyde resin) were probably too slight for resulting in appreciable fluorescence differences.

For this reason a strategy to enhance the difference perceived when comparing original and inpainted areas under UV light, was studied and the Europium (III) complex was added to the inpainting formulations. When exposed to the light of the Wood's lamp, this complex actually shows a strong red luminescence (with the main emission at 612 nm).

Even though all the formulations were added with the same amount of the complex (2% by weight), the color and intensity of the naked-eye discernible luminescence varied considering different paint layers.
In order to optimize the luminescence, higher amounts of the complex should be add to the commercial paints or to those formulations containing pigments that, as the Phthalocyanine Green (PG7), absorb the red light emitted by the complex itself. Lower amount of the complex could be used when working with formulations containing the Quinacridone Red pigment.

Despite the quality of the luminescence, the use of the Europium (III) complex in the conservation field should satisfy a number of further criteria: it should not influence the quality of the inpainting aesthetic results (thus not affecting the color and texture of the paint layers), it should not affect the stability of the retouching materials, it should be finally characterized by high durability to the weathering conditions it will be exposed to.

Generally, the aesthetic properties reached when using the retouching formulations were not affected by the addition of the Europium (III) complex.
No variations in the handling properties of the retouching formulations nor in the morphology of the dry paint layers were induced by the addition of this compound.

Slight color variations were actually perceived only when considering the white formulations, with those containing the complex looking warmer (more yellowish and reddish). When dealing with white paints it is therefore preferable to use lower complex amounts.

The potential role played by the complex in enhancing the degradation processes of the retouching paints should be further explored. In fact, minor differences were sometimes detected when comparing the FTIR spectra collected from the aged pure formulations to those collected from the aged formulations added with the complex (especially when considering those based on the Aquazol 200® resin).
It could be however noticed that the discoloration rates of the formulations added with the luminescent compound were very close to those detected for the pure formulations.[88] Moreover, the complex did not affect the solubility properties of both, unaged and slightly aged paint layers.

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[88] When not so, the differences were likely due to factors not directly related to the presence of the Europium (III) complex (such as an uneven distribution of the pigments in the binding media).

It is therefore reasonable to suppose that, when considering the macroscopic properties of the painted surfaces, the influence of the complex on the stability of the retouching paint is actually negligible.

The main concerns as far as the use the Europium(III) complex to enhance the discernibility of the retouching materials, is related to the stability of the complex itself.
In the majority of the cases, a significant drop in the intensity of the naked-eye discernible luminescence was detected upon a moderate ageing (sometimes after only 100 hours of exposure). Data coming from FTIR spectroscopy and SEM-EDX analysis suggested that UVA-light exposure promoted the degradation of the coordination ligands, thus affecting the *antenna effect* and causing the luminescence decrease.

In order to enhance the stability of the Eu(III) β-diketonate complex it could be possible to embed it in a optically transparent inorganic or organic material (as silica nanoparticles, zeolites, polymers, etc…).[89]

In order to quantitatively evaluate the properties of the complex (and its stability to the ageing), photoluminescence emission (PL) and excitation (PLE) measurements are being carried out on samples cast on canvas supports.[90]

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[89] The properties of lanthanide based organic-inorganic hybrid materials have been deeply reported. If compared to the pure complexes, hybrid materials are actually characterized by superior mechanical properties, better processability, higher thermal stability and luminescence output. Despite the review presented by Binnemans, 2009; the reader is also referred to Sigoli *et al.*, 2001.
Referring to the luminescence properties of lanthanide complexes doped in polymer matrix: Liu *et al.* 2003, Liu *et al.* 2004

[90] Thanks to the collaboration between Ca' Foscari University and C.I.V.E.N. (Dr. Francesco Enrichi).

Chapter 4

CASE STUDIES

4.1 Italian contemporary murals

Over the past 50 years a large number of murals have been created by contemporary artists throughout Italy.[1] Nowadays, more than 200 villages can be considered as a special kind of outdoor public galleries.[2]

This widespread creation of mural paintings followed different pathways. On one hand, murals arose in a totally spontaneous way, complying the artists' wish to create highly message-bearing, democratic works of art expressing social and political commitments. On the other hand, carrying out a mere decorative function, murals were created as public forms of art, aiming community outreach and neighborhood beautification.

In most of the cases, relatively little though was given to the conservation of these works of art at the time of their creation. The artists did not take enough care of the support condition before painting and they often used inadequate materials, not always manufactured for longevity in outdoor conditions.
After few decades exposed to harsh weathering, the paintings start showing clear deterioration marks and, in the worst of the cases, are targets of vandalism.

Fortunately, the murals were sometimes created as part of well organized site specific projects coordinated by local foundations which are also involved in their documentation and maintenance.
This is for instance the case of Dozza (Bologna) where, since 1960, contemporary artists have been painting their murals during an event called *Biennale del Muro Dipinto*.[3]

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[1] In the past years, different studies dealing with contemporary Italian murals were carried out: Baraldi, Della Monica, Pelosi, 2011; Chiantore, *et al.* 2006; Ferriani, Marrel, Rava, 2008; Gurgone *et al.* 2005; Iazurlo, 2010; Zendri, Melchiorre Di Crescenzo, Perusini, 2008.
Some of the murals located in San Sperate (Sardinia), were recently characterized by Pintus *et al.* The result of this study were preliminary reported during the *Modern and contemporary mural painting conference* (Valencia, 4-5 May 2012).

[2] According to a survey carried out by AIPD (*Associazione Italiana Paesi Dipinti*). http://www.paesidipinti.it/home.asp?LK=1

[3] It is interesting to remember that, during the last two editions of the *Biennale* (those taking place in 2007 and 2009), the organizing committee asked famous writers to realize their street-artworks on the walls of Toscanella (a suburb grown in Dozza surroundings). Despite the worthwhile collaboration between our Institution and *Dozza Città d'Arte* Foundation, it is not possible to include in this thesis the results coming from the characterization of the samples taken from Dozza and Toscanella works of art. These results will be presented in future publications.
Further information about Dozza mural paintings is available at: Pasquali (ed), 2008; Naldi (ed), 2010; http://www.fondazionedozza.it/; http://www.murodipinto.it/

Another case is that of Maglione (Turin), base of the M.A.C.A.M. museum. Some of the murals belonging to this museum were studied as part of this thesis and are presented in the following section.

4.1.1 M.A.C.A.M.

In 1985, Maurizio Corgnati founded the M.A.C.A.M. (*Museo d'Arte Contemporanea all' Aperto di Maglione*) an open air museum and non-profit organization intended for encouraging the diffusion and free enjoyment of contemporary art.[4]

Since then, in occasion of the annual *Festa dell' Artista*, new outdoor works of art have been created by Italian and foreign artists (including well-known names, such as Ugo Nespolo, Armando Testa, Giò Pomodoro or Maurizio Cattelan…). According to an inventory dating back to 2007, the streets of Maglione present about 168 works of art encompassing installations, sculptures and above all, mural paintings.

Most of these were created with modern paints and actually suffered for early degradation.[5]

In July 2010, a number of micro-samples were taken from 7 murals belonging to the M.A.C.A.M. museum. The first aim was to chemically characterize the paint layers, thus allowing a proper definition of the painting technique (most of the murals are generally described as *acrylic paintings*).[6] The second purpose was to gain some pieces of information as far as the condition of the murals. Particular attention was directed to those case-studies affected by discoloration, lifting of the paint layers and surface deposits of white materials, possibly related to the exudation of paints water-soluble components.

It is to remember that the characterization of these case studies and the trials carried out on laboratory samples, were developed at the same time. As it will be properly pointed out in the conclusions, the results gathered from the laboratory mock-ups allowed a better understanding of the degradation processes affecting the real murals.

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[4] Recalling Maurizio Corgnati words: *"Ecco il perché di questo museo a Maglione: i bambini di un tempo sono cresciuti in mezzo a immagini piene di mucche, pecore, ruscelli, nani, conigli e fate; i bambini futuri di Maglione avranno occhi pieni di queste immagini che stanno sui muri delle loro case"*. http://www.macam.org; Di Maio Corgnati and Di Vuolo (eds), 2002

[5] In the past years, some of M.A.C.A.M. murals were treated by Antonio Rava whose collaboration was invaluable for a proper development of this part of the thesis. Some conservation case studies were presented in: Rava, 2010.

[6] The results of a previous characterization study concerning the works of art at M.A.C.A.M. in: Chiantore, Ploeger and Rava, 2006.

The experimental approach used for studying the murals is described below, and a selection of the three most representative case studies is briefly discussed.[7]

Prior to sampling, the surfaces of the murals were examined *in situ*, using a USB connected Digital Microscope.[8]

The samples were preliminary examined using a Light Microscope (LM)[9] and divided into representative fragments for further characterization. Some of these fragments were imbedded in a polyester resin in order to allow the investigation of their cross-sections through Light and Scanning Electron Microscopy (SEM)[10] examinations.

The other fragments were studied using a number of complementary analytical techniques. The identification of the binders was carried out through Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FTIR)[11] and Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS)[12] analysis. The composition of the other materials (such as pigments) was assessed through ATR-FTIR spectroscopy and Energy Dispersive X-Ray microanalysis (EDX)[9]. If of interest, the surface morphology of the paint layers was further studied using SEM.

4.1.1.1 *Untitled* (Gianni Asdrubali, 1988)

In 1988 Gianni Asdrubali created this “acrylic” mural (140cmx320cm) in P.zza XX Settembre. Through the years, because of the occurrence of early discoloration processes, the black areas were overpainted by the artists himself.

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[7] Even if not shown here, the results coming from the characterization of a painting by Ruggeri were presented during the AiAr conference, *Science for Contemporary Art* (Ferrara, March 1st-4th 2011): *Ruggeri’s paintings on metal sheets at MACAM (Museo d’Arte Contemporanea di Maglione Canavese)*.

[8] Dino-Lite, AM313*plus* (AMNO Electronics Corporation). The same Microscope was also used for studying the cross-sections and measuring the thickness of the paint layers. These were calculated as an average of 5 measurements.

[9] This preliminary characterization and the subsequent study of the cross-sections were carried out using the Olympus SZ X9 Light Microscope.

[10] The characterization was carried out using the JEOL JSM-5600 LV Scanning Electron Microscope (working conditions described in Chapter 2, section *2.4 Investigation Techniques*).

[11] The analysis were carried out using the Perkin Elmer Spectrum 100 spectrometer (working conditions described in Chapter 2, section *2.4. Investigation Techiniques*).

[12] This part of the study was carried out thanks to the collaboration of Prof. Oscar Chiantore and Dr. Rebecca Ploeger (Department of Chemistry IFM, University of Turin).

The Py-GC/MS analysis were performed with an Agilent Technologies 6890N Network GC system combined with an Agilent 5973 Network Mass Selective Detector, and used along with a CDS Analytical Inc. Pyroprobe 1000 heated filament pyroliser. The capillary column was a HP-5ms (5% diphenyl 95% dimethylpolysiloxane) with 0.25 mm internal diameter, 0.25µm film thickness, and 30m length. The helium gas flow was set at 1 mL/min. Samples were prepared in CDS analytical quartz tubes with quartz wool. The analysis were carried out using a typical program for painting (50°C, 2 min; 10°C/min to 300°C; 300°C, 5 min) with 2 minutes solvent delay. Data were collected with Agilent Technologies’ Enhanced ChemStation software version D.00.00.38 and analysed with MS Data Analysis Version C.03.00 HP software.

As shown in the following figure (B enlarged detail), due to the delamination and partial loss of the most recent layers, the black areas look totally uneven.
This could be considered the perfect example of the potential drawbacks related to the choice of preserving the “fresh” image of a mural through a partial repainting, carried out with a medium characterized by an ageing rate which differs to much from that of the original paint.

The original black paint is affected by heavy discoloration an chalking.
The surface of the mural is moreover affected by lichens, which especially concentrate in the white areas (A enlarged detail).

Fig. 4.1-1: Asdrubali’ s mural as it looks today. A and B: enlarged details documenting the condition of the mural. The red dots mark the sampling points.

The **GA12** sample was taken in order to study the sequence of the original paint layers and to assess the cause of the discoloration of the black paint.

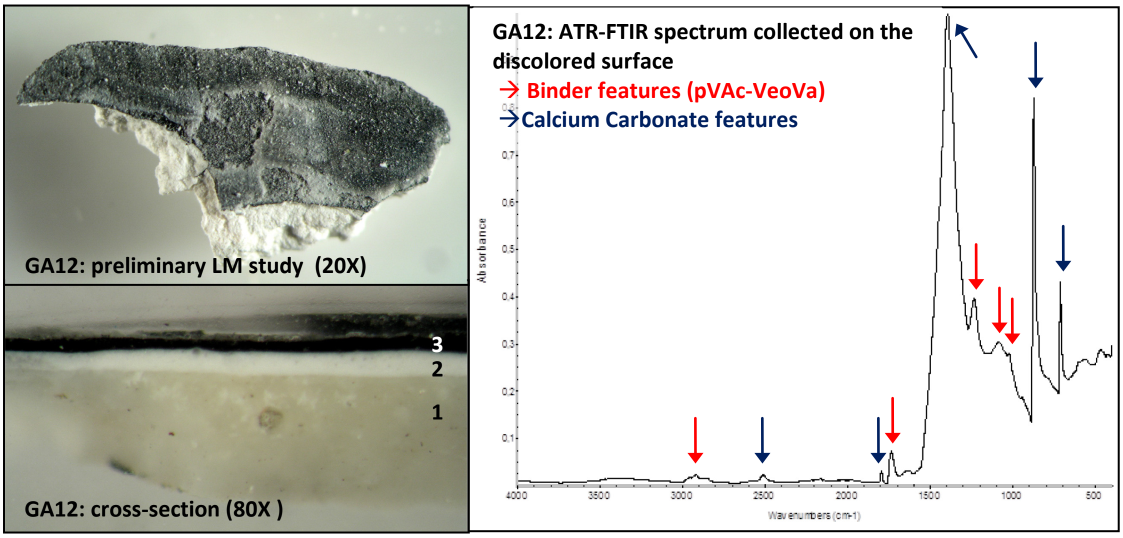


Fig. 4.1-2: A selection of the most relevant results gathered from the characterization of GA12 sample.

The original painting sequence encompasses three layers:

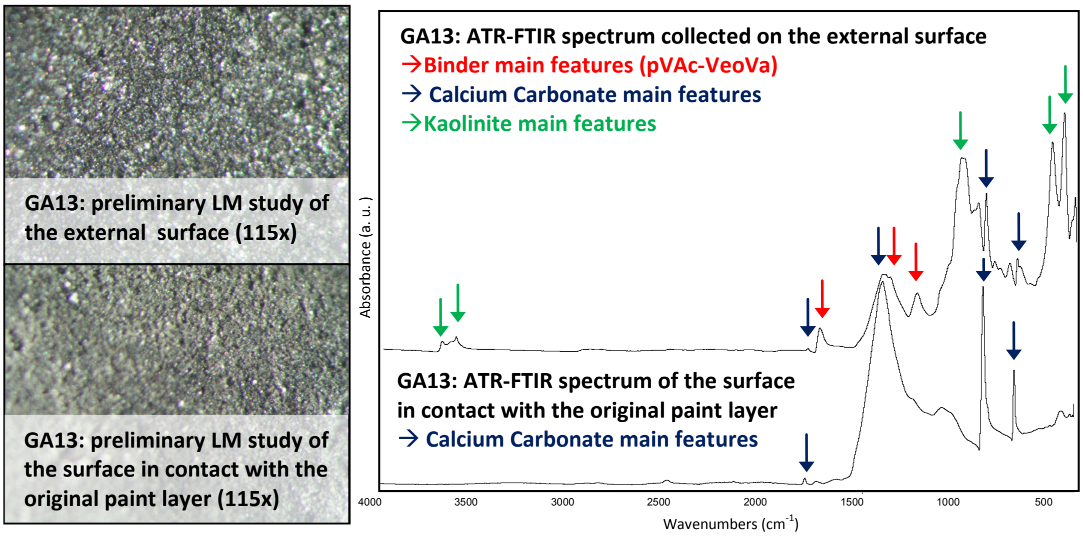
1- a well carbonated lime plaster, characterized by Silicon based sand inerts (quartz and other silicates)

2- a white paint layer (thickness of 77±10 µm), which possibly consists of an **acrylic binder** (p(EA-MMA)), a Titanium White pigment (TiO_2) and a calcium carbonate ($CaCO_3$) extender

3- a black paint layer (thickness of 43±9 µm), which possibly consists of a **vinyl binder** (p(VAc-VeoVa)), a carbon based black pigment and a calcium carbonate ($CaCO_3$) extender.

As clearly pointed out by LM surface examinations, the discoloration of the original black layers is due to the presence of some white material on their surfaces. As suggested by ATR-FTIR spectroscopy analysis and confirmed through SEM-EDX examinations, this material is calcium carbonate ($CaCO_3$). It possibly originates from both, the surface appearance of the paint extender (due to binder degradation) and the carbonation processes of the calcium hydroxide carried by the aqueous solutions which percolate on the paint surface. No evidences of paint water-soluble components (surfactants or other additives) were detected on the surface of the discolored paint layer.

The **GA13** sample was instead taken in order to characterize the black paint used during the overpainting and to assess the causes of its delamination.


GA13: preliminary LM study of the external surface (115x)

GA13: preliminary LM study of the surface in contact with the original paint layer (115x)

GA13: ATR-FTIR spectrum collected on the external surface
→Binder main features (pVAc-VeoVa)
→ Calcium Carbonate main features
→Kaolinite main features

GA13: ATR-FTIR spectrum of the surface in contact with the original paint layer
→ Calcium Carbonate main features

Fig. 4.1-3: A selection of the most relevant results gathered from the characterization of GA13 sample.

The paint used to overpaint the original black areas was possibly based on a **vinyl binder** (p(VAc-VeoVA)), a carbon based black pigment and kaolinite ($Al_2Si_2H_4O_9$) extender.

No traces of paint water-soluble components (surfactants or other additives) were detected at the interfaces of the delaminated paint film. On the contrary, the interface between this film and the original black paint was characterized by calcium carbonate ($CaCO_3$).

The delamination of the most recent paint layers is not due to the phase-separation process of paint water-soluble components but to the poor surface cohesion of the underneath original black paint layer.

4.1.1.2 Untitled (Gian Franco Asveri, 1991)

In 1991, Gian Franco Asveri created this “acrylic” mural (230 X 460 cm), located in Via Borgo d’ Ale.

Fig. 4.1-4: Asveri’ s mural as it looks today. A and B: enlarged details documenting the condition of the mural. The blue dots mark the sampling points.

As clearly shown in the previous figure, the mural was painted on a support affected by structural problems (A enlarged detail). These are possibly due to water infiltrations (e.g. the drainpipe entering the wall) and to rising damp. The cracks affecting the support result in cracks of the paint layers, which lift and flake. Depending on the different areas, lifting ad losses affect the surface paint films (the red and the black ones) or extend to the overall sequence of the layers (from the mortar upwards).[13] As shown in the A enlarged detail the complete sequence consists of a number of layers (encompassing, at least, the red and black paint films and two base layers, one colored white and the other pale blue).

In addition, the paint surface is affected by an uneven bleaching (B enlarged detail), which apparently concentrates in those areas subjected to water surface percolations.

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[13] This mural could be actually considered as a perfect example of a work of art presenting considerable losses which affect well defined monochrome areas. It requires consolidation, filling in and inpaintig treatments.

Even though it was not possible to properly assess the condition of the structural support, a number of samples were taken to investigate the overall sequence of the surface plaster/ paint layers:

- the **GFA3** sample came from a red area not affected by paint layers delaminations. It was taken with the purpose of characterizing the original materials and to study the sequence of the layers (from the pale blue one upwards)
- the **GFA4** and **GFA5** samples were taken with the purpose of characterizing the white layer underneath the pale blue one
- the **GFA6** samples was taken from a lifting bleached black area, with the purpose of studying the original materials and to assess the causes of paint layer delamination and bleaching
- the **GFA7** sample was taken from a lifting bleached red area, with the purpose of assessing the causes of paint layer delamination and bleaching

A selection of the most significant results is presented and briefly discussed together with the data coming from all the analyzed samples.

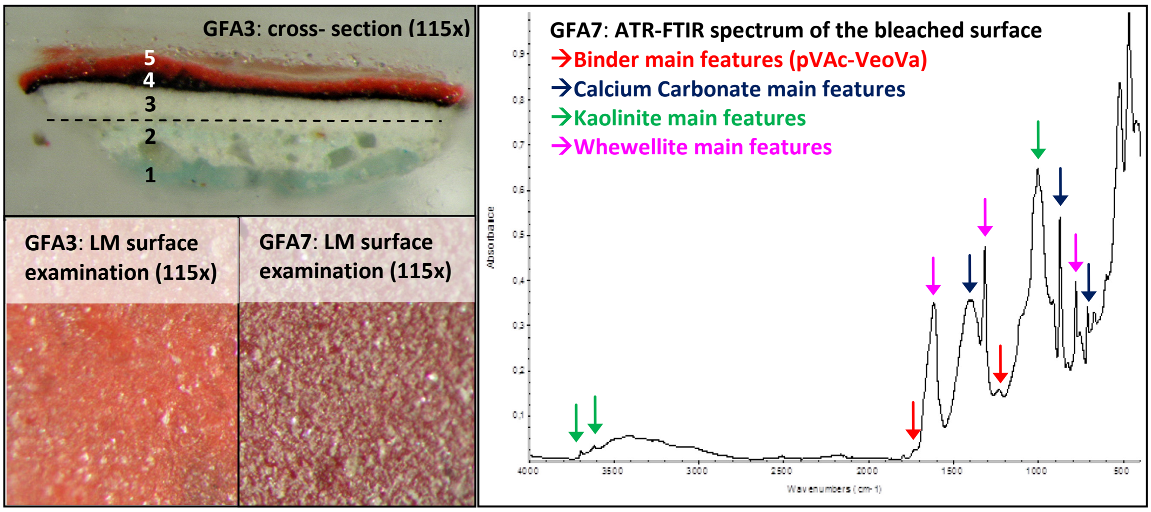

Fig. 4.1-5: A selection of the most relevant results gathered from the characterization of GFA3 and GFA7samples.

The overall sequence of the plaster/paint layers consist of:

- a mortar substrate (not better investigated)
- a thinner layer of a well carbonated lime plaster, characterized by Silicon based sand inerts and traces of gypsum ($CaSO_4 \cdot 2H_2O$), which is possibly due to soluble salt crystallization phenomena (GFA4 and GF5 samples from the white layer)
- a pale blue exterior house paint, characterized by a high content of inorganic components (layer 1 in the GFA3 cross-section). Among these there are some Silicon based compounds (possibly a SiO_2 extender), calcium carbonate and magnesium

carbonate extenders ($CaCO_3$ and $MgCO_3$ respectively). It was not possible to properly identify the nature of the blue pigment nor that of the paint binder, whose amounts is quite low (the cohesion of the layer is actually very poor)

- a white exterior house paint, characterized by a high content of inorganic components (layer 2 in the GFA3 cross-section, 74±9 µm thick). Among these there are Titanium Dioxide (TiO_2), calcium carbonate ($CaCO_3$) and a considerable amount of a Silicon based extender (possibly a large particle sized silica, SiO_2). It was not possible to properly identify the binder of this layer, which is characterized by poor cohesion. Notwithstanding the fact that most of the delaminations occur at this level, no traces of water-soluble compounds were detected at the interface between this layer and the next one
- a white paint (layer 3 in the GFA3 cross-section, 67±16 µm thick) consisting of a **vinyl binder** (p(VAc-VeoVa)), a Titanium Dioxide pigment (TiO_2), calcium carbonate ($CaCO_3$) and a Silicon based extender (possibly kaolinite, $Al_2Si_2H_4O_9$)
- a black paint (layer 4 in the GFA3 cross-section, 30±9 µm thick) consisting of a **vinyl binder** (p(VAc-VeoVa)), an Iron based pigment (likely magnetite, Fe_3O_4), calcium carbonate ($CaCO_3$) and one or more Silicon based extenders (such as kaolinite, $Al_2Si_2H_4O_9$ and silica, SiO_2). The same composition was assessed for the black paint of the GFA6 sample
- a red paint (layer 5 in the GFA3 cross-section, 36±10 µm thick) consisting of a **vinyl binder** (p(VAc-VeoVa)), calcium carbonate ($CaCO_3$) one or more Silicon based extenders (such as kaolinite, $Al_2Si_2H_4O_9$ and silica, SiO_2) and a red pigment. Even though traces of Iron were detected through SEM-EDX analysis, the interpretation of the red pigment as hematite (Fe_2O_3) is uncertain.

On the base of these results it seems possible to relate the lifting phenomenon to the presence of the numerous paint films, which overlay each other and lead to a total thickness of about 210 µm. The presence of this multilayer system could reduce the water vapor permeability of the support (which is affected by water infiltration), thus promoting delaminations. These mainly occur where the adhesion between the layers is lower (e.g. between the poorly bound house paint and the subsequent stronger and more elastic white layer).

As shown in figure 4.1-5, the surface bleaching of the red paint is not due to the exudation of paint water-soluble components (such as surfactants). As suggested by the ATR-FTIR spectral features falling at about 1620 cm^{-1}, 1315 cm^{-1} and 780 cm^{-1}, this white material could be tentatively identified as whewellite ($Ca(C_2O_4)\cdot H_2O$, with the three absorptions ascribable to ν_{as} CO_2, ν_s CO_2 and δ O-C-O).[14] Similar results were gathered from the surface of the GFA6 black sample.

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[14] Cariati, *et al.*, 2000

The formation of the calcium oxalate should be thoroughly investigated: it could originate from biogenic processes or from the oxidative degradation of the organic binder in presence of the calcium carbonate extender.[15]

4.1.1.3 *Natura Morta* (Flavio De Marco, 2001)

In 2001, Flavio De Marco painted this "acrylic" mural (200 X 400 cm) in Via Cossano.
After 9 years from its creation, the general condition of the mural is fairly good.
The surface is however characterized by an uneven bleaching, related to the surface presence of a translucent material, which locally forms quite thick layers.
Three samples were taken with the purpose of characterizing the original materials (the FD9 was taken from a brown area and the FD11 from a green one) and to assess the causes of the bleaching (the FD9 and FD10 samples).

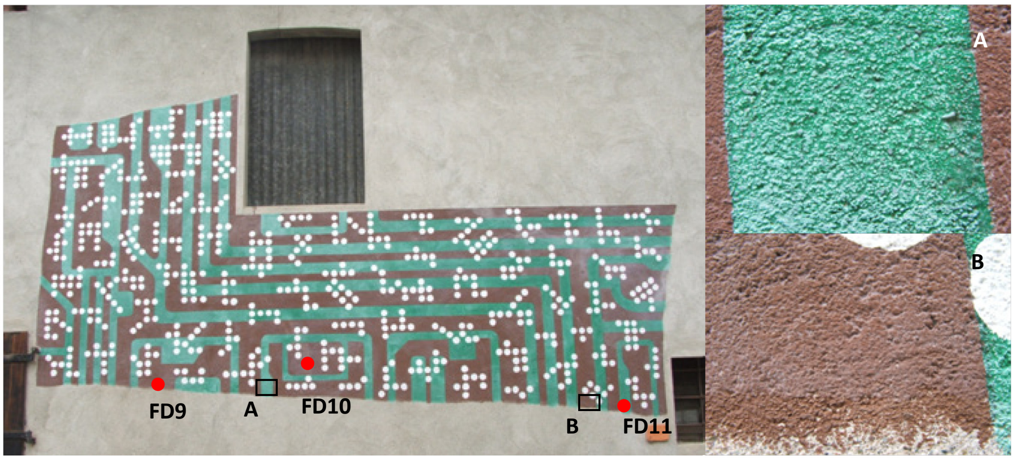

Fig. 4.1-6: De Marco' s mural as it looks today. A and B: enlarged details documenting the condition of the mural. The red dots mark the sampling points.

The analysis pointed out that the brown paint consist of a **vinyl binder** (p(VAc-VeoVa)), calcium carbonate ($CaCO_3$) and kaolinite ($Al_2Si_2H_4O_9$) extenders. Even though the exact nature of the brown pigment is still uncertain, the analysis suggested the presence of an Umber (a pigment coming from the combination of manganese and iron oxide with silicious material). The green paint is instead based on a **vinyl binder** (p(VAc-VeoVa)), a chlorinated phthalocyanine pigment (possibly PG7), calcium carbonate ($CaCO_3$), kaolinite ($Al_2Si_2H_4O_9$) and gypsum ($CaSO_4 \cdot 2H_2O$).

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[15] The origin of calcium oxalates (both whewellite and weddellite) films on stone surfaces has been widely discussed: Cariati, *et. al.*2000; Rampazzi, et al., 2004; Realini and Toniolo (eds.) 1996

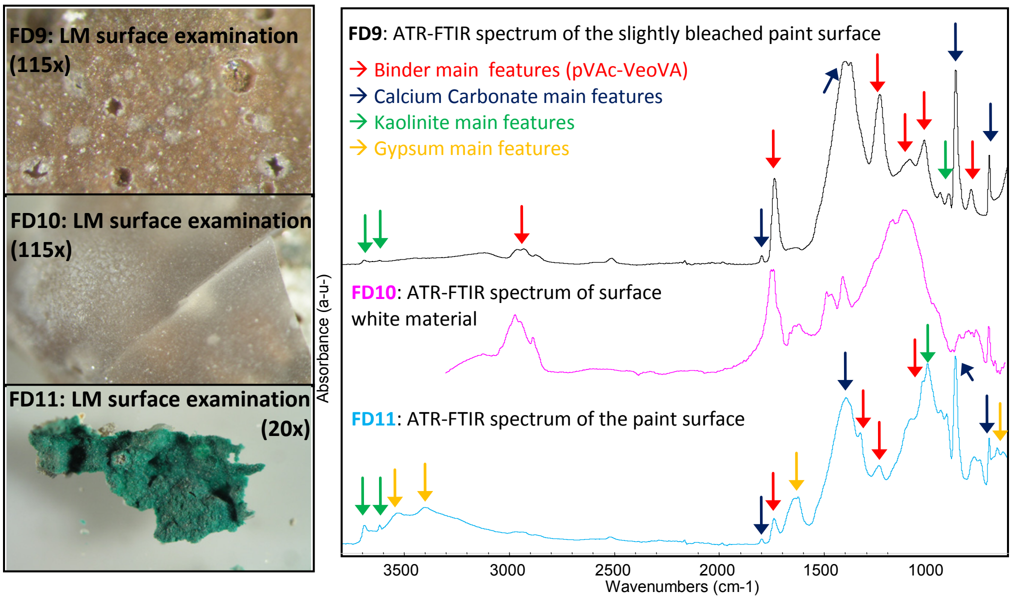

Fig. 4.1-7: A selection of the most relevant results gathered from the characterization of the FD9, FD10 and FD11 samples.

One of the causes of the bleaching is the surface appearance of the white extenders, due to the degradation of the paint binder.

The thick translucent material which partially covers the paint surface (sample FD10 and, to a less extent, sample FD9) seems instead to be due to the uneven application of a transparent coating, tentatively identified as a styrene-acrylic product added with silica.

The Py-GC/MS analysis of this sample possibly revealed a mixture of p(EA-MMA) and p(*n*BA-MMA), together with some styrene moieties. The identification of this material as a styrene-acrylic co-polymer was moreover suggested by some typical features of the ATR-FTIR spectrum (among which the aromatic C-H stretching at 3060 and 3024 cm^{-1}, the aromatic C-H out of plane bending at 763 and 702 cm^{-1}).

The presence of Silica was instead suggested by the ATR-FTIR intense band centered at about 1070 cm^{-1} and the detection of Silicon through SEM-EDX analysis.

Chapter 5

CONCLUSIONS and PRACTICAL IMPLICATIONS

5.1. Study of emulsion paints' stability

The first part of this research was developed with the purpose of exploring the degradation processes affecting contemporary murals.
These processes are actually influenced by three main features:

- the chemical composition of the paint layers
- the properties of the mural supports
- exposure conditions (potentially encompassing: water infiltrations, rising damp, significant temperature variations, surface moisture, direct exposure to heavy rain and sunlight).

Considering the media which are commonly used to create the murals, different emulsion paints were included in the study. The materials' selection encompassed 3 binders (an acrylic, a vinyl and a styrene-acrylic polymers) and 5 pigments (Titanium White -PW6-, Ultramarine Blue -PB29-, Mars Yellow -PY42-, Quinacridone Red -PV19- and Phthalocyanine Green -PG7-).

It has been deeply pointed out that emulsion paints are complex chemical systems, consisting of a number of additives (among which surfactants), included during the manufacture of the base polymer latex binders and the subsequent formulation of the paints. The majority of these compounds remain in the dry paint films and, even if present in low amounts (less than the 10%/v of the overall composition), they possibly affect the properties, stability and response of the paint layers to the conservation treatments (e.g. cleaning).
In the attempt of exploring these aspects, a number of studies have been recently carried out on both, laboratory free-film samples (cast on Mylar® supports or glass plates) and canvas paintings. It was proved that, in certain conditions, the non-ionic polyethoxylate type surfactants tend to spontaneously desorb from the bulk film and to accumulate on the surfaces of the works of art. To the best of our knowledge, poor attention was instead directed to the fate of these additives in the context of mural paintings.
For this reason, one of the aims of this research was to properly explore the phase-separation and leaching processes of emulsion paints' water-soluble components, affecting mural works of art.

After 18 weeks from the casting, no evidences of paints' water-soluble components were detected on the surface of the mural mock-ups stored under laboratory conditions

(T 20±2°C, R.H. 50±5%). It is therefore reasonable to suppose that, indoor murals are not affected by early phase-separation phenomena of surfactants or other additives. Potential differences regarding the spontaneous exudation processes may however occur considering periods of time longer than 4 months.

The rising damp trials proved that the phase-separation process is instead promoted by water, which absorbs into the support and wets relatively young (3 weeks) paint layers.
As fully discussed in Chapter 3 (section 3.1.2.3), different results were gathered for samples cast with different paints, with the Heavy Body-Liquitex® ones (acrylic binder, APE surfactant) being the most prone to the exudation process. This could be due to a number of factors: brand dependency reasons (e.g. the amount of surfactant characterizing a specific formulation); interaction between the paint components (polymer binder and surfactants); coalescence degree of the paint films; paint layers' responses to water.

Within real murals, rising damp water, moisture and rain could wet the paint layers, leading to an early exudation of their water soluble components. However, it is reasonable to suppose that, after being exuded, these components will rapidly disappear when exposed to outdoor weathering conditions (because of the leaching effect of heavy rains and photooxidative degradation processes due to UV-light exposure).[1]
This is probably the reason why no evidences of surfactants were detected on the bleached surfaces of the M.A.C.A.M.'s murals.
As confirmed by the results from both, the laboratory mock-ups and the samples taken from real case-studies, the bleaching of mural paintings could be due to a number of degradation mechanisms. For example, since the mortar support is often characterized by water soluble components, infiltrations and rising damp could become the vehicle of soluble salts and lead to surface salt crystallization (and carbonation).
For one of the case-studies (the mural created by Asveri in 1991, consisting of a vinyl paint characterized by a calcium carbonate extender), the bleaching was possibly due to the surface formation of calcium oxalates (mainly whewellite ($Ca(C_2O_4)\cdot H_2O$).

In addition, no evidences of paints water-soluble components were detected at the film-support interface. It was instead confirmed that the delaminations of the paint layers are due to the sub-superficial crystallization of water soluble salts (e.g. gypsum $CaSO_4\cdot 2H_2O$) or to the poor cohesion of the base paint layers.

Finally, the results collected studying laboratory mock-ups and real case-studies consistently suggested that the decay processes of contemporary murals are strongly influenced by the features of the support.

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[1] Scalarone, *et al.*, 2007; Ormsby, Kampakasali, *et al.*, 2009.

The selected paints were also confirmed to be quite stable to UV-light ageing conditions. After 800h of UVA-light (λ340 nm) exposure, the polymer binders were affected by minor photooxidative degradation processes.

The degradation of the binders caused some morphological variations, which concurred to the discoloration of the paint layers.

As confirmed by the data collected from both, laboratory mock-ups and samples taken from real case-studies, the discoloration is due to:

- a thinning of the polymer binding layer, leading to an increment of the roughness of the paint surfaces, which thus tend to scatter light to a greater extent (this is especially true for those paints characterized by high Pigment Volume Concentrations or by large sized pigments)
- a higher level of polymer binder degradation, which leads to the direct exposure of the white extenders (such as calcium carbonate).

No clear evidences of pigments degradation were detected, not even for the organic pigments (expected to be slightly less lightfast) or for the Ultramarine Blue one, which is expected to fade when used in mural painting (due to the alkaline character of the support).[2]

In addition, regardless of the binder typology, the degradation of the polymer was slightly more pronounced for those paints consisting of inorganic pigments, especially the Ultramarine Blue one (PB29).[3]

Besides allowing a better understanding of the degradation processes which affect mural paintings, the information coming from this first part of the experimentation led to the definition of a sort of *Best practice for mural creation*.[4]

This is a list of suggestions that contemporary artists could decide to follow in order to create long-lasting murals.[5]

These suggestions are:

- since the degradation processes are strongly influenced by the features of the support it is very important to properly assess the condition of the wall before painting (e.g. removing all the previous paint layers and avoiding those walls

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[2] This topic has been extensively studied. The reader is for example referred to: Del Federico, *et al*., 2006

[3] Similar results were detected when testing the UV-light stability of the retouching paints containing the Ultramarine Blue pigment. It could be interesting to go into the potential role played by this pigment (and /or its impurities) in promoting the photooxidative degradation of different synthetic binders.
The experimentation should be carried out on free-films, thus leaving out the potential effect of the alkaline substrate on the stability of the pigment itself.

[4] This information is consistent with that reported in the *Mural Best Practice* resulting form the *Rescue Public Murals Project* (already referenced in Chapter 1, section *1.1 Theory and practice in the conservation of contemporary murals*).

[5] Notwithstanding the soundness of these suggestions it is to remember that the *life* of an outdoor mural is destined to be definitely shorter than the life of indoor works of art.

affected by structural problems, a poor cohesion of the plasters, rising damp, infiltrations, crystallization of soluble salts)

- water plays an active role in promoting different degradation processes (among which the phase separation of paints' water soluble components). It is thus very important to prevent water from wetting the paint layers. The best preventive conservation strategies are: the correct choice of the wall (considering rising damp, infiltrations, direct exposure to heavy rain…); a correct choice of the day/hour of the day for creating the mural (it is important to work on dry walls and on walls which are not too cold); the application of a protective coating
- it is important to prevent the direct exposure to sunlight (by choosing walls not facing south and applying a protective coating)
- it is preferable to avoid those paints characterized by high pigment volume concentrations (and so by considerable amounts of extenders, as in the case of many cheap products formulated for household or industrial purposes)
- the use of paints consisting of the Ultramarine Blue pigment (PB29) is to avoid, especially when creating outdoor murals
- it is preferable to use lightfast pigment and to limit the use of the Titanium Dioxide White [6]
- it is preferable to use paints consisting of acrylic binders. Even if the styrene-acrylic paints could be efficiently used to enhance the hydrophobic character of the paint layers, they are expected to undergo harsher photooxidative processes when exposed to UV-light for prolonged periods of time

Finally, the experimentation confirmed the suitability of two portable analytical techniques for assessing (and monitoring) the condition of the murals *in situ*, according to a non-invasive approach.

Allowing the characterization of the paint surfaces, Near-Mid FTIR reflection spectroscopy is very useful to identify those murals which need a treatment (because showing the objective signs of an *unacceptable*[7] degradation) and to properly plan the maintenance of the murals (e.g. detecting the moment when a protective coating should be re-applied on the surface of the mural).

MIR active thermography was instead confirmed to be a powerful technique to detect paint layer delaminations (down to a sub-millimetric scale) and to assess the quality of the adhesion of the paint layers to the support after the consolidation treatments.

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[6] Even though, according to our results, this pigment did not influence the degradation processes of the binders in a relevant way, Titanium Dioxide has been has been often reported to be a photo-catalyst. (Ferreira, Melo and Ramos, 2010; *Rescue Public Mural Project*).

[7] The meaning of this adjective needs to be defined considering some measurable parameters.

5.2. Evaluation of innovative conservation treatments

The second part of the research was developed with the purpose of evaluating the properties of different retouching media which could be used for inpainting contemporary murals.

A suitable retouching paint should satisfy a number of visual/ aesthetic criteria (the ability to match the colour and texture of the original areas), as well as technical criteria (such as the compatibility with original materials, stability, reversibility and adequate handling properties).

A number of retouching paints were formulated in the attempt of inpainting murals based on acrylic, vinyl or styrene-acrylic emulsion paints.
Two synthetic polymers were selected as potential binders of these formulations: a poly(2-ethyl-2-oxazoline) resin, soluble in water (Aquazol 200®) and an urea-aldehyde resin, soluble in hydrocarbon solvents with a low content of aromatics (Laropal A81®).

If added with proper amounts of powder pigments, both resins led to a satisfactory color and texture match between treated and original areas (cast using different emulsion paints).
Even if the quality of the match did not significantly change after 400 hours of UVA-light exposure, both resins were affected by some early degradation processes.
Due to photooxidative reactions, the paint layers based on Laropal A81® resin became harder, more brittle and could not be dissolved in hydrocarbon solvents anymore. This polarity shift of the binder reduces the possibility of removing the treatments without affecting the original paint layers.
Aquazol 200® resin underwent concurrent photooxidative and chain-scissions processes, which did not affect the solubility of the paint layers but led to a weakening of their mechanical properties. This medium satisfies the reversibility requirement, but it is expected to result in paint layers with no durable qualities.

Even though the stability of these resins could be improved by adding a Hindered Amine Light Stabilizer (HALS) or a Ultraviolet Light Stabilizer (UVLS), both binders are unlikely to withstand outdoor weathering conditions (especially if considering Aquazol200® water-soluble and hygroscopic character).
For these reasons, nor Laropal A81® nor Aquazol200® resins satisfy all the required criteria for a medium to use for inpainting contemporary murals.

Further experimentation should be carried out, including different retouching media.

In addition, as fully discussed in Chapter 3 (section *3.2.3 Discussing results*), formulating a retouching paint by adding a pure resin with powder pigments could be quite problematic and time-consuming (especially when dealing with large losses affecting matt paint layers). For this reason, the option of inpainting the murals using commercial emulsion paints could be taken into consideration (due to high compatibility, good durability and the possibility to properly match the original paint layers, even if discolored). Nevertheless, if turning to commercial paints the reversibility would be questionable.

The presence of a resin interlayer between the mortar and the retouching paint layers may improve the reversibility of the inpainting treatments.
It was proved that, a better reversibility is achieved if using of a low molecular weight hydrocarbon resin, as the Regalrez 1094® one. Due to a slight consolidation effect, this resin does not significantly change the wettability of the mortar (it is possible to easily brush the paints on the 'treated' surface) but reduces the surface porosity of the mortar itself, thus limiting the absorption of the retouching paints into the support.
The possibility of removing a treatment without affecting the original paint layers also depends on the solubility of the binders: the presence of the Regalrez 1094® interlayer does not allow a safe removal of the inpaintings based on acrylic/vinyl/styrene-acrylic emulsion paints.

Since it is very difficult to find a medium having all the desired qualities to retouch contemporary murals, a compromise could be needed: if a medium satisfies the majority of the desired criteria, it will be worth considering even if not allowing a safe reversibility. In these cases different goals may be achieved, such as that of improving the *discernibility* of the inpainting treatments.

In order to enhance the differences perceived when comparing the original and treated areas under UV light, a molecular lanthanide compound (an Eu(III) β-diketonate complex) was added to the retouching formulations.
It was proved that, when exposed to the light emitted by a Wood's lamp (main λ 365 nm) the paint layers containing the complex are discernible, thanks to the typical red luminescence emitted by the complex itself (main λ 612 nm).
Even if adding the paints with the same amount of the complex (2% by weight), the quality of the luminescence was slightly different, depending on the binder and, above all, the pigments characterizing each paint. Since the complex occurs as a pigment, it is possible to easily vary its amount in the formulations, thus achieving the desired luminescence quality.

Despite the quality of the luminescence, the use of the Europium(III) complex in the conservation field, should satisfy a number of further criteria: it should not affect the color and texture of the paint layers, nor the stability of the retouching materials, and it should be stable to the conditions it will be exposed to.

The results of this preliminary research suggested that :

- the Europium(III) complex does not significantly influence the color and morphological properties of the paint layers
- the influence of the Europium(III) complex on the stability of the paint layers is negligible

- upon exposure to UVA-light, the complex undergoes some degradation processes (affecting the coordination ligands), which lead to a significant drop of the naked-eye discernible luminescence.

The research could be further developed testing the properties of an organic-inorganic hybrid material of the same Europium(III) β-diketonate complex or testing complexes characterized by different ligands (such as pyridine-2,6-dicarboxylate; 2-hydroxyisophthalamides, cyclen derivatives, 8-hydroxyquinolinates, scorpionates).[8] Since some of these complexes have been developed for quantum yield enhancement of solar cells, they are expected to show high stability to UV-light exposure.

Finally, inpainting contemporary works of art (among which murals) is still an open issue. The use of lanthanide complexes which absorb the UV-light of a Wood's lamp and emit a characteristic radiation in the Vis range, is a promising system to achieve *discernibility*.
If further experimentation points out that these complexes are too unstable for being used in the context of mural paintings, their use for the treatment of other works of art (such as canvas paintings) will be worth considering.

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[8] Bortoluzzi *et al.* 2011.

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APPENDIX 1

- Materials Information -

MALTA BASTARDA (GrasCalce)- CEMENT-LIME MORTAR

Malta Bastarda is a factory blend of cement, lime and siliceous sand (0/2).

USES: interior and exterior applications; laying or resetting brick, block and stone for all masonry veneer work (M5 class, UNI EN 998-1, UNI EN 998-2)

MIXING: 3 L of clean water per each bag (25Kg), mixing for not longer than 3 minutes

TESTS for FRESH MORTAR (T=20±2°C, R.H.= 60 ± 5%):
- consistence of fresh mortar (by flow table) (UNI EN 1015-3): 174 mm
- apparent specific weight (UNI EN 1015-6): 1980 kg/m^3
- air content of fresh mortar (UNI EN 1015-7): 11%
- workable life and stiffening (UNI EN 1015-9): 270 min
- chloride content (UNI EN 1015-17): 0,004%

TESTS for HARDENED MORTAR (T=20±2°C, R.H.= 60 ± 5%):
- dry bulk density (UNI EN 1015-10): 1800 kg/m^3
- flexural and compressive strength (28 days) (UNI EN 1015-11): 11 N/mm^2
- adhesive strength on substrates (UNI EN 1015-12): 0.34 N/mm^2
- water absorption coefficient due to capillary action (UNI EN 1015-18): 0.66 kg/$m^2$$min^{0.5}$
- water vapour permeability (UNI EN 1015-19): μ 14
- thermal conductivity (EN 1745 –tolerable value): λ= 0.93 W/mK
- reaction to fire tests (EN 13501-1 table value): class A1

Dangerous materials: no asbestos, water-soluble chrome VI ppm <2

Temperature of use:5-35°C

Two different 25Kg bags were purchased, respectively in June 2009 and March 2010, in Venice, Italy.

REGALREZ 1094® [1]

Regalrez 1094® is a low molecular weight (LMW) hydrogenated hydrocarbon resin.
It was originally formulated by industry (formerly manufactured by Hercules Corporation, and then by Eastman Chemicals) as a component of coatings, adhesives, sealants and caulks.
It is produced by polymerization and hydrogenation of pure monomer hydrocarbon feed stocks (such as vinyl toluene and α-methyl-styrene) to form oligomers.
By industrial standards, Regalrez 1094® is the highest quality for hydrocarbon resins in terms of stability (being indeed fully hydrogenated) and its application is suggested where the lowest color and the most stability against weathering and thermal degradation is required.

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[1] The following pieces of information come from the Technical Data Sheets (Eastman Chemical and C.T.S. srl) and from: Blackman, 2007; Borgioli and Cremonesi, 2005: 150-157; de la Rie and McGlinchey, 1990; Whitten, 1995. Further literature is referenced in these texts.
The resin was purchased from C.T.S. srl (Spain), in May 2011.

Its introduction among conservation materials came as a result of a research into stable synthetic resins that could duplicate the optical and aesthetic properties of natural resins.

PROPERTIES, STABILITY and APPLICATION

Molecular Weight (M_w= average mass): about 900 a.m.u.

Glass Transition Temperature (Tg): 40°C (product's MSDS), 33°C (Borgioli and Cremonesi, 2005)

Crystallization Temperature: 33°C (Blackman, 2007)

Softening range: 90÷ 98 °C

Refractive index: 1.519

Density at 21°C: approx. 0.99 g/cm^3

Compatibility: polyethylene, polypropylene, natural rubber, EPDM, butyl rubber, ethylene-propylene copolymers, styrene-isoprene- styrene (SIS) block copolymers, styrene-ethylene-propylene copolymers (SEP) and styrene-ethylene-butylene-styrene (SEBS) block copolymers.

Solubility: according to the MSDS, Regalrez 1094® is soluble in aliphatic and aromatic solvents, C5 and higher esters and ketones (e.g. butyl-acetate and amyl-acetate). It is insoluble in glycol ethers, glycol ether esters, and alcohols. For low/zero volatile organic content (VOC) systems it is soluble in t-butyl acetate (TBA) and perchlorobenzenetetrafluoride (PCBTF) and will tolerate some acetone and/or methyl acetate as a diluent in solvent systems based on TBA and/or PCBTF. As far as the use of the resin in the conservation field, non polar solvents like petroleum distillate (boiling 140-160°C), White Spirit D40 or other Mineral Spirits with low aromatics content (<18%) are suggested. It turned out to be soluble in solvents that evaporate quickly enough to manipulate the surface as you could with a natural resin (e.g. Sol340HT and MS146 HT, evaporation time about 1700-2050 seconds). In order to achieve matter results, Ligroin (boiling 80-120°C) could be used.

Relating properties and practice

Usually, synthetic polymer varnishes tend to sit very much on the surface because of their complex molecular structure and, when applied over textured surfaces, they conform to microscopically roughness, thus scattering light and reducing the saturation.

Compared to other synthetic polymers, low molecular weight resins result in lower viscosity solutions (even when considering high concentrations), that allow better application over the paint surface.

Saturation properties and refractive index of Regalrez 1094® resin are very similar to those of natural resins (dammar or mastic) and, for this reason, it has been extensively tested (and used) as a picture varnish.

Even if hydrogenated hydrocarbon resins are slightly more glossy and brittle than their natural counterpart, their flexibility and working properties (viscosity and flow properties) can be modified by adding various rubbers, such as those of the Kraton G series (Shell Chemical). Tests revealed that 1.5-3% concentrations by weight of these rubbers are enough to modify the working properties of the resin substantially. These rubbers (e.g. Kraton G 1650, Kraton G 1657) are typically SEBS co-polymers and, having a saturated elastomer midblock, are expected to show an excellent resistance to degradation. They actually proved stable when age tested but, to achieve the maximum stability, it is recommended to incorporate in the mixture a hindered amine light stabilizer additive (HALS) like Tinuvin 292 (Ciba Geigy), that acts as free radical scavenger (concentration of 2% are suggested).

Regalrez 1094® resin showed an excellent compatibility with paraffin and micro-crystalline waxes also, thus wax could be add to reduce surface shine.

Even if some industrial varnish formulations are now available (Regal Varnish Gloss and Matt, with polymer concentration of 25% w/v), it could be preferable to use custom-made varnishes.

In this case, it is important to discard varnish mixtures after three weeks, because resins degrade faster in solution than they do in a dried film.

Being the Glass Transition Temperature quite high, the resin is not prone to pick-up dust and dirt.

Thanks to the non polar nature of the resin, the application solvent does not affect the painting in the evaporation process. Downside, remaining soluble in the same original solvent, only the first application may be done with a brush, other layers need to be applied by spraying.

Stability

As already said, Regalrez 1094® resin shows similar qualities to natural varnishes but better stability. Tests carried out after 7 years of natural ageing, showed that the solubility of Regalrez 1094® does not significantly change with ageing, allowing good reversibility.
Actually, when ageing the resin in a solar box (and so including the UV component of light, $\lambda > 295$ nm), a certain increment in the molecular weight (maybe related to cross-linking) and the formation of some oxidation products were detected. By adding Tinuvin 292, the stability of the resin definitely improves.

Application

Regalrez 1094® resin has been extensively tested and used as a varnish (over oil, acrylic and varnished paintings). It showed to be especially suitable for resaturating synthetic and natural resins that had become dull. Because of its low viscosity, some problems can arise when applying over porous surfaces. However, it is possible to apply Regalrez 1094® varnishes on top of other varnishes with a distinctive polarity (Laropal A81®, stabilized dammar, Paraloid B-72), thus isolating different layers and facilitating future removal (one should be able to apply Regalrez 1094® over Laropal A81® using Shellsol 340HT, odorless thinners, heptanes, or hexane).
Solutions for spray and brush application are typically prepared by mixing 25-30 g of resin in 100 ml of solvent (10-15 g for solutions to apply over primary varnishes; 35-40g may lead to matte surfaces).
It has also been tested as retouching medium (30% or 20%w/v in Shellsol D40).[2]

LAROPAL A81® [3]

Laropal A81® is one of the low molecular weight resin coming from the condensation of urea and aliphatic aldehydes (isobutyealdehyde and formaldehyde), manufactured by BASF.[4]
Industrially, these resins are used as paint additives to improve properties such as hardness, gloss and resistance to yellowing. Moreover, thanks to their low viscosity, they are often used to reduce the VOC of coatings.
The use of LaropalA81® resin for conservation purposes came from a discussion about new materials for retouching, began in 1993 as the result of a previous study regarding low molecular weight resin use in picture varnish.[5]

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[2] Koneczny, 2010: 67; Sims, Cross and Smithen, 2010: 165

[3] The following pieces of information come from the Technical Data Sheets (BASF and C.T.S. srl) and from: Borgioli and Cremonesi, 2005: 146-149; Borgioli, 2008; de la Rie, *et al.* 2002.
Further literature is referenced in these texts. The resin was purchased from C.T.S. srl (Spain), in May 2011.

[4] BASF produces various urea-aldehyde resins, sold under the Laropal A trade name.

[5] de la Rie and McGlinchey, 1990

The suitability of different BASF resins as conservation media was assessed in a project which involved conservators, conservation scientists and artists' materials manufacturers (Gamblin Artist Color Co.), and which finally lead to the development of Gamblin' s retouching paints.

PROPERTIES, STABILITY and APPLICATION

Molecular Weight (M_w= average mass): 2880÷3640 a.m.u. (4300 a.m.u., according to de la Rie, *et al.* 2002)
Glass Transition Temperature (Tg): 49÷57°C
Softening range: 80 ÷ 95°C (DIN 53180)
Refractive index: 1.50
Density at 20°C: approx. 1.11 g/cm^3 (ISO 2811, DIN 53217)

Compatibility: with many coatings raw materials including alkyd resins, cellulose nitrate, cellulose acetobutyrate, vinyl chloride copolymers, chlorinated rubber, hydroxypolyacrylates, melamine-formaldehyde resins, aromatic and aliphatic epoxy resins, hydrocarbon resins, phthalate plasticizers

Solubility: it is soluble in almost all paint solvents, hydrocarbon solvents containing about 25% of aromatics and oxygenated solvents (such as isopropanol, ethanol and acetone). It is insoluble in water. Its solubility/diluent tolerance in aliphatic solvents such as mineral spirit is limited. Such solutions tend to separate, particularly at temperatures below 15 °C, but can be stabilized by the addition of 2-5% of an aromatic solvent (e.g. Solvesso® 100). A 20% by weight solution of the resin is soluble in 10% toluene/90% cyclohexane (by weight). Less or more aromatics may be required depending on resin concentration, temperature and exact composition of the solvent mixture.

Relating properties and practice

As already discussed for Regalrez 1094®, when using low molecular weight resins, better optical and handling properties can be achieved. Thanks to their low viscosity, Laropal A81® solutions level to a great extent leading to surfaces that exhibit less light scattering, higher gloss and more saturate colors (similar to those gained when using natural resins). Moreover, because of their slightly polar character, urea-aldheyde resins show excellent pigment wetting. This property together with a very pale color make Laropal A81® particularly suitable for producing all-purpose pigment preparations. The low viscosity of its solutions enable high-pigment-content pastes to be produced.

The excellent solubility and compatibility of Laropal A81®resin enable its use in many types of coating formulation. Being the Glass Transition Temperature quite high, the resin is not prone to pick-up dust and dirt.

Stability

Even if the exact composition of these aldehyde resins is unknown, the oligomeric product is supposed to contain cyclic amide groups and other functionalities. Residual aldehyde groups (which would be a source of chemical instability) were not detected in the urea-aldehyde resins by Nuclear Magnetic resonance spectrometry analysis.[6]

Extensive testing carried out to assess the durability of Laropal A81® resin revealed that it is heat resistant and photochemical stable.

After prolonged accelerated ageing (about 300 h) in an environment simulating daylight through window glass, including daylight's ultraviolet component, Laropal A81® films showed little solubility changes. Unstabilized films required 10% toluene/90% cyclohexane solvent mixtures for removal and when stabilized with 2% Tinuvin® 292, even less polar mixtures.

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[6] de la Rie, *et al.,* 2002

Infrared spectroscopy showed moderate oxidation in unstabilized films and very little oxidation in stabilized films. Size exclusion chromatography showed some reduction in the molecular weight of unstabilized films (suggesting depolymerization processes). The molecular weight of films stabilized with 2% Tinuvin® 292 remain instead unchanged. In addition, all films remain clear and colorless and do not exhibit defects such as cracking or flaking.

The stability of paints formulated with Laropal A81® resin have been further tested, showing good photochemical stability as well.

After 3000h of ageing in an environment simulating daylight through a window glass, the paints remained removable using low-aromatic hydrocarbon solvents (10% toluene/90% cyclohexane solution).

Application

Even if Laropal A81® has been successfully used as varnish, its principle use in conservation is related to the formulation of retouching paints. Meeting several criteria concerning stability, solubility in low-aromatic hydrocarbon solvents and low viscosity it was finally chosen as binding media of Gamblin's retouching colors.

Thanks to handling and optical properties comparable to those of natural resin paints, the solutions of Laropal A81® resin are suitable glazes and where relatively high color saturation is required.

Moreover, retouching paints formulated with Laropal A81® resin showed good covering power, versatility in the achievement of a variety of effects, little change in color upon drying and ease in 'editing' with a silk cloth. They revealed to be particularly useful for retouching losses in ceramics and wooden artifacts.

Using more polar solvents that are fairly fast evaporating, may prove useful when inpainting on resins that are insoluble in such solvents and when crisp brushstrokes and low gloss are desired. Among the solvent mixtures found for these paints there are: equal parts of petroleum benzene, shell TS-28 and isopropanol; dilute mixtures (1:4) of isopropanol in mineral spirits (15% aromatic), and Arcosolv ™ (propylene glycol monomethyl ether).

Retouching formulations based on Laropal A81® 45% solutions in Shellsol D40 (54.5) and ShellsolA100 (45.5) has been reported.[7]

Occasional slight fluctuations in color are unavoidable, but do not affect the performance characteristics of the product.

AQUAZOL 200 ® [8]

Aquazol® is the logo that distinguishes a family of thermoplastic polymers formed by poly(2-ethyl-2-oxazoline). Four types of Aquazol® are manufactured, differing as far as their molecular weight.

Firstly manufactured in 1986 by Dow, this polymer was originally thought as a green, hot-melt sealing adhesive for paper bags or cardboard boxes. Turning out to be too stable for soil decomposition, in 1990 it was sold to Polymer Chemistry Innovations that is still manufacturing and distributing it worldwide. As far as industrial purposes, Aquazol® is now principally used as a greenware binder in ceramics (due to its clean

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[7] Koneczny, 2010

[8] The following pieces of information come from the Technical Data Sheets (Polymer Chemistry Innovation Inc. and C.T.S. srl) and from: Appolonia, *et al.*,2009; Arslanoglu, 2005; Bernardini, 2009; Borgioli, and Cremonesi,2005: 171-172; Fasce and Carnasciali, 2009; Gagné, 2007; Shelton, 1996; Ventikou (web reference accessed 2010); Wolbers, McGinn, and Duerbeck, 1998; Wolbers, 2008. Further literature is referenced in these texts. The resin was purchased from C.T.S. srl (Spain), in May 2011.

burnout and non-ionic characteristics), even if it was also approved for use as an indirect food additive (e.g. as packaging adhesive). It is an excellent alternative to polyvinyl pyrrolidone (PVP) or polyvinyl alcohol (PVOH) in almost all applications, with the added advantage of thermal stability and so suitability for high-temperature applications (steel quench, hot-melt adhesives, etc…).

As far as conservation purposes, Aquazol® was originally investigated by Richard Wolbers as a consolidant for paintings on glass (in 1994). Since then, it gained appeal for many conservators due to its adhesive qualities, wide-ranging solubility (including water), biodegradability and non-toxic character.

PROPERTIES, STABILITY and APPLICATION

Molecular Weight (M_w= average mass): 200,000 a.m.u.[9]

Glass Transition Temperature (Tg): 69-71°C; lower Tg (55-59°C) were detected for samples cast from aqueous solutions (probably relating to the plasticizing effect of water molecules)

Refractive index: 1.52

Density: 1.14 g/cm^3

Compatibility: it can be added to epoxy resins, polyacrylic acid (with the effect of rising its Tg) and other polymers (with plasticizing effects). Polymer-Aquazol® blends show only one Tg. It is compatible with wax and waxy adhesives (e.g. BEVA 371). It is stable in weak acids and weak bases.

Solubility: it is soluble in water (25% or more by weight) and in a wide-range of polar organic solvents (alcohols, such as methanol, ethanol, isopropanol; ketones, as acetone and methyl ethyl ketone; chlorinated solvents, as methylene chloride). It is very slightly soluble (2% or less) in aliphatic solvents (toluene, *n*-pentane…). The pH of aqueous solution is neutral (6-7).

Relating properties and practice

Aquazol® has several characteristics that can be manipulated in order to adapt its properties.
Its polymers unusually combine high molecular weights, with low viscosity. Different molecular weight (5,000; 50,000; 200,000; 500,000) products show different viscosities and bond strengths (the strength decreases going to lower molecular weights). The desired properties can be thus achieved by blending different Aquazol® types. When compared to other water-based adhesives, Aquazol® shows strengths that lay between those of cellulose ethers (Klucel G) and those of acrylic or polyvinylacetate emulsions.

Due to its amide backbone, Aquazol® has electron rich and polar regions around the nitrogen atoms and the carbonyl groups which allow it to interact with materials that are electron poor or polar. It also has non-polar regions (the aliphatic ethyl group) which can interact with non-polar molecules. This explain its wide-range solubility and compatibility with many materials (which allows retreatment with other adhesives and the use of Aquazol® for adhering dirty surfaces).

Thanks to its broad solubility-range and its stability Aquazol® presents a low potential for damaging the original paint during both, its application and removal.
One of the most striking properties of this polymer is that it is perfectly soluble in water.
This sometimes turns out in low wetting properties, that can be improved by small adds of alcohols or surfactants.

Besides being soluble in water, Aquazol® has also a significant response to elevated relative humidity, absorbing more water than animal glues or polyvynilacetate emulsions over a period of time.

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[9] The target molecular weight of Aquazol 5® is 5,000 a.m.u.; that of Aquazol 50® is 50,000 a.m.u. and that of Aquazol 500® is 500,000 a.m.u.

When thinking about conservation, this hydroscopic nature is a concern but, the lack of reports of treatment failure due to high R.H. environments and many reports of satisfactory results, indicate that Aquazol® is an adhesive to be considered.
At R.H. below 84% the tensile strength is still significant (with all the molecular weights in a gel-like state).
Moreover, films made from solutions in isopropanol: water (1:1 by volume) appear to absorbs less water than pure aqueous films.
When mixed with dry pigments or when used to consolidate under bound paint layers it may form high molecular weight complexes (involving divalent ions), which are less soluble and maybe less reactive to high relative humidity.

It does not shrink as it dries nor becomes brittle (probably due to its hygroscopic nature, thus to a certain water plasticizing effect, it maintains its tensile strength over time).

Thanks to its high refractive index Aquazol® has been used for consolidating paintings on glass (glass refractive index: 1.529).

Thanks to its thermoplastic character it can be activated by heat (usually at 55°C).

Stability

Since Wolbers' first study regarding the stability of Aquazol® (1994), the ageing characteristics of this polymer have been further tested.
Tertiary amides are one of the most stable configuration for nitrogen, thus Aquazol® is expected to be relatively stable under normal conditions. The results of accelerated ageing, representing approximately 30 years in indoor museum conditions, support that Aquazol® polymers are light stable and maintain both their neutral pH (with pH shifting from 6.4 to 6.2) and their broad solubility with time. No evidence of cross-linking, oxidation processes or yellowing were detected. The molecular weight of the polymer tends instead to decrease with ageing, suggesting the occurrence of chain-scission processes, that cause an increment in the solubility but some loss of strength as well.
In the presence of divalent ions, Aquazol® forms a high molecular weight complex that could be less soluble after ageing. In a more recent study regarding inpainting materials,[10] tests carried out on Aquazol 500®, confirmed its stability and reversibility after light ageing, even when added with Ivory Black, Cadmium Orange and French Ultramarine pigments.

Aquazol® polymers are stable to heat and does not support mold growth.
They also maintain a plastic deformation with little embrittlement at low relative humidity (elongation at break of 380% at RH 8%).

Application

Thanks to its versatility, good resistance to ageing and high reversibility, in the past years Aquazol® has been recommended (and actually used) for different conservation purposes.

It is currently used in the treatment of many different types of objects, replacing traditional water-based adhesives (e.g. animal gelatin, acrylic or vinyl emulsions…) in performing a variety of functions. It has been used: as a moderate strength adhesive and consolidant; as a clear coating; in traditional gilding preparations (using solvent solutions and providing a significant alternative for reproducing the sheen of burnished water gilding); in formulating filling materials and as retouching paint binder (especially for matching matte surfaces).

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[10] Gagné, 2007.

For consolidation purposes most conservators use Aquazol 200® in a 5-10% concentration in water, ethanol, isopropanol or acetone. The use of Aquazol 500®, 4% in a mixture of water/denatured ethanol 1:2 has been successfully used for treating an unfired clay polychrome sculpture. Generally speaking, better penetration is achieved when ethanol is added in aqueous solutions. For temporary applications of paper tissues over paint surfaces a 40% solution of Aquazol 500® in water was used.

For adhesion, most conservator use Aquazol 500®, 20% stock in alcohol containing 10-50% water. Aquazol 500® solutions in denatured ethanol (ranging in concentrations 5%-20%) are also used.

For filling treatments, the use of Aquazol 500® (10% in water) added with whiting is reported. Some preliminary study was also carried out adding Aquazol® solutions (15% and 20% concentrations in mixtures of water/alcohol, 80:20) with whiting and gesso.

For inpainting, saturated solutions of Aquazol 50® or Aquaol 200® are commonly used (67% or 50% for the former; 33% for the latter, in water or in alcohol with 0-20% of water). For these purposes, the use of Aquazol 500® 17%w/v, 20% w/v or 10% w/v in water is also reported.
When dealing with retouching issues, conservators would mix the Aquazol® solution with dry pigments or add the solution to water color or gouche paints. In order to decrease the reactivity to elevated R.H. and to protect the inpainting against abrasion, inpainted areas are sealed with varnish. Aquazol® paint displayed properties in between gums and oils.

Recently, the use of Aquazol® as polymer plasticizer has been proposed and studied.

MICRONIZED SILICA LO-VEL 27

This very fine white powder is an amorphous, pure silicon dioxide (SiO_2) obtained from the pyrohydrolysis of silicon compounds. Thanks to its hydrophilic and inert character it can be added to a number of materials (such as resins, varnishes, silicone rubbers…) behaving as a suitable thickening agent and improving the thixotropic result. Particle surface has no pores.

Surface area: 180 m^2/g
Main particle size: 19 nm

The product was purchased from C.T.S. srl (Spain). (Information coming from the Technical Data Sheet).

CALCIUM CARBONATE POWDER

Ground and selected white marble granulates. Grain size ranging from 0.0 mm to 0.7 mm.

The product was purchased from C.T.S. srl (Spain). (Information coming from the Technical Data Sheet).

TWEEN 20®

Neutral non ionic surfactant (polyoxyethylene(20)monolaurate sorbitan).

Density: 1.1 kg/l (20°C)
Soluble in water, alcohols, ethylene and propylene glycol. Insoluble in mineral oils.

H.L.B.[11]: 16.7
C.M.C.[11]: 0.06 mM (at 20-25°C)

The product was purchased from C.T.S. srl (Spain). (Information coming from the Technical Data Sheet).

SHELLSOL® D40

Shellsol® D40 is derived from Low Aromatic White Spirits which has been highly refined and reacted with hydrogen to convert aromatics to cycloparaffins. It predominantly consists of C-9 to C-11 paraffins and napthenics. Its solving power is lower than that of the aromatic hydrocarbon solvents but much higher than that of the products obtained from extraction processes.

Boiling range (°C): 145-205
Aromatic content: < 0.4 Wt.-%
Flash point (°C): > 38
Sulphur: <1 ppm
Density at 15°C, g/ml: 0.760-0.795
Refractive Index (nD20): 1.4250-1.4360
Relative evaporation rate (Ether:1): 55-70
Kauri-Butanol number (value): 30-31

The solvent was purchased from Kremer Pigmente GmbH & Co.KG (information coming from the Technical Data Sheet).

SHELLSOL ®A

Solvent naphta (petroleum).

Boiling range (°C): 155-181
Aromatic content: > 97 Wt.-%
Flash point (°C): > 40
Sulphur: <5 ppm
Density at 15°C, g/ml: 0.868-0.880
Refractive Index (nD20): 1.4950-1.5020
Relative evaporation rate (Ether:1): 42-45
Benzol content: < 0.01 Wt.-%
Kauri-Butanol number (value): 90

The solvent was purchased from Kremer Pigmente GmbH & Co.KG (information coming from the Technical Data Sheet).

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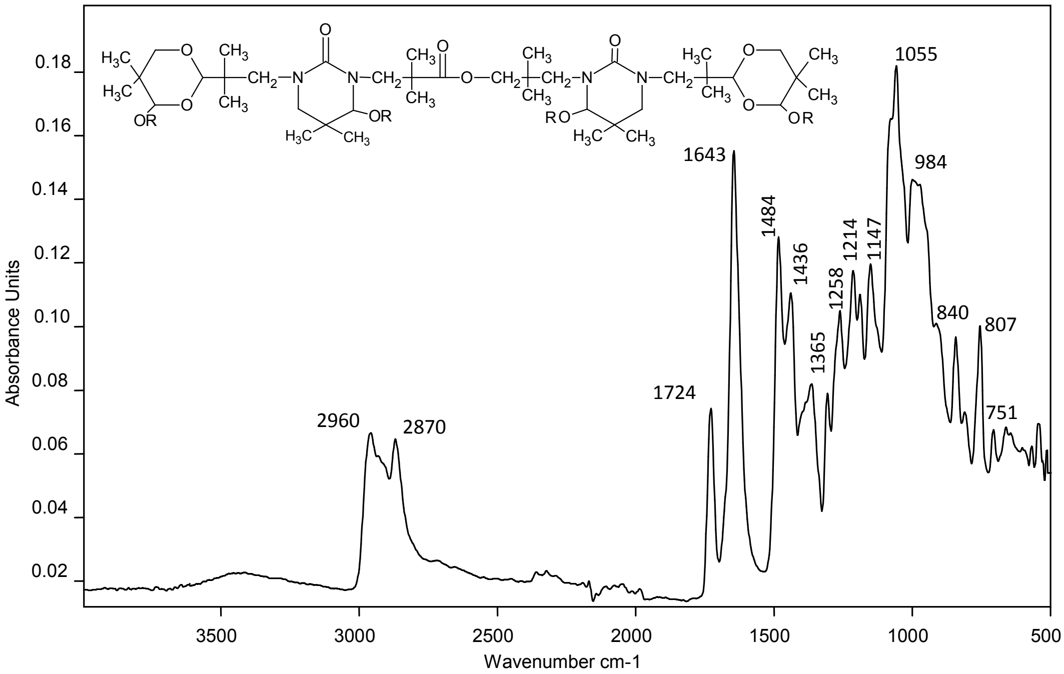
[11] H.L.B: Hydrophilic-Lipophilic Balance. When considering non ionic surfactants, the H.L.B. value ranges from 0 to 20, with 0 corresponding to the highest lipophilic character and 20 the highest hydrophilic character.
C.M.C: critical micelle concentration. It is the concentration above which micelle are spontaneously formed.
Since the C.T.S technical data Sheet do not show these important parameters, they were gathered from Sigma Aldrich.

APPENDIX 2

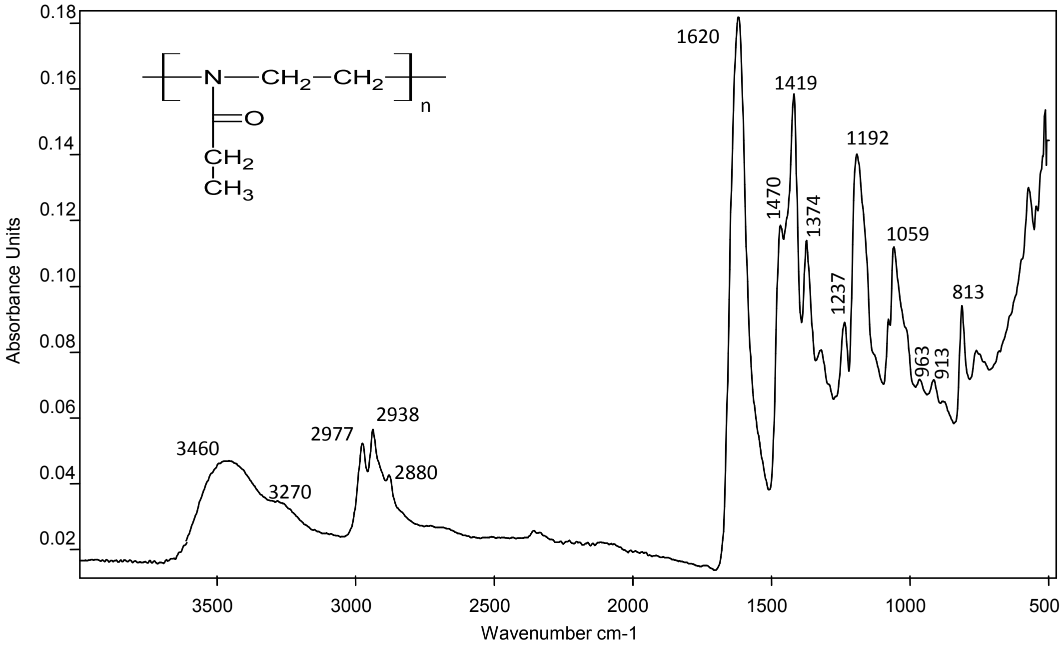
- Reference FTIR spectra -

RESINS

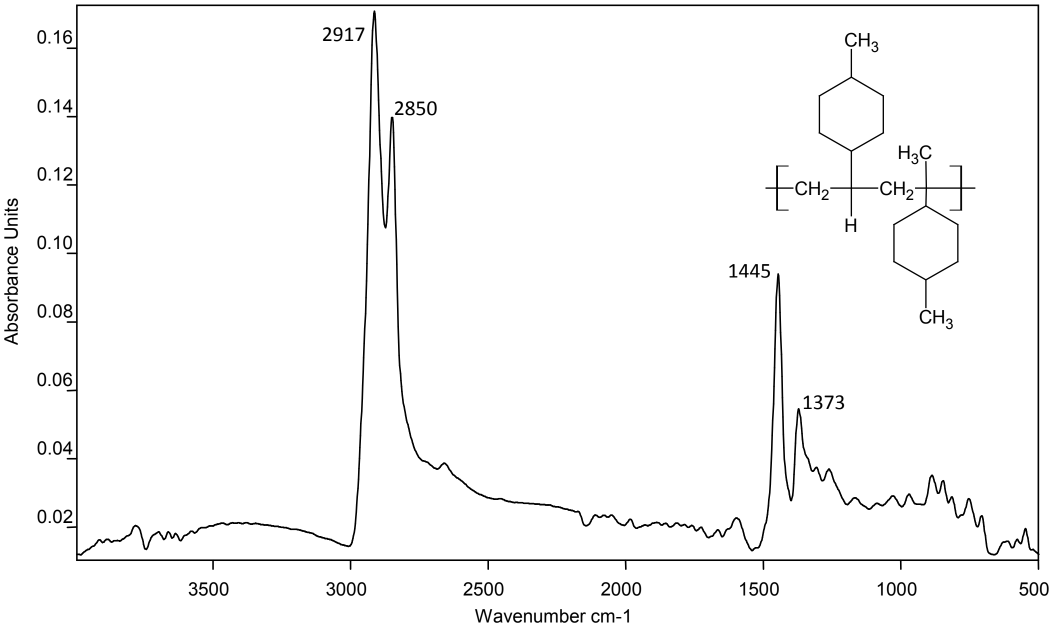
Laropal A81®



Aquazol 200®

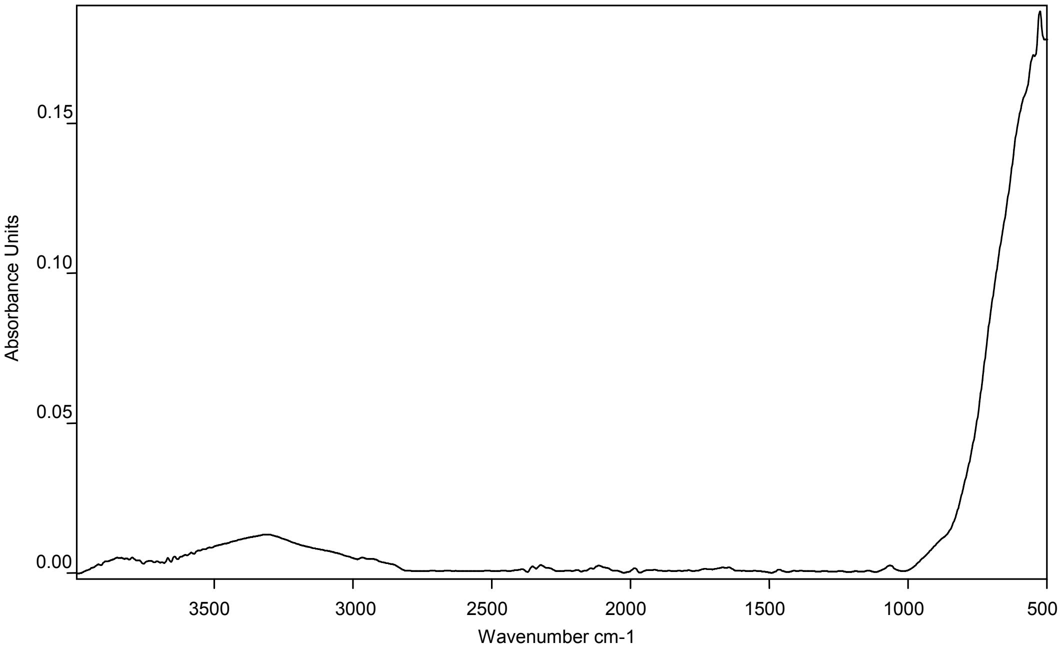


Regalrez 1094®

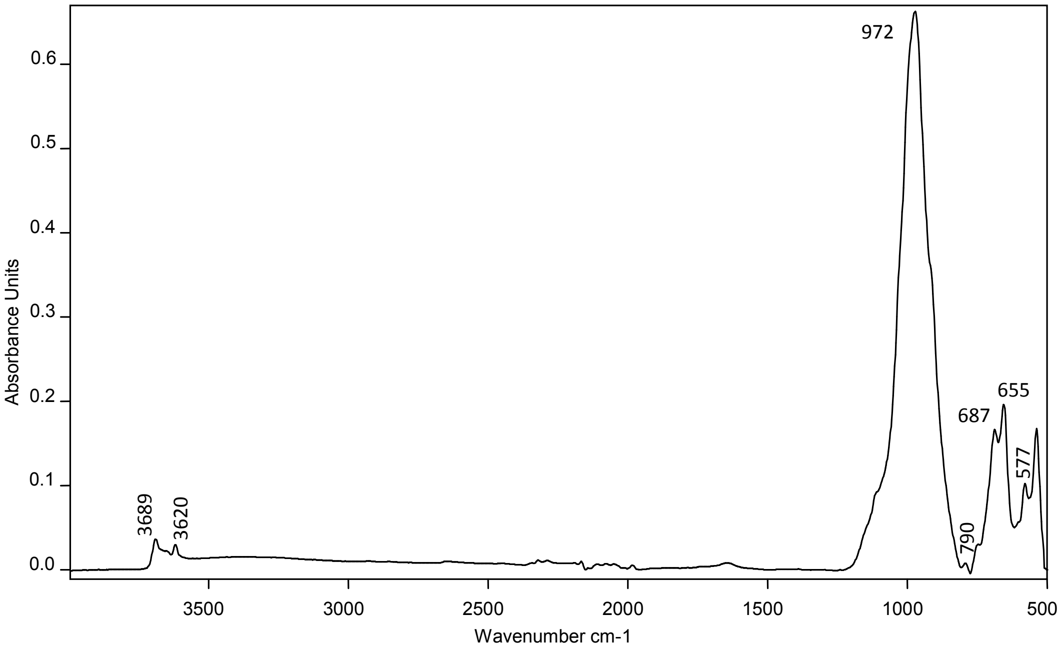


PIGMENTS

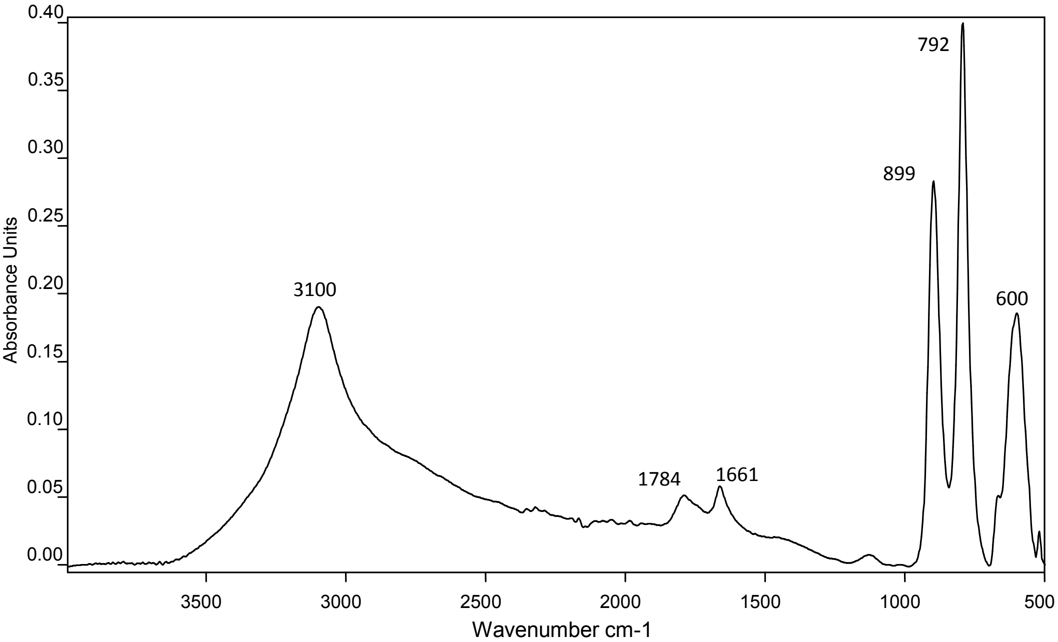
018 –Titanium White (PW6) – Maimeri



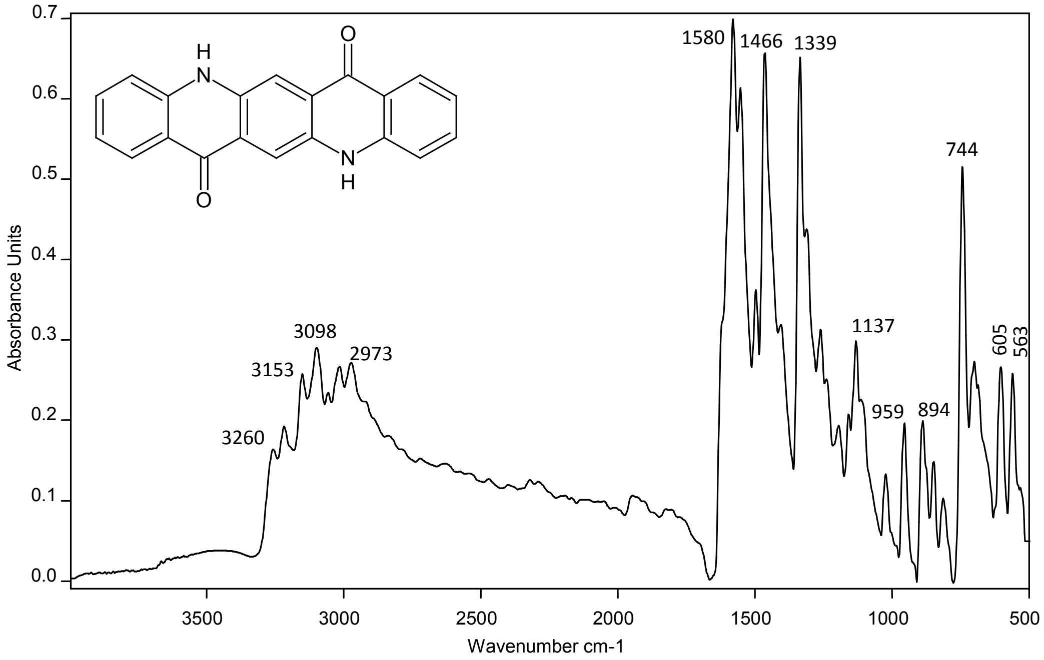
392 - Ultramarine Deep (PB29) – Maimeri



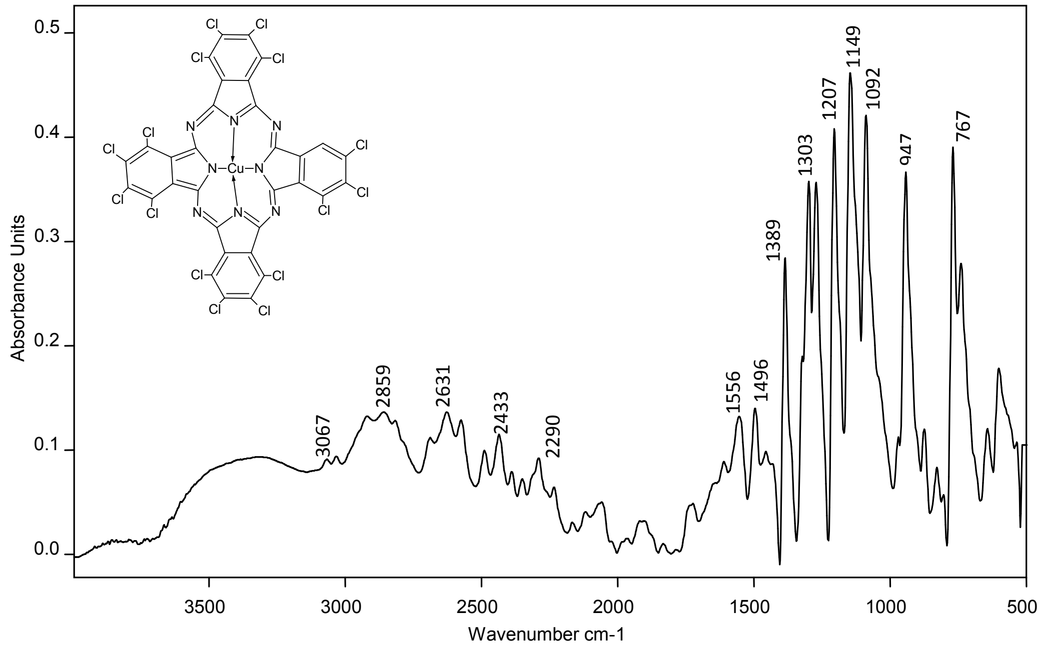
102 – Mars Yellow (PY42) – Maimeri



212 – Quinacridone (PV19) – Maimeri

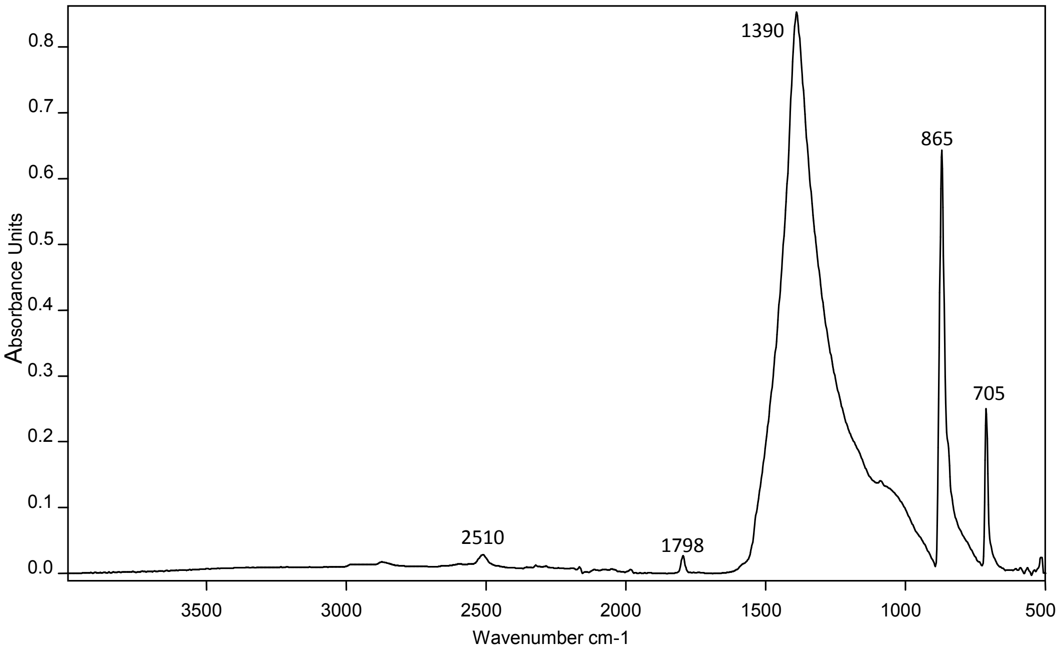


321- Phtalo Green (PG7) – Maimeri

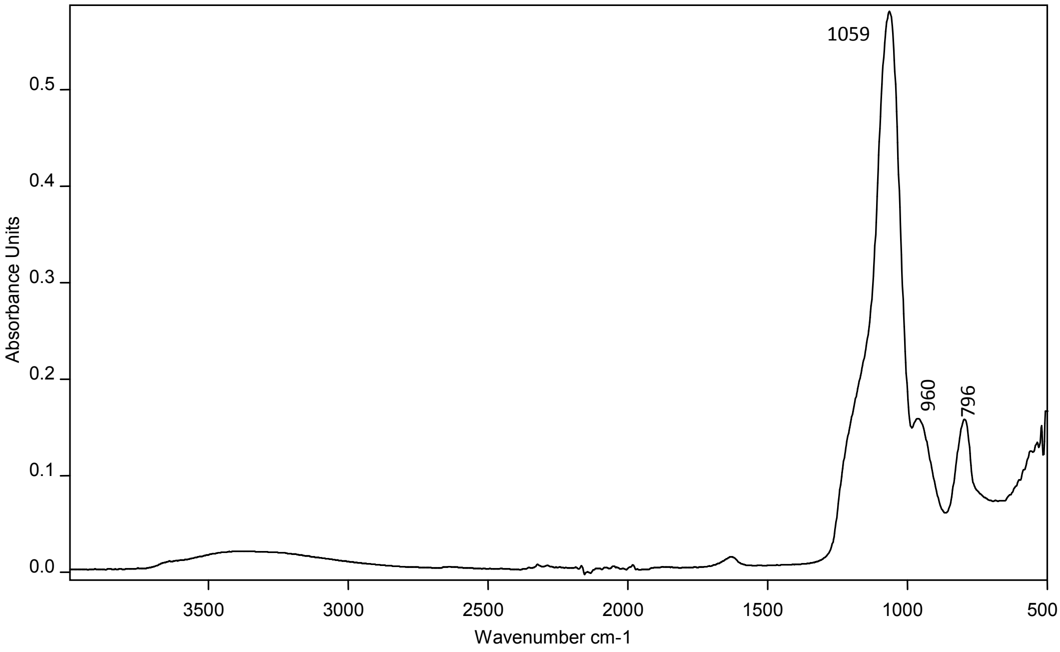


EXTENDERS

Calcium Carbonate ($CaCO_3$)



Micronized Silica LO-VEL 27 (SiO_2)



EUROPIUM (III) COMPLEX

Eu(DBM)$_3$phen