Analytical study of accelerated light ageing and cleaning effects on acrylic and PVAc dispersion paints used in Modern and Contemporary Art

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PART I

1- Abstract
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1- Abstract

In this study, analytical techniques were used for the characterization of acrylic and poly(vinyl acetate) (PVAc) products before and after accelerated aging and wet cleaning treatments.

For this purpose, analytical techniques such as Fourier Transformed Infrared Spectroscopy-Attenuated Total Reflection (FTIR-ATR) and *in-situ* thermally assisted Pyrolysis-Silylation-Gas Chromatography-Mass Spectrometry (Py-Silylation-GC-MS) were used for chemical characterization. Scanning Electron Microscope with Energy Dispersion X-ray fluorescence analysis (SEM-EDX) and tensile tests were run for morphological and mechanical characterization.

For studying the degradation processes caused by light exposure, a set of acrylic and PVAc products were subjected to two accelerated aging protocols. In order to represent normal aging conditions these were conducted at environmental Temperature (T) and Relative Humidity (RH) conditions. Consistent information on the aging of these products has been obtained by contrasting the resulting chemical and mechanical data from both aging programs. Specific degradation pathways such as chain-scissions or cross-linking were detected in this way. In general, acrylics were fairly more stable to artificial aging than PVAc and styrene-acrylics.

Finally, the effects of wet cleaning treatments were evaluated, with special focus on the action of water. Other cleaning treatments, comprising gels and emulsions were tested as well. The results indicate that water can cause changes in the morphology and mechanical properties of the samples as well as leaching of additives. These effects were significantly reduced when water was used in a gelled form. FTIR-ATR and Py-Silylation-GC-MS were used to study the additives extracted from the samples after cleaning treatments. Octyphenol and fatty alcohols non-ionic surfactants with poly(ethoxylated) chains have been detected, as well as anionic sulphonate type surfactants. Cellulose ether, poly(vinyl alcohol) and polyacrylic based thickeners were detected in the solid extracts from different test specimens.

1- Resumen

En el presente trabajo se han empleado diferentes técnicas analíticas con el fin de optimizar protocolos experimentales para la caracterización de la estabilidad de acrílicos y acetatos de polivinilo (PVAc) frente a ensayos de envejecimiento acelerado y tratamientos de limpieza.

Para la caracterización química de las muestras se ha utilizado la Espectroscopía de Infrarrojo por Transformada de Fourier en modo Reflexión Total Atenuada (FTIR-ATR) y Pirólisis-Sililación-Gas Cromatografía–Espectrometria de Masas (Py-Silylation-GC-MS). Para el estudio de las propiedades mecánicas de las muestras se han realizado ensayos mecánicos a tracción, y para el estudio morfológico la Microscopía Electrónica de Barrido con microanálisis por fluorescencia de Rayos-X (SEM-EDX).

Igualmente, el estudio de los procesos de degradación causados por la exposición a la luz se ha desarrollado sobre una amplia serie de muestras acrílicas y vinílicas expuestas a dos tipos de envejecimiento acelerado. Para ello, se seleccionaron las condiciones de envejecimiento artificial que resultaban más representativas y similares a las causadas por un envejecimiento natural provocado por la acción de la luz. La información química y mecánica obtenida por ambos ensayos de envejecimiento acelerado es consistente. Ejemplo de ello es que se han identificado en diferentes tipos de especimenes procesos de degradación específicos tales como entrecruzamiento (polimerización) o escisión de cadenas. Las conclusiones obtenidas de forma general apuntan que los acrílicos son materiales más estables que los vinílicos y los estireno-acrílicos.

Asimismo, en este estudio se han abordado los efectos de los tratamientos de limpieza bien de base acuosa, bien con disolventes organicos, en las propiedades físico-químicas en muestras acrílicas y vinílicas. También se han evaluaron otros métodos de limpieza tales como geles e emulsiones. Los resultados indican que los tratamientos acuosos extraen aditivos, afectan la morfología e inducen cambios en las propiedades mecánicas de las muestras. Estos efectos pueden ser reducidos con el uso de sistemas alternativos de limpieza. Los materiales extraídos de los films se han caracterizado por FTIR-ATR y Py-Sililación-GC-MS pudiendo identificarse surfactantes no-iónicos como octilfenol y alcoholes etoxilados así como surfactantes aniónicos de tipo sulfonado. Finalmente, se han identificado espesantes de tipo éter de celulosa, alcohol poli(vinílico) y ácidos poli(acrílicos).

1- Resum

En el treball açí presentat s´han empleat diferents tècniques analítiques i s´han optimitzat protocols experimentals per a la caracterització de l´estabilitat d´acrílics i acetats de polivinilo (PVAc) mitjançant assajos d´envelliment accelerat i tractaments de neteja.

Per a la caracterització química de les mostres s´han utilitzat l´Espectroscòpia d´Infraroig per Transformada de Fourier en mode Reflexió Total Atenuada (FTIR-ATR) i Pirólisis-Sililación-Gas Cromatografía-Espectrometria de Masses (Py-Silylation-GC-MS). Per a l'estudi de les propietats mecàniques de les mostres s'han empleat assajos mecànics a tracció, i per a l'estudi morfològic la Microscòpia Electrònica de Rastreig amb microanàlisi per fluorescència de Rayos-X (SEM-EDX).

Altres tècniques que van complementar a les anteriors i de les quals es va obtindre informació valuosa van ser la Microscòpia de Força Atòmica i Microscòpia òptica.

D'altra banda, l'estudi dels processos de degradació causats per l'exposició a la llum es va desenvolupar en una àmplia sèrie de mostres acríliques i viníliques exposades a dos tipus d'envelliment accelerat. Es van seleccionar les condicions d'envelliment artificial que resultaven més representatives i semblants a les causades per un envelliment natural provocat per l'acció de la llum. La informació química i mecànica obtinguda per ambdós assajos d'envelliment accelerat és consistent. Exemple d'això és que s'han identificat en diferents tipus de productes processos de degradació específics com ara entrecreuament (polimerizació) o escissió de cadenes. Les conclusions obtingudes de forma general apunten que els acrílics són productes més estables que els vinílics i els estiré-acrílics.

Així mateix, en aquest estudi s'han abordat els efectes de neteges amb aigua i dissolvents en les propietats fisicoquímiques en mostres acríliques i vinílicas. Altres mètodes de neteja com ara gels i emulsions també han sigut avaluats. Els resultats indiquen que els tractaments aquosos extrauen additius, afecten la morfologia i induïxen canvis en les propietats mecàniques de les mostres. Estos efectes poden ser reduïts amb l'ús de sistemes alternatius de neteja. Els materials extrets dels films han sigut caracteritzats per FTIR-ATR i Py-Silylation-GC-MS identificant-se amb els dits procediments surfactantes no-iònics com octilfenol i dodecil-polietoxilados i surfactantes aniónicos de tipus sulfonado.

Finalment, s´han identificat espessants de tipus èter de cel·lulosa, alcohol poli(vinílico) i àcids poli(acrílicos).

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3- Objectives

This project is focused on the analytical study of the stability of Modern and Contemporary paints of acrylic and PVAc type exposed to environmental agents or subjected to conservative treatments.

More specifically:

- Study of the changes in chemical, morphological and mechanical properties induced in films of acrylic and PVAc dispersion paints when they are subjected to accelerated light ageing.

- Study of the changes in chemical, morphological and mechanical properties induced in films of acrylic and PVAc dispersion paints when they are subjected to aqueous cleaning treatments.

- Study of the changes in chemical, morphological and mechanical properties induced in films of acrylic and PVAc dispersion paints when they are subjected to cleaning treatments with organic solvents.

- Study of the changes in chemical, morphological and mechanical properties induced in films of acrylic and PVAc dispersion paints when they are subjected to cleaning treatments based on gel systems.

From the results obtained, a correlation between the changes observed in chemical, morphological and mechanical properties of the films can be carried out. This enables the comparison of the behavior of both types of acrylic and PVAc paint films when they are subjected to accelerated light ageing or the above mentioned cleaning treatments.

For accomplishing these objectives, the following steps were developed:

Workplan

1. Preparation of paint specimens

1.1 - Selection of a wide number of acrylic and PVAc paints and media.

1.2 - Preparation of paint specimens from commercial acrylic and PVAc paints and media as thin films over Mylar® sheets.

2. Analytical characterization of paint films

2.1 - Chemical and morphological characterization of the paint films by means of analytical tecniques such as FTIR-ATR spectroscopy, scanning electron microscopy (SEM), and in situ thermally assisted Pyrolysis-Silylation-Gas chromatography-Mass Spectrometry (Py-GC-MS).

2.2 - Characterization of the mechanical properties of the aged paint films by means of tensile tests.

3. Analytical characterization of the light aging behaviour of paint films

3.1- Aging of paint films under two artificial aging programs that simulate indoor light exposure conditions.

3.2 - Chemical characterization of the paint films after ageing treatments by means of FTIR-ATR spectroscopy and scanning electron microscopy (SEM).

3.3 - Characterization of the mechanical properties by means of tensile tests.

4. Analytical characterization of the effects of cleaning with water, organic solvents and gel systems on paint films

4.1 - Immersion tests performed in paint films using water, selected organic solvents and gel systems.

4.2 - Cotton swab tests performed in a selection of acrylic and PVAc paint films using water.

4.3 - Study of water uptake and material leached from paint films after water immersion by determining the absorption and drying curves during immersion in water.

4.4 - Study of water uptake and material leached from a selection of paint films after application of gel systems and emulsions by determining the absorption and drying curves during immersion in water.

4.5 - Identification of the leached materials from the paint films subjected to the test of water immersion by means of FTIR-ATR spectroscopy.

4.6 - Characterization of the surface morphology of paint films after water and organic solvent immersion tests and application of gel systems and emulsions by means of SEM.

4.7 - Study of the effects of water immersion in the mechanical properties of the studied paint films.

4.8 - Study of the effects of the immersion of paint films in a number of organic solvent on their mechanical properties.

4.9 - Study of the effects of the application of gel systems and emulsions in a selection of paint films on their mechanical properties.

5. Analytical study of paintings

5.1 - Characterization of the surface morphology of samples from an acrylic painting subjected to cleaning of water and gel systems by means of SEM.

5.2 - Characterization of the surface morphology of samples from a PVAc painting subjected to cleaning of water and gel systems by means of SEM.

PART II

4- Introduction

4- Introduction: acrylic and poly(vinylacetate) paints

This introduction is a general overview of both the history and chemistry of the synthetic materials called acrylics and poly (vinylacetates) (PVAc). The chapter will start with a discussion of the wide range of products that can be included as they are used by artists in the production of their artworks. A summary of some results obtained from an on-line survey of conservators and artists is also presented. Even though this survey obtained limited participation, it is interesting to compare the opinions of conservators and artists on the use and durability of these materials.

Also included in this chapter is a brief history of the introduction of these materials in industry and the arts,. The chemistry of these products, how they are prepared and what ingredients can be found in these formulations, are also described. The chapter is finalized with a description of the drying processes of these products and a general overview of the mechanical properties of acrylics and PVAc products. It is intended that the information gathered here is useful for both conservators and conservation scientists.

4.1- Acrylic and Poly(vinyl acetate) paints: an overview

The full understandment of the chemical and physical properties of acrylics and vinyl products that may have been or are being used by artists in the production of artworks is a complex subject. Nowadays, acrylics quality artists' paints are supplied by different paint manufacturers. For example, in Spain, brands such as Titan®, Talens®, Vallejo®, LeFranc & Bourgeois® and Winsor & Newton® are probably the most well known artists' acrylic products, while other international brands such as Golden® or Liquitex® have found more popularity in other countries, despite their historic importance. Many commercial stores also produce their own acrylic colours. For example "Casa Viguer" (Valencia, Spain), which carries its own acrylic Viguer® brand has a wide selection of colours. Many other commercial brands produce acrylic colours and varnishes that are not always artists' quality.

Other acrylics dispersion paints and non pigmented resins can come from industrial products, which can go from dispersion media used for protection of exterior walls to household exterior paints [1]. The artist's have, thus, a wide selection of products. On the other hand the conservator and conservator scientist are faced with a wide variety of different materials under a general heading of "acrylic products".

The poly(vinyl acetate) types of paints have a similar background. They were introduced into the market prior to the acrylic dispersion paints, and have been used by artists in the past, and found in many works of art[1] [2-5]. Ferreira *et al* have studied the work of Joaquim Rodrigo, a Portuguese painter who used a PVAc glue (Vulcano®) by Favrel® to formulate his own paints [5]. This same brand produced early artists' PVAc based paints (a Favrel® Lisbonense) [5]. Today only LeFranc and Bourgeois produces a PVAc type of paint of artists' quality named Flashe® [2,6]. However, artists use PVAc products from industry that are not especially formulated for artistic work. These include Conrayt® or Vinavil®, which are common in Spain [3-4], or others such as Robbialac® (household paint brand) in the Portuguese context [5]. Other well kown brands are sold under the classification of PVAc dispersions, are actually copolymers of vinyl acetate (Vac) and acrylics, or other type of monomers [3,4].

It is also interesting that many artists use PVAc type materials under the term "latex", often considering them as acrylics [5,7]. In the survey conducted on-line to 40 artists, only one artist questioned if the terms "latex", "vinyl" or "acrylic" were the same, or related. The rest of the artists considered latex as another type of paint medium they used in their production. Even though this is not a thorough study, it is an indication of the technical knowledge some contemporary artists may have of the products they are handling. A description of some interesting results of this on-line survey is presented later in this chapter.

It has become clear that studying the properties of acrylic and vinyl paints is a very complex subject in many ways. Either due to the wide range of products existing nowadays in the market, or to the changes in formulation these products underwent throughout the years. There is much proprietary information that does not help researchers fully understand the chemical and physical properties of these products and predict their future durability or behaviour. There are, nevertheless, general characteristics common to all acrylic and poly(vinyl acetate) dispersion paints. These products are emulsions (or dispersion) and they represent a range of known monomers, pigments, fillers, and additives that are being characterized by conservation scientists.

[1, 2] See summary of on-line enquiry, presented later in this chapter.

4.2- Artists and conservators: on-line survey

In May 2010, an on-line survey was sent to both international and national conservators. In this survey, a series of questions were asked with the aim of determining the opinions conservators may have about modern materials, their composition, forms of degradation and, consequently, treatments applied. Some questions under the title "the composition of contemporary paintings" have been designed to compare results with similar questions asked of artists. Ultimately, the scope of this survey was to determine if conservators' ideas are in tune with those of artists. Unfortunately, and similarly to what has happened with the survey by Klein in 2000, only about 40 responses were sent back [7] [8]. The same response was seen by artists. Nevertheless, the data obtained by this survey are considered of general interest, and a short summary of the results are presented here.

The first part the surveys consisted of a series of questions about the nature of the materials applied in paintings as supports, ground and paint layers. Overall, the understanding of the main materials used in the production of artworks, by the groups of artists, was similar to those pointed out by conservators. Firstly, the main supports favored were generally canvas, followed by plywood, paper and photographic material. Around 78% of the artists responding claimed that they applied ground layers, and these were preferencially commercial acrylic gessoes, latex (acrylic and PVAc based) or traditional homemade grounds with rabbit skin and calcium carbonate. The rest expressed the convenience of buying commercially prepared canvases. In figure 4.1 is a barchart corresponding to the opinion of conservators on the most common products used as binding media. Similar information is included from artists to the question of what materials they mostly used for painting. The preferred paint brands have also been enquired and the results are present in figure 4.2.

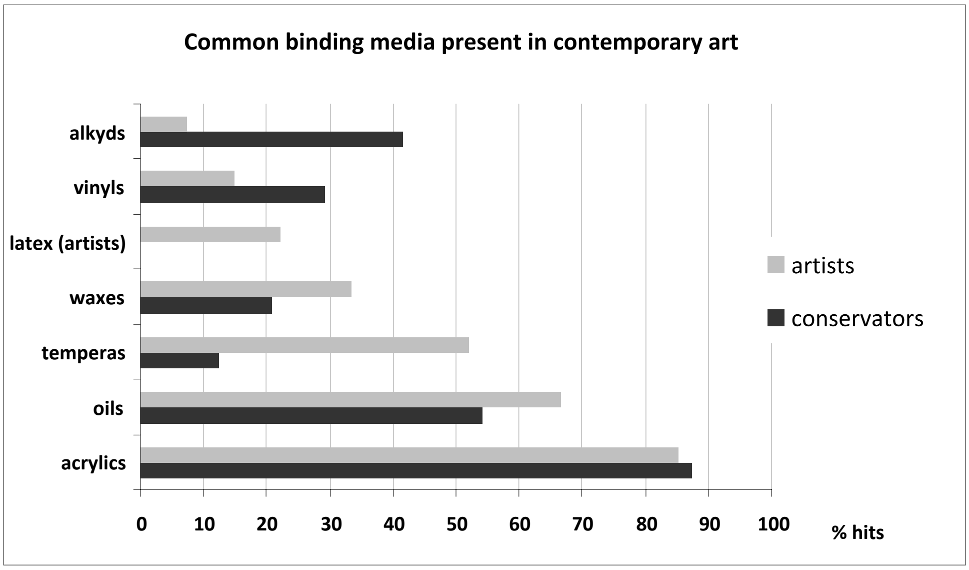

Figure 4.1: barchart of the hits corresponding to the most common materials used as binding medium in paint layers. Overall there is a good agreement between artists and conservators. Acrylics are the most voted binding medium. It is interesting to notice that artists consider latex different from either acrylics or vinyls. Also, alkyd paints were not a much voted choice for artists, even though conservators point this as the third main binding medium for paints. Since there could be multiple answers to the same question, the results have been plotted in percentage (%) for each option (i.e. 88% of the 40 artists answered acrylics, but may have answered also on other binding medium, such as 15 % in vinyl paints).

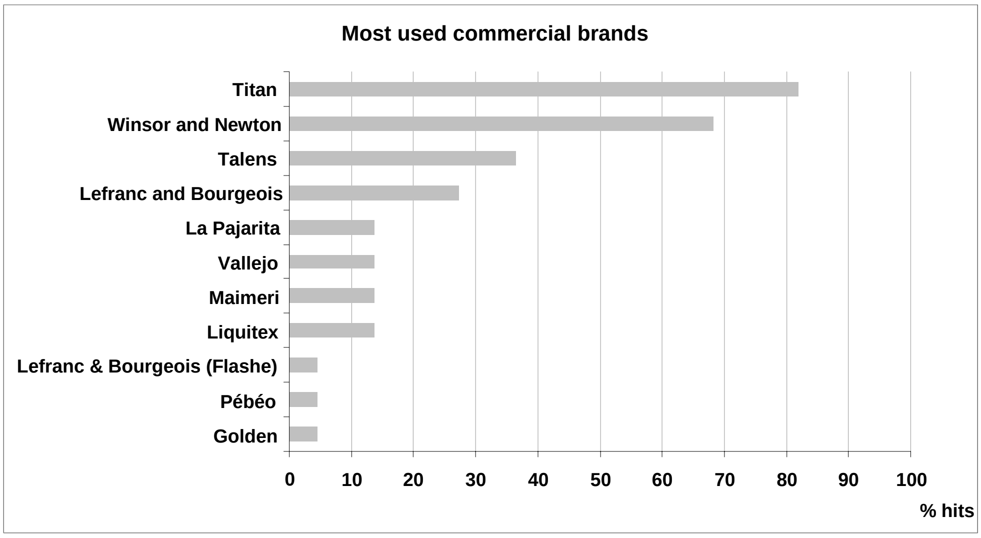

Figure 4.2: barchart of the most used paint brands by the artists that participated in this survey. It should be noted that there is no specification if the brand is related to a specific type of paint (example acrylic or vinyl), except for Flashe®. Titan® and Winsor & Newton®, followed by Talens® appear to be the most used commercial paint brands. The results are expressed in % as explained in the prior graphic.

On the subject of varnishing (most artists did not specify which type of varnishes they use), 46% of the artists answered that they applied varnish layers, whereas a 23% said no. The rest of artists answered that, occasionally, they applied varnish layers or in some specific areas from a painting. This is in good agreement with a series of interviews to several contemporary artists, where a 75% used varnishing in their painting process. These artists were mainly acrylic users. Interestingly, this information went against the general understanding of contemporary paintings, in which matte or non varnished surfaces dominate [9]. On the other hand, 50% of the conservators answered positively to the presence of varnishes in the paintings they work with. One conservator gave an answer with a statistic value (possibly from his institution) that 40% of modern paintings were varnished (which type of varnishes were not specified). These varnishes are preferently applied in spray, brush or roll.

Generally, artists still mistrust the durability of acrylics and other synthetic products, and prefer oils as the more stable painting material. These results have been compared with the materials conservators say exhibit more damage. The results are presented in figure 4.3. Interestingly, the materials claimed by artists as more stable are the ones conservators indicate present more damage.

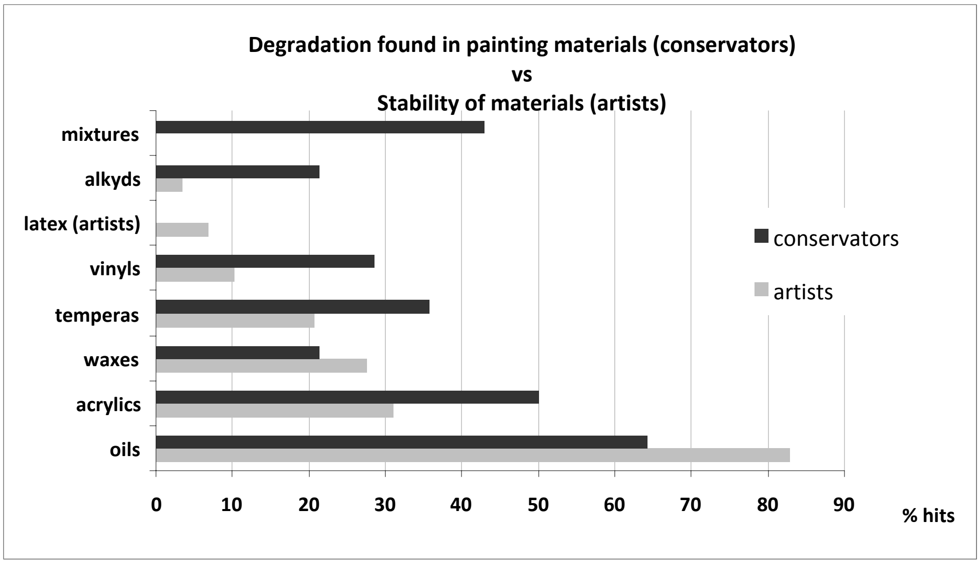

Figure 4.3: shows the concept of stability of materials from the artists point of view contrasted to the degradation found in works of art by conservators. Interestingly the trend shows that conservators find more conservation problems in those materials considered more stable by artists. Conservators also find much damage in mixtures of materials (normally water/oil incompatibility, or industrial varnishes over fragile paint layers). Results are expressed as explained in the previous graphic.

When asked on the most common forms of degradation found in their paintings, 85% of the artists answered that dust/dirt acumulation on the surface was the most common problem, and for that they normally stored paintings in the vertical position, with some plastic paper covering or wrapping. Similarly, a 100% of the conservators pointed out that they have done dusting or mechanical cleaning in contemporary works of art either in oils, acrylics or PVAc paints. Water-based cleaning procedures are common to these three types of products (aprox. 75% for all types of paints), whereas solvent based cleaning is mostly restricted to oils. Other conservation treatments such as consolidation, fixation of paint layers and application of filling materials are also stated in a great number, which indicate that acrylics or PVAc products may suffer alteration even though very young.

Finally, when artists were asked if they were concerned about the conservation of their paintings, a 93% answered yes, and 83% were of the opinion that an intervention should be made by a conservator. On the other hand, 37% of conservators answered they were always in contact with living artists for conservation treatments, only 4% answered no. Many failed to answer this question.

4.3- Synthetic media in the 20th century: use and evolution of acrylic and vinyl dispersion paints

The introduction of the acrylic and vinyl paints along with other new synthetic products in the artistic production can be regarded as a combination of factors. Originally these materials were introduced in the post-World War II era as industrial products, where art materials were scarce and considered luxury products. This forced many artists to turn to the materials availabe for industrial purposes (for example, painters often started using household paints) [10,11,14]. There was, nevertheless, an intentional mindset from many artists to search for new materials. An interesting description of the introduction of synthetic media in the art world has been published by Crook and Learner [11].

The first non traditional product used as a binding medium in the 20th century was nitrocellulose. This is a semi-synthetic product obtained from the reaction of cellulose with nitric acid. According to the degree of nitro groups, these products could attain various ranges of properties. For example, high degrees of substitution can lead to explosive properties. After the World War II, this product was no longer used for belligerent purposes, and was transformed into car paint, having wide application. Dupont produced nitrocellulose car paints called *Duco*® [11,14]. Nitrocellulose paints were fairly well accepted in the art field, especially after a workshop organized by Siqueiros in New York in the 1930’s. In this workshop new materials and new forms of application were discussed and presented to many artists, among them Jackson Pollock, who later adopted nitrocellulose paints in his works [11].

In the early 1930's, alkyd paints were produced as alternatives to nitrocellulose due to safety reasons. Their drying time was longer than nitrocellulose though they showed more gloss and resistance to weathering [11-14]. After World War II, alkyds were introduced in the marker of household paints in the USA and, by the early 1960's they had become best-seller oil-based paints [11,12,13]. Artists such as Willem de Kooning, Pollock, Frank Stella, Peter Blake used alkyds in their works [11-14].

The polyvinyl acetates (PVAc) were developed in 1913 and used mainly as adhesives in the following years. In the 1930's *Union Carbide* Corporation produced *Vinylite®*, a mixture of vinyl compounds in which PVAc was included. Vinyl products were commercialized as dispersion in water between 1946 and 1950. These resins dispersed in water were used in high resistance paints by Germany, as substitution to natural rubber [12,16-18]. These emulsions were then introduced in the industrial market of paint. Nevertheless, these emulsions were introduced in a *do-it-yourself* fashion, where the resins and the pigments were mixed by the buyer. *Polymer Tempera*®, a commercial PVAc paint, was available in 1945 by Borden Co. In the early 1960's, Rowney (UK) produced a PVAc based medium to which pigments could be ground (Rowney PVA [19]), which had problems in effective pigment dispersion. These paints were not very successful in the artistic world, especially considering that, soon after, the acrylic paints were introduced in the market and offered better properties. Some artists such as Alfred Duca, James Brook, Karl Zerbe, Syd Solomen, Hyman Boolm, Sidney Nolan, Keneth Nolan used PVAc mediums and paints in their works. Alberto Burri (1950's) used *Vinavil®* PVAc medium, a product with the same name is still available in the market today [3]. PVAc waterborne paints remain the principal type of paint for household paints, especially for interior coatings. It is also frequent to find copolymers of VAc and acrylics in these types of paints. The copolymerization with an acrylic monomer usually adds stability and overall resistance to the final product. Nevertheless, these paints are known to posses less resistance to wheathering and low binding properties when compared to 100% acrylic products [20,21].

Acrylics were develop industrially in 1927 by Rhöm in Germany [14,16]. In 1949, the first artists' acrylic solution paints (a poly(butyl methacrylate) dissolved in turpentine) were commercialised by the tradename Magna® [7,11]. The creators, Leonard Bocour and Sam Golden, advertised these acrylic products as the "first new painting medium in 500 years" [11]. The first acrylic emulsion paints were developed for exterior housepaints in 1953, by Rhöm and Haas. The acrylic dispersion was named *Rhoplex AC-34®*. Soon after, in 1955, the company Permanent Pigments Inc. (Cincinnaty, Ohio), run by Henry Levinson, launched a new artists' colour formulated with the same acrylic resin and named it *Liquitex®*. This paint had a very thin and liquid texture but soon after, in 1963, a range of textures were introduced, resembling those of oils. Moreover, Levinson launched a campaign of workshops and lectures throughout the country. These paints achieved good acceptance by some of the most well known artists of the 20th century such as David Hockney or Andy Warhol [11,22]. After 1964, just in the USA, there were already Magna® and Aquatec® (solution and dispersion acrylic paints by Bocour Artists Colors) and Liquitex® (Permanent Pigments Inc.), as well as, New Masters® (California Products), Hyplar® (Grumbacher), politec® (Politec) and Shiva Artists Colors® (Shiva Artists Colors) [10].

A study performed by Learner at the Tate on a wide number of modern paintings from the last 50 years revealed a variety of compositions ranging from pure PVAc resins, to vinyl-acrylic copolymers and pure acrylics. Among the latter, poly(ethyl acrylate/methyl methacrylate) and poly(*n*-butyl acrylate/methyl methacrylate) copolymers [23,24]. In the present day, the acrylic medium composed of poly(*n*-butyl acrylate/methyl methacrylate) is possibly one of the most used binding medium in paint formulations used for artists' paints [2,7,23]. Nevertheless, other media such as poly(ethyl acrylate/methyl methacrylate), or acrylic-styrene copolymers can still be found. A chemical description of acrylic and vinyl products is presented in the next section of this work.

4.4- The chemistry of acrylic and vinyl resins and paints

A paint or coating can be defined as a complex formulation of a finely dispersed solid in a liquid medium containing additives that can cover a substrate and form a protective or decorative film. A typical acrylic or vinyl dispersion paint formulation will include ingredients such as a resin as a binder, pigment(s) for color, surfactants, solvents and other additives that are added at different stages of the paint manufacture.

The following section of this work will adress the basic formulation concepts of acrylic and vinyl dispersion paints. The paints are normally produced in two steps: the production of the resin, and the production of the paint. This is normally done by different manufacturers [23].
Below, a general description of acrylic and vinyl monomers is given, as well as a presentation of how these are converted into waterborne resins. Finally, the additions necessary to convert the binding medium into a paint, or coating, are also adressed.

4.4.1- The acrylic and vinyl monomers

The resins obtained from vinyl and acrylic monomers are among the most common groups used in coatings. These resins can be used alone or in combination with other types of products. Normally, they can be divided in two categories: thermoplastic and thermosetting. The thermoplastic resins harden by solvent evaporation and vary their mechanical properties with temperature, whereas thermosetting resins harden by chemical reaction. The acrylic and vinyl products studied in this work are included in the thermoplastic polymeric group of resins [25]. The second group will not be discussed, since it is out of the scope of this thesis.

These resins are long chain polymers with high molecular weight, produced by emulsion polymerization of acrylic and vinyl monomers. The polymerization process is possible due to the presence of double bonds (-C=C-) in the monomers, which are capable to react to form long units of stable carbon-carbon covalent bond (-C-C-) bonds. If the polymer consists of one single monomer, it will be a homopolymer, if the chain comprises two, or more, different monomers it will be a copolymer, terpolymer, etc [25,26].

Acrylic resin is a broad term that includes polymers produced from monomers that derive either from acrylic or methacrylic acid. The resulting monomers are esters of these acids termed acrylates and methacrylates, respectively, and are shown in Figure 4.4.

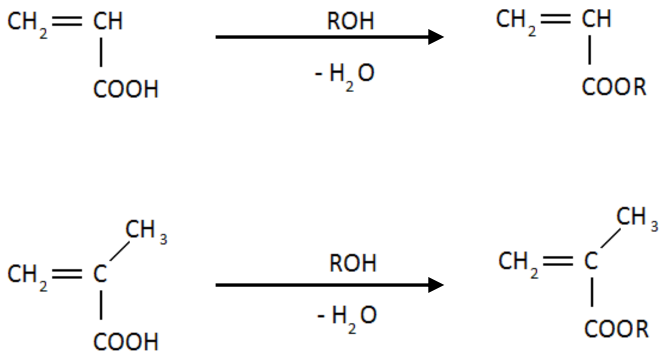

Figure 4.4: a schematic representation of the acrylates (above) and methacrylates (below) monomers resulting from the reaction of acrylic and methacrylic acid with an alcohol.

The nature of the side group can be used according to the functionality that the manufacturer wishes to obtain. For example, longer side chains are associated with flexibility or water resistence, whether shorter alkyl chains produre harder polymers [25].

On the other hand, vinyl monomers can be represented by the formula present in figure 4.5, where R is usually a hydrogen atom (-H) or a methyl (-CH_3) group. X can include a wide variety os species, including aromatic rings, halogens, amides, and ester or susbstituted esters. If X is an acetate group, the resulting monomer is vinyl acetate. If there is an aromatic ring, the resulting monomer is styrene [25].

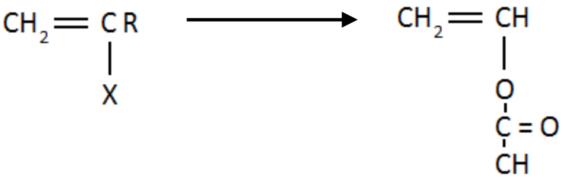

Figure 4.5: schematic representation of the vinyl monomer structure (left). A vinyl acetate monomer is also depicted (right).

The selection of monomers used in the preparation of a resin can be dictated by the performance requirements and also by cost. Resins prepared for the purpose of binding media for paints are normally combinations of two or more monomers (copolymers), chosen in order to give a compromise of their properties, such as film formation, elasticity, gloss, etc. For example, PVAc has been produced has a homopolymer and used in the production of paint. Nevertheless, the homopolymer produces brittle films and one or more external plasticizers are normally added in order to render flexibility. Nowadays, internal plasticizement is prefered to external plasticizement[2], which is accomplished by adding a *softer* comonomer. These can be products such as acrylic or a vinyl comonomer with a bulky alkyl side chain. In dispersion acrylic resins used as binding media or varnishes it is common to find comonomers such as butyl acrylate-methyl methacrylate (BA-MMA), ethyl acrylate-methyl methacrylate (EA-MMA) or styrene-butyl acrylate (Sty-BA). On the other hand, PVAc copolymers can include vinyl versatates (VAc-VeoVa) [11,28], butyl acrylate (VAc-BA) [25,27,28]. In these examples, the union of the two distinct monomers is in view of a specific purpose. In table 4.1, is a summary of common acrylic and vinyl monomers along with some general properties they may contribute with to the resulting polymer film.

---

[2] See external plasticizers later in this chapter.

Monomer	Abbreviation	Film property	Tg (ºC)[3]
methyl methacrylate	MMA	exterior durability hardness stain and water resistance	105
butyl acrylate	BA	flexibility and water resistance	-56
ethyl acrylate	EA	flexibility and water resistance	-22
ethylhexyl acrylate	EHA	flexibility and water resistance	-50
Vinyl neodecanoate	VeoVa	flexibility	-3
styrene	Sty	cost reduction hardness	100
vinyl acetate	VAc	hardness	29
acrylic acids	Ac	stabilizer	106
methacrylic acids	MAc	stabilizer	200

Table 4.1: typical monomers found in industrial copolymer dispersions [25,27,28].

4.4.2- The emulsion polymerization process of acrylic and vinyl resins

The emulsion polymerization process involves the brakeing of the C=C bond present in either the acrylic or vinyl monomer. This reaction is very exothermic and needs constant and vigorous agitation as well as control of the temperature, as it strongly influences the molecular weight of the resulting polymer. This forces the process to be conducted in a solvent or water medium to dissipate the heat produced in the reaction. There are several types of polymerization techniques, including bulk polymerization, suspension polymerization, solution polymerization and emulsion (or dispersion) polymerization. For the scope of this thesis, only dispersion polymerization will be adressed, since it is the process used in the production of the acrylic and PVAc resins used for artists' paints and media.

In a simplified model[4], dispersion polymerization occurs in the presence of a minimum of four components: water, surfactant(s), monomer(s) and an initiator. A protective colloid[5] can also be

---

[3] The concept of Tg will be discussed later in the section devoted to the mechanical properties of acrylics and PVAc products.

[4] Emulsion polymerization is a far more complex process than the summary presented here. Furthermore, the knowledge on this theme is still somewhat empirical [25]

[5] A protective colloid is water soluble materials with a high molecular weight used to stabilize the dispersion and avoid flocculation during polymerization. These can include cellulose ether derivates, poly(vinyl alcohol) or polyacrylic acids [28]. These products are normally used in PVAc dispersion polymerization, but rarely are needed in the case of acrylics and styrene-acrylic resin dispersion polymerization due to pre-polymerization processes.

added at this stage to protect the particle surface avoiding agglomeration and flocculation of the growing polymer particles [16,25-28]. The first part of the process consists of the addition of surfactant[6] to the stirring water until it reaches its specific critical micelle concentration (CMC)[7], and starts forming micelles. The micelles have their polar, or hidrophilic groups, oriented to the water, and the hidrophobic domain is forced together in an agglomerate [25]. A typical micelle is formed by 50 to 100 surfactant molecules [28]. The monomers are then added to the stirring solution and are either dissolved in water as individual molecules, or brake into droplets, stabilized with surfactant, or absorbed into the existing surfactant micelles, due to affinity by polarity. The micelles containing monomer are, at this stage, smaller than the monomer droplets stabilized by the surfactants. The initiator[8] is then added to the mix and starts the consumption of monomer. The theories on the mechanisms of polymerization vary, but generally, it is accepted that the polymer particles grow either in the aqueous phase, which require stabilization by surfactants, or inside the micelles. In order to achieve equilibrium, the monomer present in the droplets will diffuse from the micelle to the water phase. This allows the growing polymer to keep growing by consumption of the monomer present in the acqueous phase. As the polymer particles grow, there is a consumption of surfactant for its stabilization. When the concentration of surfactant is below their CMC, the micelles disappear, and further polymerization only occurs in the already formed particles. At this point it is typically claimed that a 15-25 % of the monomer has been converted into polymer. This phase is called *nucleation* due to the small particle size in comparison to the final particles, generally in the range of 100-500 nm [27]. The monomers are then consumed until no droplets exist, and the rate of polymerization decreases only when trace amounts of monomer remain. A schematic representation of this process is represented in figure 4.6. The final product, the dispersion resin, or *latex*, will present solids content above 45 %, low volatile content, and it is expected to have a shelf-life of a minimum of 6 months, but preferably of 1-2 years.

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[6] Surfactant (surface active agent) is an anphoteric molecule that contains an hydrophilic and hydrophobic groups which align depending on their surrondings [25]. Surfactants will be adressed later in this chapter.

[7] CMC is the value of concentration, expresed in milimolar (mM) or also in grams per liter (g/L) that indicates the concentration at which a specific surfactant forms agreggates named micelles [25]. Below this value, the surfactant is present in solution as individual molecules with limited solubility [28]. The CMC varies according to each particular surfactant.

[8] Initiators will be adressed later in this chapter.

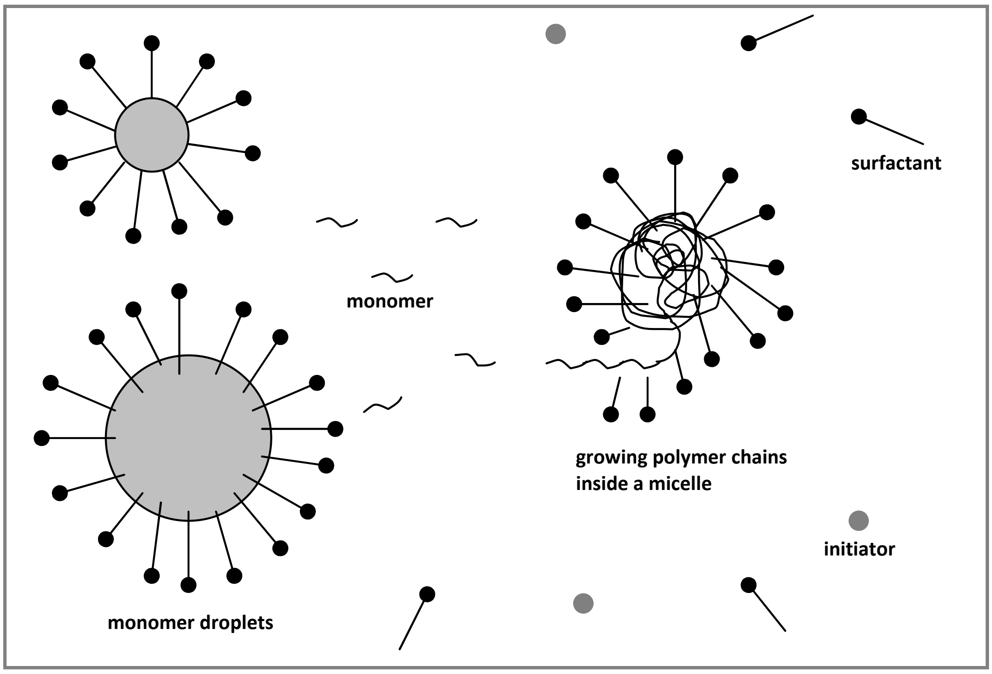

Figure 4.6: a schematic representation of the species present during the emulsion (dispersion) polymerization. Monomer droplets, initiators and growing particles inside the surfactant micelles are depicted. Adapted from [28].

4.4.3- The components used in the dispersion polymerization processes of acrylic and vinyl resins

Besides water and monomers, the most important components used in the polymerization processes are surfactants and initiators. There are also other additives commonly present at this stage include protective colloids and buffers. These components will be shortly described, since they are present in many stages of the paint formulation and the dried paint.

4.4.3.1- Surfactants

A surfactant is a contemporary term for *surface-active agent* compounds. These molecules present groups of opposite polarity (polar and non polar) and, thus, are capable of interacting with both polar and non-polar environments. Surfactants can be classified according to the nature of the polar group as non-ionic, anionic, cationic and anphoteric, as depicted in figure 4.7 [27]. For dispersion resins, both non-ionic and anionic surfactants are commonly used. Some surfactants used in the production of dispersion resins and paints are presented in table 4.2 [25-28].

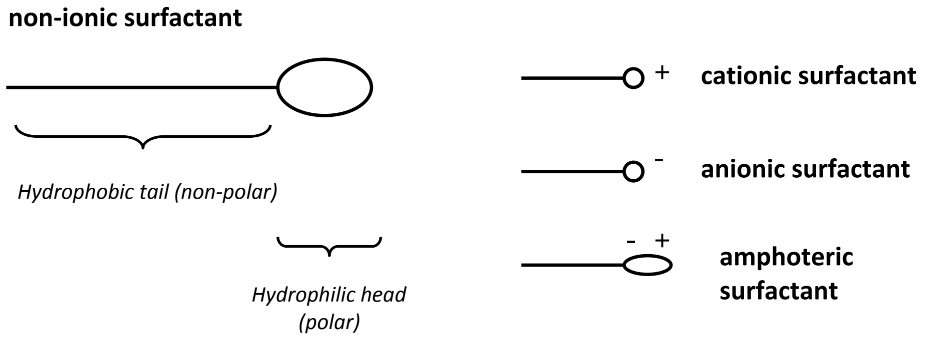

Figure 4.7: generic types of surfactants according to the polar group type.

Classification of polar group	General name
Non-ionic	ethoxylated alkyl alcohol
	ethoxylated alkyl phenol
Anionic	alkyl/aryl sulphonates
	alkyl/aryl sulphates
	ethoxylated sulphonates
	ethoxylated sulphates
	phosphates
	salts of carboxylic acids (C_{12}-C_{18})

Table 4.2: examples of common surfactants present in the polymerization process. These are divided according to the non-ionic or anionic polar group

Usually, a mixture of anionic and non-ionic surfactants are used in the latex preparation [27,29,30]. The reason for this is that both types of surfactants work together in synergistic way, and the manufacturer is able to take advantage of each surfactant property, rather than from the compounds individually. An ionic surfactant will contribute to the stabilization of the latex particle by means of electrostatic repulsion, and the non-ionic surfactant will contribute with steric repulsion.

The non-ionic surfactant most commonly used in the past has been alkyphenol ethoxylate, but due to environmental concerns, since it is not easily biodegradable, this product has been substituted to other ethoxylated type of surfactants, such as ethoxylated alkyl alcohols, of fatty acids monoethanolamide ethoxylates. The ethoxylated surfactant is the main responsible for the dispersion stabilization. For this, relatively long polyoxyethylene (PEO or PEG) chain should be in the order of 10 to 30 in number of ethylene oxide units (EO). This increases water solubility of the polar group of the surfactant, whilst the nonpolar chains are oriented towards the polymer particle surface.

An anionic surfactant is also included to confer thermal stability of the ethoxylated surfactants, since their solubility is temperature dependent[9], as well as electrostatic stabilization. This is especially important during the initial stages of polymerization, where the system is at high temperatures, as discussed previously in this chapter. Anionic surfactants significantly lose their properties with increasing electrolyte content of water and in the film formation stages [25,27]. A scheme representing a polymer particle stabilized by a surfactant layer is presented in Figure 4.8.

Another type of surfactants that may be used in order to improve the film resitance to water and queous solutions are the copolymerizable surfactants [27,31-34]. These compounds present a reactive group, such as a double bond, that can participate in the polymerization reactions. As it is included in the polymer chain, these type of surfactants can avoid the typical water sensitivity that other surfactant presents when the film is dried [27,31-34].

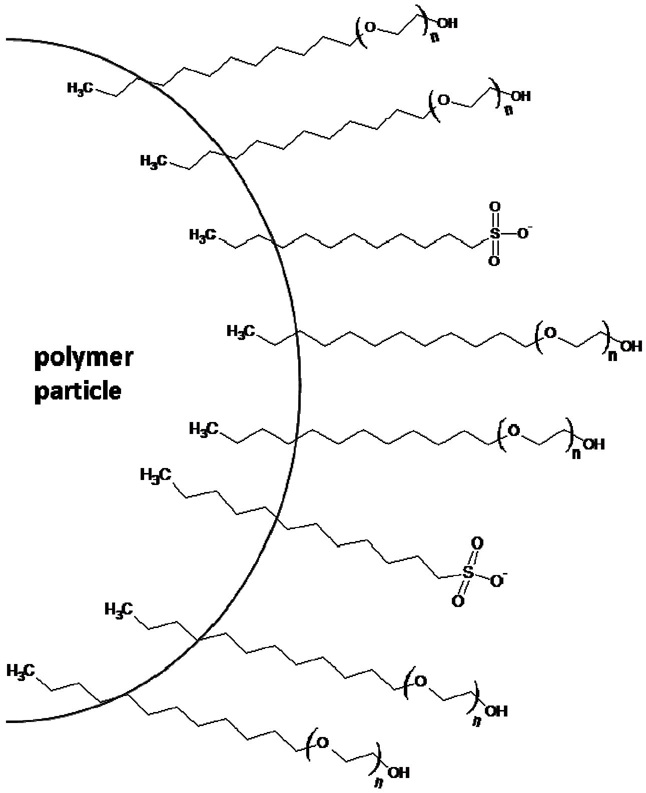

Figure 4.8: representation of a polymer droplet stabilized by an anionic and non-ionic surfactant. Both surfactants are used in order to achieve a sinergy between of steric (non-ionic) and electrostatic (anionic) stabilization of the latex particle. (Adapted from [27])

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[9] PEO-type surfactants decrease solubility in water with increasing temperatures [27].

4.4.3.2- Initiators

Also present in the dispersion polymerization process is the *initiator*. This compound is necessary to start the *addition* polymerization process, since it is the agent that produces the cleavage of the C=C bond present in the monomers and start a radical chain reaction that forms the polymer (figure 4.9). The polymerization is bound to undergo three main steps: *initiation*, *propagation* and *termination*.

$$\underset{\textit{Initiation}}{\mathbf{RH}} \longrightarrow \underset{\textit{free radical}}{\mathbf{R^{\cdot} + CH_2 = CHX}} \longrightarrow \underset{\textit{intiated species}}{\mathbf{RCH_2 - C^{\cdot}HX}}$$

Figure 4.9: summary of the the three main steps of the polymerization via radical initiation. R represents a general initiator

The initiation process can be brought about by free radical initiation, anionic initiation an cationic initiation. Nevertheless, for emulsion polymerization, the initiator is exclusively of the free radical type, and must be water soluble. The initiators most frequently used in acrylic dispersion polymerization are persulphates of sodium, potassium and, particularly, ammonium, which is much soluble in water, and also with the presence of small amounts of peroxide. The reactive sulphate radical anions are generated by the cleavage of the peroxy linkages by thermal induction or by the use of a *redox* couple and activators. The reslult are sulphate radicals. Reducing agents can include sodium bisulphite, metabisulphite, thiosulphate, and hydrosulphite and formaldehyde sulphoxylate. Activators can count upon salts of polyvalent metals, such as iron (II) salts (sulphate and ammonium suphate) [25].

$$\mathbf{{}^{-}O_3 - S - O - O - SO_3^{-} \longrightarrow 2S^{\cdot}O_4^{-}}$$

Figure 4.10: representation of the brakedown of a peroxide bond that starts a polymerization process via radical reaction.

Other common initiators can also be used in the polymerization industry, including di-benzoyl peroxides (Diacyl peroxides), azo-bis-isoisobutyronitrile (AZO initiators), t-butyl peroxybenzoate (Peresters), t-butyl hydroperoxide (Alkyl hydroperoxides), di-t-butyl peroxide (Dialkyl peroxides), and peridicarbonates, among others [25]. All these initiators work in a similar fashion, by the formation of a free radical.

Once the initiation occurs, the propagation undergoes rapidly with the successively addition of monomers to the growing polymer chain. In this process, the radical is held at the termination of the polymer growing chain. This means that the polymerization process is not affected by the polymer chain length. The termination of a growing polymer is then achieved by elimination of the radical specie present at the end of the chain. This may be accomplished by several mechanisms such as termination *by combination*, termination *by disproportionation* and termination by *chain transferring*. In practice, termination by combination occurs when two polymer chains react by their radical ends and form a larger polymer. Termination by disproportionation occurs when a radical polymer chain abstracts a H atom from another radical chain, causing extintion of both, with a consequent formation of a terminal double bond in one chain, and a saturated chain in the other. Finally, termination by chain transferring occurs when the radical is removed by another chemical species. These processes will not be discussed here, but general representations are present in figure 4.11 [25].

$$\mathbf{R_1 - HXC^{\cdot} + {}^{\cdot}CHX - R_2 \longrightarrow R_1 - CHX - CHX - R_2}$$

Termination by combination: the formation of a head-to-head polymer

$$\mathbf{R_1 - HXC^{\cdot} + {}^{\cdot}CHX - R_2 \longrightarrow R_1 = CHX + CH_2X - R_2}$$

Termination by disproportionation: the formation of unsaturated and saturated chain ends

$$\mathbf{R_1 - HXC^{\cdot} + AB \longrightarrow R_1 - HXCA + B^{\cdot}}$$

Termination by chain transfer: termination of a growing chain, but not the free radical

Figure 4.11: *termination* reactions that stop chain growth during emulsion polymerization, including termination by combination, disproportionation, and chain transfer

4.4.3.3- Buffers

A buffer will be included in the dispersion to control the pH. This is an usual addition since some surfactants and initiators are sensitive to pH. Controlling the pH also stabilizes some monomers such as vinyl acetate, which hydrolyse in alkaline environments. Control of pH can also optimize the copolymerization processes, since it influences the polymerization efficiency. For example, the acrylic and methacrylic acids do not copolymerize easily at pH above 5 [28]. Common buffers may include borax, sodium hydrogen phosphate and sodium bicarbonate salts. Most latices are used a pH above 7.5. Whereas during the polymerization processes the pH is normally kept acidic, after this process is complete, the pH is readjusted to higher values. This is normally accomplished by carefully adding a volatile base such as ammonia [28]. Acrylics are particularly unaffected by low pH (especially if containing acidic co-monomers). On the other hand, vinyl acetate are prone to suffer hydrolysis at pH below 4 and above 9 [25].

Beyond the four main compounds present in the polymerisation of a dispersion resin, other additions are also included in the coating in view of improving film formation properties and overall performance of the film. These can include external plasticisers, co-solvents, biocides, thickeners, among others. Such additives will be adressed later in the next section of this chapter. Some examples of acrylic or PVAc waterborne dispersion formulations are presented in table 4.3, which have been taken from specific literature [25]. These are illustrative of the ingredients present in the dispersion polymerization of an acrylic or vinyl resin.

Formulation 1: preparation of methyl methacrylate homopolymer

Ingredient	**Quantity (% weight)**	**Function**
De-ionised water	59.5	medium
Sodium lauryl sulphate	0.8	surfactant
Ammonium persulphate	0.1	initiator
Methyl methacrylate	39.6	monomer
	100	

Formulation 2: preparation of a vinyl acetate homopolymer

Ingredient	**Quantity (% weight)**	**Function**
De-ionised water	43.49	medium
Nonyl phenol + 35 EO	2.07	surfactant
Nonyl phenol + 9.5 EO	1.03	surfactant
Sodium acetate	0.04	pH control
Hydroxyethyl cellulose	1.55	protective colloid
Vinyl acetate	51.76	monomer
Ammonium persulphate	0.06	initiator
	100	

Formulation 3: preparation of a vinyl acetate internally plasticized

Ingredient	**Quantity (% weight)**	**Function**
De-ionised water	42.98	medium
Sodium dodecylbenzene sulphonate	0.26	surfactant
Nonyl phenol + 15 EO	0.87	surfactant
Sodium bicarbonate	0.17	pH control
Hydroxy ethyl cellulose	1.22	protective colloid
Vinyl acetate	46.03	monomer
VeoVa 911	8.25	monomer
Ammonium persulphate	0.22	initiator
	100	

Table 4.3: general recipes for the formulation of dispersion latexes added for illustration purposes of the most common components present in a base formulation. In all formulations are present water monomers, an initiator, a surfactant or more. A protective colloid is also common in these formulations.

4.5- The components used in the production of acrylic and vinyl dispersion paints

When it comes to producing paint, the manufacturer is bound to add other ingredients to the previously prepared acrylic or vinyl dispersion. The general list of ingredients for paint would include the previously prepared water dispersed resin, the pigment(s) for coloration, additives for enhancement of the films properties, solvents to provide fluidity of dispersion and surfactants for wetting and dispersing solids. For the scope of this project, it is of special interest to understand how pigments are introduced in the dispersion by means of surfactants, since the presence of these largely affect the final properties of the dry paint films [26,27,28,35-44].

4.5.1- Pigments (and wetting/dispersion agents)

Pigments are used in paint to confer a desired color, promote hiding characteristics and other optical properties. These particles also impart mechanical strength and protective properties to the paint. In the industry there is a wide selection of pigments available to the paint manufacturers, which can be roughly divided into inorganic or organic pigments. A detailed description of both groups of pigments used in art, with emphasys in modern paints, has been presented by several authors [45-51]. The vast amount of pigments is standardised and listed in the Colour Index (C.I.). To every pigment is associated a a C.I. name composed of two initials and a number, that correspond to the color and tye of pigment, respectively. For example PG 36 is a Pigment Green, where the number 36 stands for a phthalocyanine (chlorinated and brominated). This information is gathered in the Color Index, published by the Society of Dyers and Colourists [52].

The inorganic pigments used today are similar to those traditionally used in oils, such as siennas, umbers, ochres and mars pigments, many types of black pigments such as lamp, mars and bone black. Cadmium, cobalt and chrome compounds are still used as pigments. As for white pigments, titanium white is the most common pigment used in modern formulations, even though zinc white is also available. In table 4.4 are some of the pigments used today in acrylic paints [28,53].

Pigment	**C.I.**	**Chemical composition**
Titanium White	PW6	TiO_2
Zinc White	PW4	ZnO
Cadmium Yellow	PY37	CdS
Mars Yellow	PY42	$Fe_2O_3.H_2O$
Yellow Ochre	PY43	$Fe_2O_3.H_2O$
Cadmium Red	PR108	CdS.xCdSe
Cadmium Orange	PO20	CdS.xCdSe
Chromium Oxide Green	PG17	Cr_2O_3
Ultramarine Blue	PB29	$Na_8Al_6Si_6O_{24}S_x$
Cobalt Blue	PB28	$CoO.Al_2O_3$
Cerulean Blue	PB35	$CoO.SnO_2$
Raw Umber	PBr7	$Fe_2O_3.H_2O.MnO_2$
Burnt Umber	PBr7	$Fe_2O_3.H_2O.MnO_2$
Raw Sienna	PBr7	$Fe_2O_3.H_2O$
Burnt Sienna	PBr7	$Fe_2O_3.H_2O$
Lamp Black	PBk6/7	C
Mars Black	PBk11	Fe_3O_4
Bone Black	PBk9	$Ca_3(PO_4)_2$+C+$CaCO_3$

Table 4.4: inorganic pigments commonly found in modern acrylic and PVAc paints

Organic synthetic pigments are the second major class of pigments. These are true pigments[10], not dyes, and are composed of carbon structures, many aromatic or conjugated double bonds that confere the color of these substances (chromophores). They can also present auxochrome groups that alter the main Hue of the pigment such as keto, thio, nitro and nitroso [46]. Among these pigments, the most numerous class is that associated with the presence of a nitrogen double bond (N=N) named AZO (azoic). This can be divided into monoazo or diazo if there is the presence of one or two N=N bonds in the structure of the compound. On the other hand, the rest of the organic synthetic pigments which do not have N=N bond are classified as non-azoic. These can as well be divided into phthalocyanine, oxazine, anthraquinones, quinacridones and nitroso [48]. A diagram presenting the main families of synthetic organic pigments, as well as some common examples of these compounds are presented in figure 4.12-13, but a more detailed description of these groups of pigments, history, and chemical formulas has been presented elsewhere [46,54].

---

[10] A pigment is a solid particle which is unsoluble in the binding medium.

- **Azoic**
  - Arylide
  - Diarylide
  - ß-Naphthol
  - Naphthol Red
  - Benzimidazolones
  - Disazo
  - Pyrazolone
  - Nickel Azo
- **Non-azoic**
  - Pthalocyanine
  - Quinacridone
  - Perylene/perinone
  - Isoindoline
  - Diketopyrrolo-pyrrole
  - Thioindigo
  - Dioxacine Violet

Figure 4.12: diagram of the main families of synthetic organic pigments, according to the azoic or non-azoic classification.

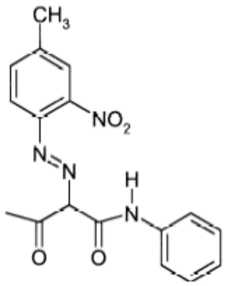
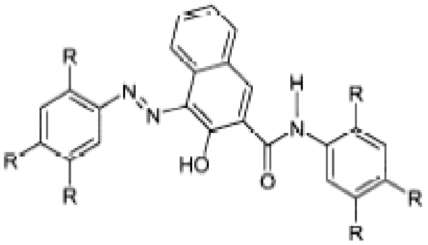
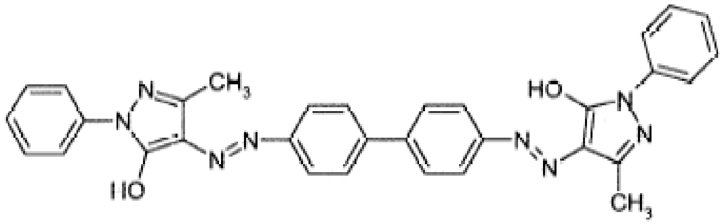
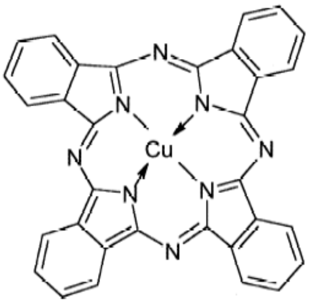
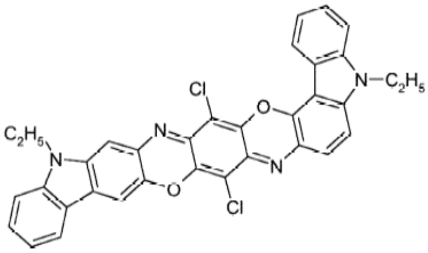
<table>
<tr><td colspan="2"><i>Azoic pigments</i></td></tr>
<tr><td>Arylide yellow (acetoacetic arylide type) (example PY3)</td><td>Naphthol red (PR112, PR146)
R = H, Cl, CH_3, OCH_3, OC_2H_5, NO_2, $NHCOCH_3$, $SO_2N(C_2H_5)_2$, CONHPh, CO_2CH_3</td></tr>
<tr><td colspan="2">Pyrazolone orange (example PO 13)</td></tr>
<tr><td colspan="2"><i>Non-azoic pigments</i></td></tr>
<tr><td>Blue copper pthalocyanine
(example PB 15:3)</td><td>Dixacine violet (PV 23)</td></tr>
</table>

Figure 4.13: a diagram with the most common families of organic synthetic pigments. Some general stuctures of these pigments are also shown. The examples included: PY3, PR112, PR146, PB15:3, PV23, are present in some of the acrylic and PVAc paints prepared in this study (see experimental section). Figures adapted from [46].

For a pigment to have hiding power (absorb light and scatter the incoming light), it must have a higher refractive index than the binding medium. Most pigments posess a refractive index above 2, while the majority of resins have a index of 1.4-1.6. The perfect size of a pigment for maximum scattering is reported to be equal to the length of light inside the particle, which roughly corresponds to half of the wavelength in the air (0.2-0.4 µm). Pigments which have lower refractive index (below 1.65) and poor hiding power with large average particle size are usually referred to as extenders. These can include silica, barium and calcium sulphate, calcium carbonates and silicates such as china clay, talc, mica and bentonite. These are used in paint formulations for lowering the cost of production of the product, and also for controlling rheological properties, gloss reduction and improve mechanical properties [27].

Pigments used in dispersion paints are not added directly to the resin. They are supplied in pastes that are added to the binding medium. These pastes are composed of pigment with surfactants in water (and a small portion of binding medium). The mixture is treated in order to finely separate the particles and stabilize them prior to the addition to the dispersion resin. This is also true for fillers. The process of pigment dispersion in the paste consists of three steps: wetting the particles, physical brakedown of agglomerates and aggregates into primary particles and dispersion of the pigment in water.

Pigments are usually supplied as flocculates and agglomerates of primary particles that are separated by cavities filled with water and air. The wetting stage consists of adding a surfactant that will adsorb onto the pigment surface. Considering that the pigment surface is less polar than water, when the surfactant/wetting agent is introduced in the water medium, it will orient the non-polar end towards the pigment, and the polar group towards the water. This will remove the air and water between pigments and lead to a brake-up of the flocculates and most agglomerates. At this stage, dispersion by mechanical and physicochemical means is used to further separate agglomerates to a fine dispersed state. At this stage the surfactants maintain the stability of the dispersion and avoid reagglomeration (see figure 4.13) [27]. A review of the effects of dispersion latexes in the stabilization of the pigments has been presented by Steward et al [101].

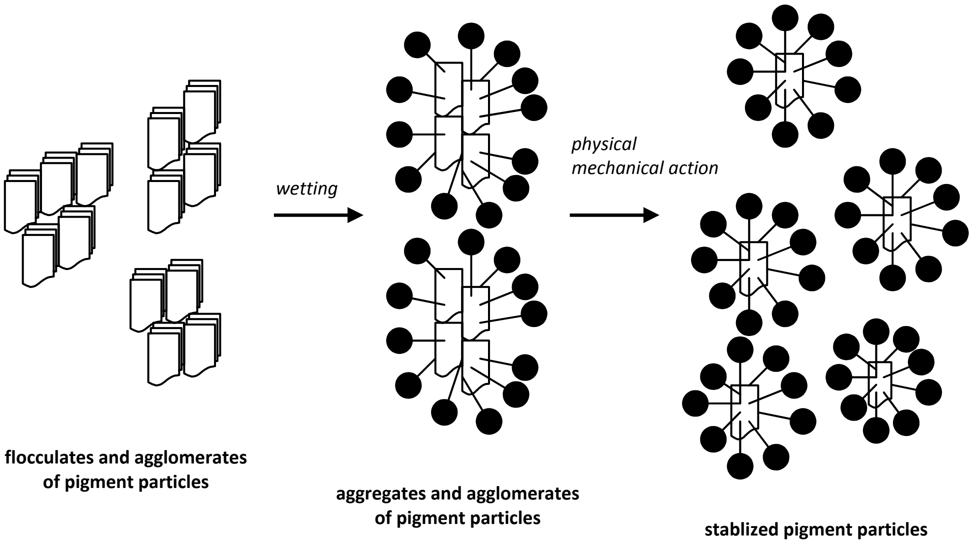


Figure 4.14: simplified representation of the wetting, dispersion and stabilization of the pigment particles in an aqueous medium. The process shown here is representative of pigment wetting and dispersion in waterborne paints

The surfactants used as wetting agents can vary according to the type of pigment. Generally, the inorganic and organic nature of the pigment will govern the selection of the surfactant in the paint making.

For inorganic particles such as titanium dioxide and fillers/extenders, the most effective type of dispersant is polyelectrolytes. There is the inorganic type such as the polymeric phosphates, and the organic type including polyacrylates, copolymers of maleic acid and styrene-acrylic polymers. The organic types are usually oligomers of low molecular weight. Also, many types of amino alcohols are excelent dispersants for waterborne paint formulations. In this case, amino diols are often preferred to simple amino alcohols [27].

Organic pigments are normally far more hydrophobic than inorganic pigments. Often the inorganic polyelectrolytes do not bind satisfactorly onto the pigments surface. Usually, a mixture of anionic and non-ionic surfactants is required to maintain the electrosteric and steric stability of the dispersion, respectively. Similarly to the surfactants present in the latex preparation, the main type of surfactants used is alkylbenzene sulphonates (anionic), alkyl phenol ethoxylates and fatty alcohol ethoxylates (non-ionic). Monoethanolamides ethoxylates of polyunsaturated fatty acids are also used for these purposes. Lecitin as also been reported as a traditional zwitterionic surfactant for organic pigments (normally used in alkyds). Other surfactants that are being used in the paint manufacturing business are the anionic sufactant sodium bis (2-ethylhexyl) sulfosuccinate (AOT) and the non-ionic based on acetylenediol (Surfynol) type surfactants [27].

Other products are added to the paint system to modify and optimize its properties, these include thickeners, solvents, biocides, which are generally in lower concentration than the binder, pigments and surfactants. Neverless, the presence of these additives may affect the final properties of the film. For examples, Murray *et al*. have shown that the addition of Natrosol® (a cellulose type thickener) to an acrylic dispersion (Primal® AC 634) medium can drastically change the resistance to yellowing of the acrylic system after suffering an artificial light aging trial [55]. Some common additives will be adressed in the following section.

4.5.2- Thickeners

Thickeners are used as rheological modifiers. This means they change the viscosity of the dispersion. The viscosity of dispersions varies according to the application intended for each formulation. Thus, rheology modifiers are of the utmost importance. For example, the viscosity at low shear rate is critical, if the paint has too low viscosity, the paint will sag, if too thick the paint will leave brush/roller marks. If the paint is applied in spray then it should have low viscosity. Traditionally, thickeners, or rheology modifiers, include cellulose derivatives such as the non-ionic ethylhydroxyethylcellulose (EHEC), carboxymethylcellulose (CMC). Nowadays, these compounds have been substituted by polymers that exhibit more surface activity. The most important types are named *associative thickeners*, and include the hydrofobically modified ethylhydroxyethylcellulose (HM-EHEC) and the hydrofobically modified ethoxylated urethane (HEUR) [25-28,56-64].

HM-EHEC are ethylhydroxyethylcellulose compounds modified 2-5% with a long-chain alky or alkylaryl substitutent, such as presented in figure 4.14.

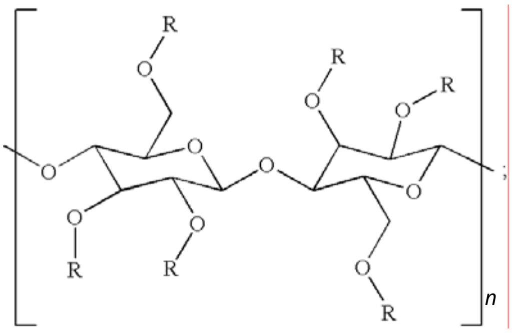


Figure 4.15: general structure of cellulose that can be substituted in R with Ethyl, hydroxyethyl, and also 2-5% long-chain ethoxylated alkyl aryl among others.

HEUR thickeners are prepared by addition of a long-chain alkylmonoisocyanate to polyethylene glycol (PEG). They present a general formula:

C_nH_{2n+1} – NCO – [PEG] – OCN – C_nH_{2n+1}

Associative thickeners can be regarded as very high molecular weight non-ionic surfactants. They interact with all surfaces of the dispersion (pigment and latex) and form networks that increase substantially the viscosity of the formulations [25-28,56-64].

4.5.3- Anti-foam agents

The surfactants present in dispersion formulations that tend to form stable foam, which is generally not desired for the paint manufacturer. Thus, an antifoaming (or defoamer) agent can be included in the paint formulation that can prevent the foam production or destroy foam already formed. Among a variety of compounds that can be used for this purpose there are simple molecules such as octanol, and other more complex compounds such as modified polydimethyldisiloxane, ethoxylated siloxanes (superspreaders), perfluorinated compounds and a series of other surfactants [27,28].

4.5.4- Solvents

Solvents are often added for controling freeze-thaw and coalescing properties. Paints are often tested for freeze-thaw stability, and they should survive five cycles of temperatures going to -16 ºC [25]. At these low temperatures, water freezes and forms crystals. Consequently, the polymer particles are forced together and often coagulate. This process may increase when the water starts to thaw. The manufacturer can add water soluble solvents such as glycols (ethylene and propylene glycol) to lower the freezing point of the system. At the present day, due to toxicity issues, propylene glycol is the most used additive for this purpose [25,28,65,66].

High-boiling solvents can also be added to the dispersion in order to aid the coalescing process and assist in the film formation. These are called coalescing solvents. In the past, ethylene glycol had both the freeze-thaw and coalescing solvent functionalities. Other solvents present in early formulations could include dialkyl succinates, cellosolves (methyl, butyl), and carbitols. In PVAc emulsions, dibutylphthalate or tricresyl phosphate has been used for this purpose. In the mid 60’s, Texanol® was introduced into the market, which is still widely used in paint formulations. The incorporation of solvents such as carbitols may also be necessary for controlling the solubility of associative thickneners (viscosity and capacity for mixing with the dispersion paint) [56]

4.5.5- Biocides

Biocides, or preservatives, are toxic materials used to prevent the biological growth for the time the paint remains in the container. In the 70's, mercury based compunds have been used for this purpose but have been banned in both commercial interior and exterior household paints. This is not the case for artists' paints. Biocides count upon phenyl mercury acetate, oleate and di-phenyl mercury dodecenyl succinate and dioxin (banned). Copper compounds are also used as biocides but give coloration, thus limiting their use. Tin and zinc oxide can also be used even though less efective as biocides. Other non mercurial products are also cited in the literature such as 2-n-octyl-4-isothiazolin-3-one, acrylamide, trademark products such as Skane® (Rhöm and Haas), Super Ad-It® (Tenneco), Nopcocide® (Henkel), Dowicil® (Dow), Preventol® (Bayer) [28,57,67]

4.5.6- External plasticizers

Plasticizers are introduced in formulation of resins to soften the final film according to the desired application. These products have been widely used in PVAc fomulations, since the homopolymer particles are too hard and, at normal temperatures, form brittle products [25]. The formulations were thus softened with plasticizers up to 20% (w/w), which could include dibutyl or diethylphthalates, benzoates, triphenyl phosphate and sulfonamides [3,6,28,68]. External plasticizement may cause conservation problems with the aging of these resins. Typically, a plasticizer will migrate to the surface of the film leaving a non-plasticized film with a tacky and greasy surface that is prone to attract matter and change its appearence [28,69]. In the 1960's, the copolymerization of VAc monomers with other softer monomers such as acrylics and VeoVa helped overcome these problems. Nevertheless, and even though external plasticizement is attributed to past formulations, they have been found in products that are produced nowadays [3,6].

Some examples of acrylic and PVAc water dispersion paint formulations are presented in table 4.5. These have been taken from the same reference as the waterborne resins present in table 4.3 [25]. Some of the additives discussed previously can be readily identified in these products.

Formulation 1: white emulsion paint based on PVAc homopolymer

Ingredient	**Quantity (% weight)**	**Function**
Titanium white	11.79	pigment
Talc	5.89	filler (cost reduction)
Chalk	5.89	filler (cost reduction)
Lithopone (30%ZnS)	15.72	pigment/filler
Methylcellulose (4%)	5.89	thickener/protective colloid
Sodium hexamethaphosphate (5%)	2.36	wetting/stabilizing agent
Water	9.82	medium/solvent
Ammonia (25%)	until pH=8	pH control
grind and then add:		
PVAc (60%)	23.58	polymer/binding medium
Plasticiser (not specified)	3.14	plasticizer
Methyl cellulose (4%)	3.93	protective colloid/thickener
Water	11.79	medium/solvent
Fungicide (not specified)	0.20	preservative
ammonia (25%)	until pH=8	pH control
	100	

Formulation 2: preparation of an exterior acrylic white paint

Ingredient	**Quantity (% weight)**	**Function**
Hydroxy ethyl cellulose (2.5%)	8.370	protective colloid/thickener
Water	5.860	medium/solvent
Tamol 731 (25%)	1.260	dispersant agent
Triton CF-10	0.209	surfactant/wetting agent
Anti-foam (not specified)	0.084	anti-foam/defoamer
Ethylene glycol	2.090	coalescing solvent
Titanium white (rutile)	20.930	pigment
talc	17.580	filler (cost reduction)
grind then add:		
Rhoplex AC-388 (50% non volatile contents)	38.511	polymer/binding medium
Anti-foam (not specified)	0.084	anti-foam/defoamer
Ammonia solution (28%)	0.167	pH control
Tri-butyl phosphate	0.921	
Propylene glycol	2.930	coalescing solvent
Preservative (not specified)	0.167	preservative
Water	0.837	medium/solvent
	100	

4.6- Film formation and mid-to-long term performance and stability of acrylic and vinyl dispersion paints

The drying process of waterborne polymeric systems has been studied over 50 years without universal agreement on the exact mechanisms involved [70,71]. Nevertheless, the basic process can be simplified in three major steps for an ideal latex film and is the general view on film formation of the conservation community. The first step of the drying process is the evaporation of water, at the same rate as pure water or a dilute surfactant solution. Consequently, the spherical particles suspended in the waterborne dispersion become close packed with water filling the intertices between them. The second step begins when further evaporation of water forces the particles to be in contact with each other and deform. The deformation of the particles into polyhedra shape is accompanied by polymer coalescense and subsequent formation of a continuous film. Reviews on the theories and mathematical models of latexes film formation processes have been published elsewhere and are out of the scope of this work [59,60,72].

There are many factors affecting the film formation processes previously described, including particle size, temperature (T), relative humidity (RH) and type of substrate. Temperature and RH affect influence the evaporation rate of water, and, also, the porosity of the substate can absorb or retain water and influence in this process. Particle size is also known to be decisive in the film formation of latexes, as small particles tend to form a more tight arrangement that facilitates the coalescence process. Nevertheless, temperature appears to be the main factor affecting the film formation process. For particles to deform into polyhedra and coalesce, the capillary forces between the spheres must be higher than the forces needed for the polymer particle to deform. This implies that the temperature of the surroundings (and hence the paint itself) must be above the glass temperature of the polymer (Tgº)[11], Below the Tgº, the particles spheres are hard and resist deformation, resulting in a non-fully formed film. The minimum temperature necessary to form a coherent film is named the minimum film formation temperature (MFFT) below which the film does not form. Even though the values of the MFFT varies according to the Tºg of the products (MFFT can be around 12ºC for many acrylic and PVAc formulations) they can be regulated by the use of coalescing solvents.

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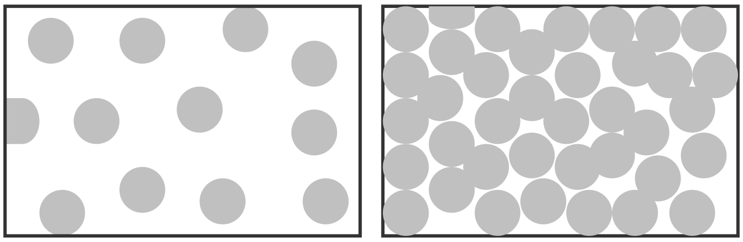
[11] A more detailed description of the glass transition temperature will be given in the section dedicated to the mechanical properties of acrylic and PVAc materials.

I. Dispersion product. The polymer particles are suspended in water

II. Evaporation of water and close-packing of polymer particles



III. Deformation of the polymer particles into polyhedra with further water evaporation

IV. Entanglement of the polymer chains and formation of a continous film - coalescence

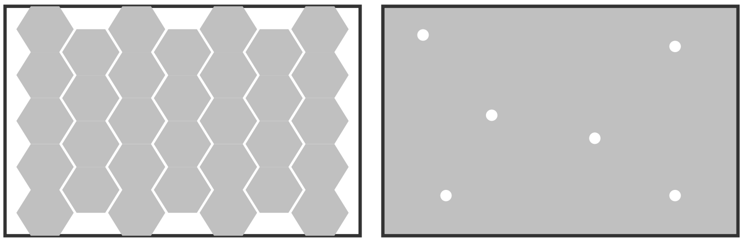


Figure 4.16: traditional representation of the drying and film formation of a dispersion latex

As an acrylic dispersion is a complex system composed of much more than water and the polymer. The presence of other additives, such as surfactants, necessary for the dispersion and polymerization process of the polymer in water should be taken into account. The mutual diffusion mechanism developed by Voyutskii takes into account the presence of surfactants in the drying process of the acrylic dispersion systems. According to this mechanism, during the close packing of the polymers spheres there is an increasing concentration of surfactant in the aqueous phase. This forces the surfactant to move from the polymer-water interface and either dissolve in the polymer phase, or form aggregates between the polymer particles [37,38,73]. As the surfactant is no longer surronding the polymer particles, there can be coalescence.

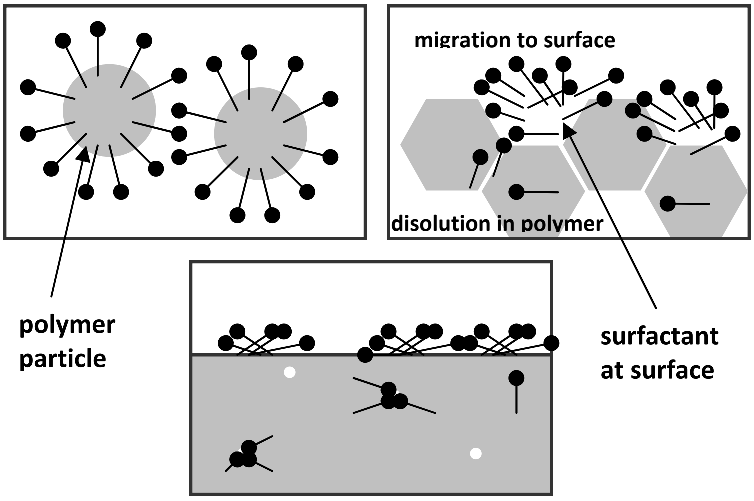


Figure 4.17: the drying and film formation of a dispersion latex taking into account the presence of surfactants. At particle packing, the surfactants are forced to go to the surface or to redissolve into the polymer matrix, allowing particle coalescence [22]

In paint systems, where the pigments (and other additives) are involved, the film formation process presents more variables. Pigments, for instance, can be considered as non deformable particles, and the polymer spheres must be able to deform and flow around these particles and into each other (coalesce). Thus, the polymer must be softer than in an unpigmented system, and water evaporation has to be slow enough to allow this process to happen. The pigment nature, surface, the particle size of the polymer (the smaller and softer particles coalesce first), Tgº, surfactant levels are very important in the film formation of latex pigmented systems.

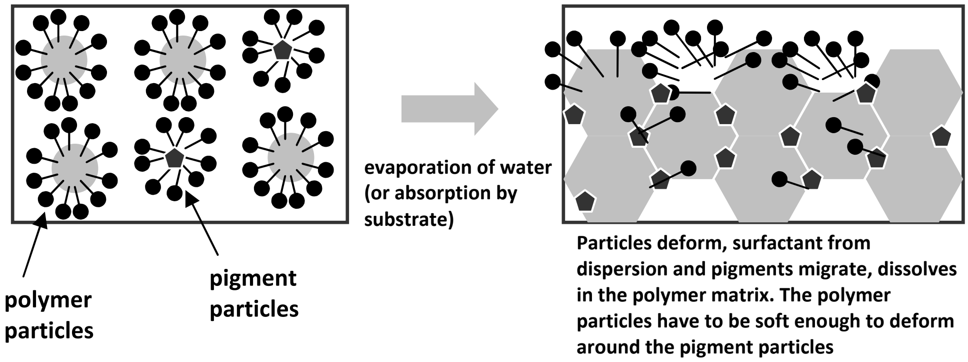


Figure 4.18: a proposed scheme for drying of a dispersion paint taking into accounts the surfactants and pigments (many other additives can be present). The polymer particles have to deform around the pigments so that film formation is achieved. The migration and dissolution of surfactants, as previously described, may also take place [22]

In painting practise, either according to paint manufacturers or from personal interviews with several artists, it appears that it is general belief that acrylic paints dry to the touch over a short period of time (20 minutes to 1 hour). They are said to cure, or achieve full film properties, within three days for thin films, or two to three weeks for thicker applications [22]. In a study coducted by Whitmore, the mechanical properties of Liquitex® medium films were measured periodically during dark storage for several days [73].The films exhibited an increasing Young's modulous[12] until 50 days, when the mechanical properties finally stabilized. This information leads to think that the processes of film formation may take longer than initially expected. These findings can well be compared with other data obtained from the drying of acrylics in studies by Tumosa and Mecklenburg [74]. The authors have shown that acrylic paints and gessoes can loose up to 45% weight from first applying the product over a non porous substrate (polyester sheet) until it is fully dried. The major amount of weight loss was determined in the first 6 hours and has been related to the loss of water and volatile solvents. Overall weight of the test samples stabilized in the first year of drying, but some weight losses raging from 0,1% to 0,6% were detected in the consecutive four years. Not until 4 years drying have the weight of the samples finally reached a stable value. Furthermore, these results are in very good agreement with the data obtained by Down *et al*. whom identified several volatile emissions for both PVAc and acrylic products during the drying stages of these products during period of weeks, which roughly correspond to the curing of the films. Interestingly, the authors also found that PVAc films exhibited the highest amounts of volatile emission when compared to acrylic products, especially related to the emission of acetic acid volatile emissions [75]. The mechanical properties of acrylic paints during the initial weeks of the curing process have been studied by Hagan [76]. The films studied that strength and stiffness increase over the first few weeks with a sudden increase in this trend achieved in the first 2 to 3 weeks, after casting. After 13 months the mechanical properties were still stabilizing, though in a slow linear manner. This has been attributed to the curing (drying and film formation) of these paints.

The studies above mentioned show clearly that both acrylic and poly(vinyl acetate) dispersion paints have an initial stage of evaporation of water and solvents that are associated to the stabilization of the mechanical properties of the film. In figure 4.18 are presented experimental drying curves representative of three Talens® products, a titanium white (high pigment volume concentration (PVC), naphthol red (low PVC) and a gloss binding medium. The weight variation measured is in good agreement with data obtained by Mecklenburg [74] and can be correlated to the data presented by

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[12] Young's Modulus is a measure of stiffness. The higher Young's Modulus value means it takes more stress (or force) to deform the sample, when compared to a material that has a lower Modulus. This concept will be described later in this chapter, in section 4.7.1.

Hagan [76]. These results proved of the outmost importance when testing the performance of these products, especially if the test specimens produced must simulate naturally aged or cured films. Also, this is relevant for the planning adecuate aging trials. Taking into account this data, the samples tested for the scope of this thesis were at least one to two years old or, in many cases, they were three years old.

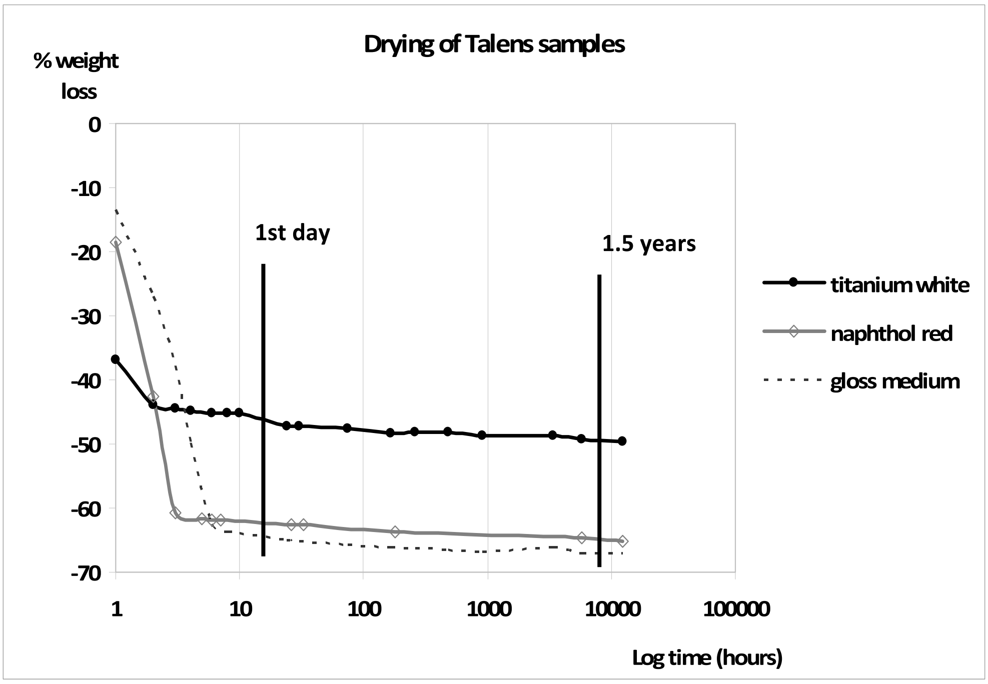

Figure 4.19: the experimental drying curve of three Talens® products, cast over mylar® sheets and left to dry at laboratory conditions. The products were weighted from the first moment of casting (0 hours not shown here due to logarithm scale). The products include titanium white, naphthol red and a gloss medium. After one year and a half of drying, all products are still loosing considerable amounts of weight, which can be related to volatles such as residual water and additives (coalescing solvents). This is in good agreement with the data by Mecklenburg [74]. Also appreciable in this figure is the difference in amount of solids present in titanium white (aprox. 55% solids) and naphtol red (aprox. 35% solids). The latter presents similar solids content to the gloss medium.

4.7- The mechanical properties of acrylic and PVAc paint films in conservation science

The study of the mechanical properties of materials used in cultural heritage is of great interest for conservation science, and has been an approach undertaken by many authors. For instance, Mecklenburg has studied the mechanical properties of the distinct materials present in a painting structure in order to understand their individual roles in the general physical behaviour and deterioration processes when exposed to different environmental conditions [77]. Other authors such as Roche, Hedley and Berger have also studied the mechanical properties of model paints in order to understand the general physical behaviour of canvas paintings [78,79]. These studies are the very basis for the current more permissive environmental and conservation guidelines used in museums all over the world.

But the characterization of the mechanical properties of materials found in cultural heritage can also be used to follow the chemical-physical changes that occur during ageing and conservation treatments such as cleaning. One clear example of this are the studies published by Mecklenburg on the mechanical properties of drying oils mixed with different pigments [81]. The characterization of the different mechanical behaviour during drying and curing of oil films with the presence of different metal ions has been the basis for the understandment of phenomena such as delamination zinc white oil paints, the durability of oils painted with lead white and the weakness of earth colours. Recently, migration of ions across distinct paint layers has been proved to be also affecting the physical properties of paints [82].

Similarly, measuring the mechanical properties of acrylic products has been a useful approach to understand and predict the physical response of such materials with changes in environmental factors such as temperature (T), relative humidity (RH), light and thermal aging [73,75,76,83-88]. The mechanical approach to undertanding materials has also been used to monitor the physical changes occuring after cleaning treatments with water based treatments and solvents [36,60,73,76,89-91]. It is therefore considered interesting to present some basic theory of the mechanical properties of polymers such as the acrylics and PVAcs and the tests conducted in this work to characterize them.

4.7.1- The viscoelastic properties of acrylics and PVAc resins

Acrylics and PVAc paints and coatings are viscoelastic materials [92]. Recognizing this property is the basis to understand the mechanical properties of such materials. A solid can deform either in an elastic and/or viscous way. An ideal elastic deformation (Hookean deformation) is produced when a material elongates under a tensile stress in direct proportion to the stress applied. When the stress is released the material returns to its original dimensions almost instantaneously. This behaviour is usually illustrated by a steel spring. An elastic deformation behaviour obeys Hook's law.

$$\sigma = E.\ \varepsilon$$

σ = *stress* (MPa)
ε = *strain* (deformation units, %)
E = *Young's Modulus* (N/mm^2, MPa)

Where:
$\varepsilon = (L_f - L_0)/L_0$ L_o = original longitud of the test specimen
L_f = streched length

$\sigma = F/A$ F = force apllied
A = cross-sectional area

Figure 4.20: Hook's law, where the linear relationship between the stress and the strain is determined by *E*, the Young's Modulus. The definitions of stress and strain are also presented.

An ideal viscous material (Newtonian fluid) also elongates in direct proportion to the stress is applied. In contrast it does not return to, or even toward, its original dimensions when the stress is released; it experiences permanent deformation. In a viscoelastic material, that has time-depended properties, a deformation can fully recover if the stress is released but it requires time. However, permanent deformation occurs irrespectively of its viscoelastic properties [92,94].

4.7.2- The mechanical properties obtained by stress and strain tests

For the scope of this study are considered essentially the mechancial properties obtained by *stress-strain* tests. In such tests, a strain (deformation/elongation) is applied to a sample of known dimentions, and the stress (force per unit of the original cross-section area) developed by the sample are measured, or vice-versa. A schematic a stress-strain curve depicted in figure 4.21.

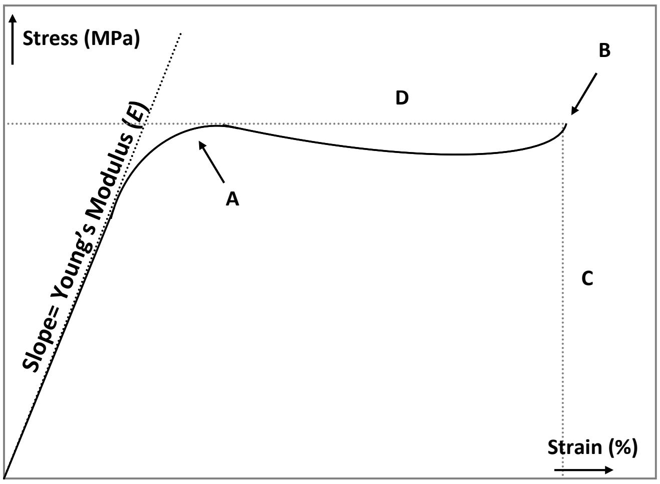

Figure 4.21: a schematic representation of a stress-strain curve for a typical polymer. Pointed out in the figure is [92,94]:

Initial slope *= Young's Modulus (elastic region)*

A *= Yield point (change from elastic to plastic behaviour)*

B *= rupture point*

C *= elongation at brake*
D *= tensile strength*

From this type of curves, information about the elastic and plastic behaviour can be obtained, as well as elongation at brake, tensile strength (how much a sample stretches and how much force does it withstand before rupture) and yield.

The elastic behaviour, or *elasticity*, is the capacity of a material to return to its original shape after a deformation or force has been applied[13]. The elasticity is represented by the Young's modulus (*E*) measured normally in Mega or Giga Pascal (MPa or GPa). *E* is extracted from the linear relationship between stress and strain, obtained from the slope of the initial and linear part of a stress-strain curve, as shown in figure 4.21. The higher Young's Modulus value means it takes more stress (or force) to deform the sample, when compared to a material that has a lower Modulus. This value represents a measure of *stiffness*. The strength of a material is the stress at which it fails. It is possible to have a very stiff material (high modulus) and, at the same time, have a very weak material. Stiffness and strength are independent.

The *elongation at brake* is the amount of deformation the sample exhibits at the moment it brakes. The *tensile strength*, on the other hand, is the value of stress exhibited by the sample at the moment of rupture. If a material has an increasing stiffness and a decreasing ability to stretch when loaded, it is said to become increasingly brittle [92-95].

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[13] This is related to the deformation of carbon-carbon angles in cristaline materials, or due to the separation of chains held by electrostatic forces in amorphous materials.

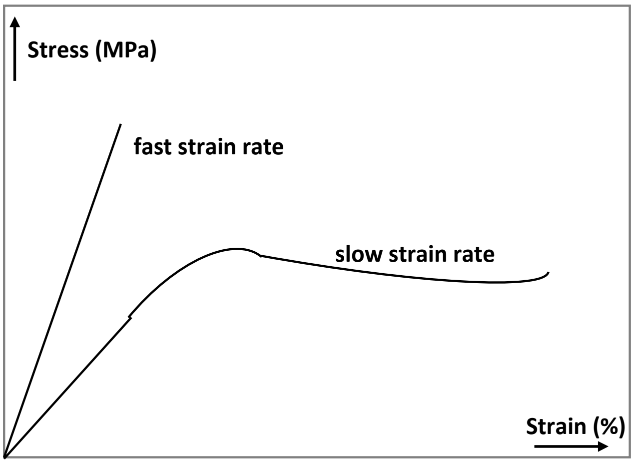

Figure 4.22: representation of the effects of strain rate in the mechanical properties of viscoelastic materials [92-95].

It is important to mention that the mechanical behaviour of viscoelastic materials are dependent on the rate of the application of the strain or stress. The rate of deformation is dependent on the viscosity of the material which, by turn, depends on temperature. Thus, in a viscoelastic material, the rate of deformation and temperature will affect the resulting mechanical properties. In figure 4.22, is presented a schematic result of two similar samples at the same temperature, and measured at two strain rates, fast and slow [92]. At very fast rates of strain application these products may present a glassy behaviour with a brake without showing yield, whereas at low strain rates these materials are rubbery and present yield and larger deformation values [95].

When a viscoelastic material is subjected to a constant deformation at the same environmental (T and RH) conditions, the stress decreases rapidly until it stabilizes into a constant value. This value is the equilibrium between the cohesion forces of the material and the external agent (strain, in this case)[14] and is called *relaxation*, shown in Figure 4.23 [94,95]. A stress-strain test can thus be obtained by several relaxation tests after a strain or load application, as shown in figure 4.24. This procedure was adopted in the mechanical tests in this work, as explained in the experimental section.

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[14] In polymers this is related to a rearrangement of the molecules to minimize energy and re-equilibrate with the strain.

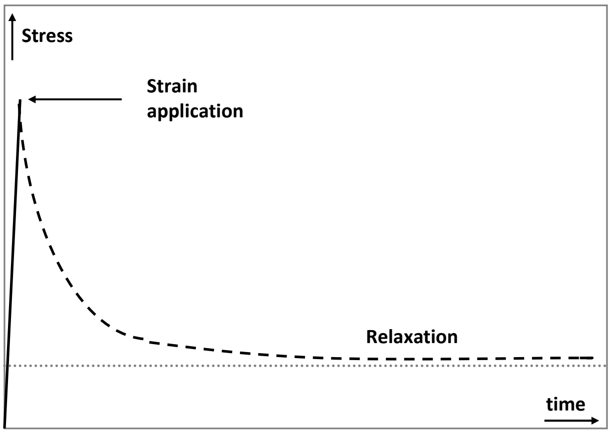

Figure 4.23: a schematic representation of a relaxation test. An initial strain is applied and maintained; whereas the changes in stress are measured with time. It is also visible that the stress tends to an equilibrium after a certain amount of time [94,95].

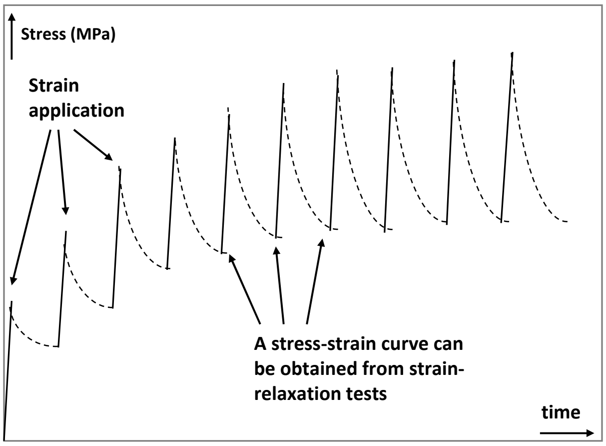

Figure 4.24: a schematic representation of a stress-strain curve obtained by several relaxation tests. The strains are applied periodically after the material relaxes. According to the time of relaxation the material can be tested at full equilibrium, or semi-equilibrium. If the values of stress obtained from relaxation (roughly represented in the black line) are plotted into a stress-strain curve, the mechanical properties of materials at relaxation conditions can be obtained [94,95].

Mecklenburg has shown, for different materials, that low strain rates and equilibrium conditions, or relaxation, can be used for characterizing materials exposed to normal changes in environmental conditions. He also showed that values of modulus and elongation at brake and strength in these materials strongly depended on the test conditions (strain rate, relaxation time, and control of enviromental conditions) [95]. This was also stated by Hagan, who claimed the necessity of specification of test conditions for testing acrylic paint samples [76].

4.7.3- The glass transition temperature and its influence in the mechanical properties of acrylic and PVAc products

Acrylics and PVAcs are thermoplastic resins. This means that they can present different physical properties according to temperature. The most important value in the study of thermoplastic polymers is the glass transition temperature (Tg). It represents the value, or most accurately the range of values, of temperatures where a polymer changes from a glassy to a rubbery behaviour. Consequently, a polymer below its Tg is stiff and brittle, whereas above its Tg it is flexible and has a high elongation at brake. The general trends in the mechanical properties of thermoplastic polymers with temperature, focusing in the regions immediately above and below the Tg are presented in figure 4.25 [25].

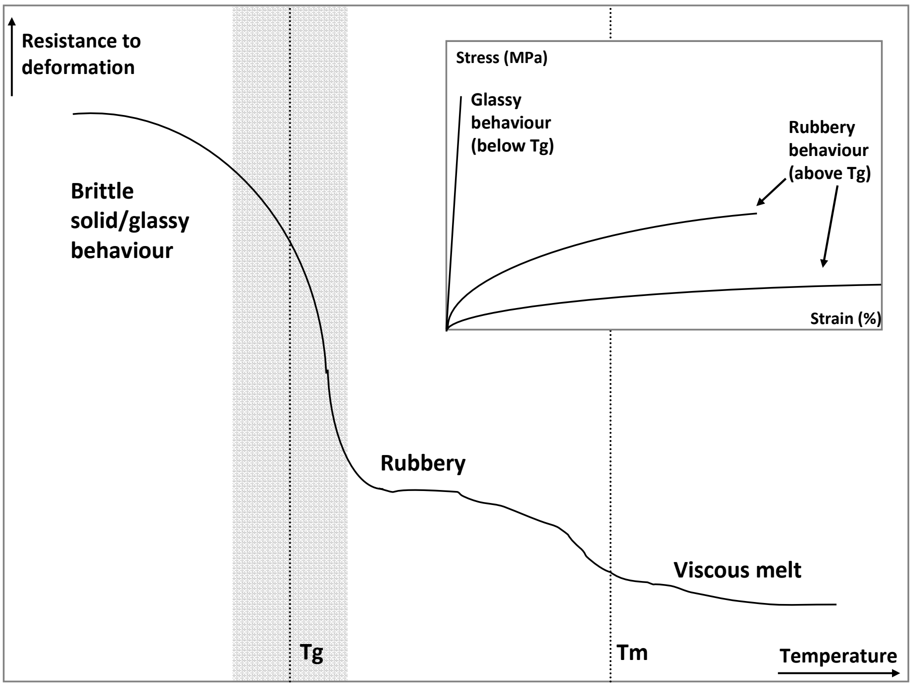

Figure 4.25: the resistance to deformation behaviour of thermoplastic polymers with changes in temperature. In this figure is pointed out the visible the glass temperature (Tg) range. In this range the polymer changes from a brittle solid (glassy behaviour) to a rubbery state. With increasing temperature the material may melt if it does not deteriorate first.

The effects of temperature on the mechanical properties of coatings and its relation to the Tg is fairly known in the industry [86,77,92,94]: acrylic paints increase their stiffness as the temperature is lowered with some reduction in the capacity for elongation. When the temperatures reach values below the Tg, the samples evidenced a significant decrease in elongation properties (and increase in stiffness), thus turning into a brittle material. Several authors have measured the mechanical properties of acrylic paint samples and showed that they are above their Tg at normal environmental temperature, as expected [86,87,92,93,99,100]. Usually, Tg of acrylics is around 5-15ºC (these values vary according to formulation and type of analysis performed). However, Mecklenburg has shown that the Tg is strongly affected by relative humidity (%RH), and this will be referenced later in this chapter [93,100].

4.7.4- Other factors that influence the mechanical properties of acrylic and PVAc products

In the previous section the effects of temperature in mechanical properties of acrylic and PVAc paint films have been described. Nevertheless, other factors such as moisture content (or exposure to different relative humidity environmental conditions) or pigment volume concentration (PVC) can affect the mechanical properties of a paint sample [25,84,96-97].

Hagan has described the behaviour of some acrylic dispersion paints at different values of relative humidities with constant temperature. For the specimens tested it was evident that acrylics loose elongation properties at low RH values, whereas increase elongation at brake in high RH conditions. The stiffness of the test specimens accordingly increases at low RH values and decreases at higher HR values. The effect of the moisture content in the mechanical properties of acrylic films was related to a plasticizement effect and rupture of hydrogen bonding with the presence of water in the polymer chains and this can be increased with the presence of hygroscopic additives [84].

Mecklenburg, on the other hand, has characterized the mechanical behaviour of acrylic paint samples at low temperatures at 5% RH and at 50% RH. From the data derived from the stress-strain, it was shown that acrylic paints lose the ability to plastically deform in response to an applied force below temperatures of 5° C at 50% RH, and below 11° C at 5% RH. These results show that the Tg of these products is RH dependent [93]:

> *"The modulus and strength of acrylic paints rise with decreasing temperature. At 50 % (%RH) some acrylic paints became brittle at 5° C, and all acrylic paint types were brittle below -1 . 4° C. At 5% RH, some acrylic paint types became brittle at 11° C, and all had become brittle below 5° C. Correlation of the brittleness of acrylic paints with the Tg, of acrylic paints perhaps indicates that acrylic paints pass through a Tg, near 5° at 50% RH and 10° C at 5% RH. Atmospheric water would then be acting like a plasticizer and would lower the Tg."*

The effects of pigment volume concentration in the mechanical properties of acrylic paint films have also been studied by Hagan [72,76]. The pigment particles are hard solids and add constraint to the polymer binder, decreasing mobility of the polymer chains. With increasing concentration of pigment, the paint films experience an increase of stiffness. When the amount of pigment reaches a point named critical pigment volume concentration (CPVC), the pigment particles become poorly bound and the film starts loosing structural integrity. This is reflected in the mechanical properties, with resulting films above CPVC showing low strength and elongation at brake [42,83,96-98].

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PART III

5- Experimental

5- Reference materials

5.1.1- Reference acrylics products

The waterborne acrylic colours and media prepared in this study are summarized in table 5.1. The acrylic paint brands include Liquitex® (Heavy Body), Royal Talens® (Amsterdam), Vallejo® (Studio) and Pébéo® (Studio). The name and the description of each colour as described in the manufacturer's catalog. All colours were labelled as *professional* artists' acrylic colours. The products were purchased in 2008, in Valencia, Spain.

Commercial brand	**Colour**	**composition declared by the manufacturer**
Liquitex®	titanium white	titanium dioxide (PW 6)
	transparent mixing white	zinc white (PW 4)
	cadmium yellow medium	cadmium yellow (PY 35)
	cadmium red medium	cadmium red (PR 108)
	ultramarine blue	complex silicate of sodium and aluminum with sulfur (PB 29)
	ivory black	bone black (PBk 9)
	burnt umber	calcined iron oxide containing manganese (PBr 7)
	raw umber	natural iron oxide containing Manganese (PBr 7)
	burnt sienna	calcined iron oxide (PBr 7)
	iron oxide (PBr 7)	synthetic red iron oxide (PR 101)
	raw sienna	natural iron oxide (PBr 7)
	cerulean blue cobalt blue	oxides of cobalt and aluminum (PB 28)
	phthalocyanine blue (red shade)	phthalocyanine blue epsilon (PB15:6)
	yellow Light hansa	arylide yellow 10G (PY 3)
	naphthol crimson	naphthol carbamide (PR 170 F5RK)
	dioxazine purple	carbazole dioxozine (PV 23 RS)
	gloss medium and varnish	acrylic medium and varnish
Royal Talens®	titanium white	titanium dioxide (PW 6)
	zinc oxide	zinc white (PW 4)
	raw sienna	natural iron oxide (PBr 7)
	black oxide	synthetic iron oxide (PBk11)
	naphthol red	naphthol red (PR112)
	phthalocyanine blue	phthalocyanine blue (PB15)
	extra gel medium	acrylic medium
	gloss medium	acrylic medium
Vallejo®	titanium white rutile	titanium dioxide (PW6)
	ultramarine blue	polysulphide of sodium alumino silicate (PB29)
	permanent violet	dioxazine (PV23)
	mars red	synthetic iron oxide (PR101)
	mars black	synthetic iron oxide (PBk11)
	phthalo blue	copper phthalocyanine (PB15:3)
	naphthol crimson	monoazo (PR146)
Pébéo®	dark ultramarine blue	(PB29-PR19-PB15:3)
	raw sienna	(PY42-PR101-PBk11)
	red ochre	(PR101)
	titanium white	(PW6)
	raw umber	(PY42-PY83-PR22-PBk7)
	burnt umber	(PR101-PBk11-PBk7- PR22)
	naphtol carmin crimsom	(PR146-PR112-PO13)
	phthalocyanine blue	(PB15:3)

Table 5.1: waterborne acrylic paints sorted by brand and type of pigments. All colours were prepared as thin films over Mylar® sheets.

5.1.2- Reference poly(vinyl acetate) (PVAc) products

The PVAc waterborne products prepared as thin films over Mylar® sheets are summarized in table 5.2. These comprise the artists' paint brand Flashe® from LeFranc & Bourgeois, and three unpigmented products Mowilith® DMC2 (Hoechst), Vinavil® 59 (Società Rhodiatoce of the Montecatini Group), and Conrayt®(Rayt SA).

Commercial brand	colour	composition declared by the manufacturer
Flashe®	white	(PW5-PW6)
	raw sienna	(PY42-PR101)
	burnt sienna	(PR101)
	raw umber	(PY42-PBr7)
	burnt umber	(PBr7)
	ultramarine blue	(PB29)
	armour green	(PG7)
	senegal yellow	(PY74)
	oriental red	(PR112)
Mowilith®	Mowilith® DMC2	VAc-butylmaleate
Vinavil®	Vinavil® 59	PVAc
Conrayt®	Conrayt®	PVAc

Table 5.2- list of the PVAc products prepared over Mylar® sheets.

5.1.3- Other reference materials

Ligroin, white spirit and ethanol were supplied by Panreac®; acetone, Triton® X-100 and Brij® 30 were suplied by Sigma–Aldrich®. Carbopol® Ultrez 21, Agar-agar®, Vanzan® NF-C and Klucel® G and Mylar® (120 micron thick) were purchased in CTS, Spain.

5.2- Sample preparation

Acrylics and PVAc products were prepared as draw-downs over 120 µm non-siliconed polyester sheets (Mylar®). The sheets were placed horizontally over laboratory stands and six tape stripes were used to control thickness. The materials were applied over the Mylar® with a spatula. The films obtained were 300-400 mm long and 50 mm wide. The average thickness after drying ranges from 0.10 to 0.15 mm for most colours and media. After one day of drying, the tape stripes were removed from the polyester sheets in order to avoid eventual interferences in the natural aging of the paint film specimens. The films were left to dry vertically for approximately one to two years before testing.

5.3- Analytical techniques

5.3.1- Weight measurements

Weight measurements were performed with a Precisa® XT 120-A precision balance with a weighting range of 120 g and readability of 0.001 g.

5.3.2- Fourier Transformed Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR)

The infrared (IR) spectra in ATR mode were obtained using a Vertex® 70 Fourier transform infrared spectrometer with an fast-recovery deuterated triglycine sulphate, temperature-stabilised coated detector and a MKII Golden Gate ATR accessory. A total of 32 scans were collected at a resolution of 4 cm^{-1}, and the spectra were processed using the OPUS/IR software. The sample preparation consisted of introducing the material desired for testing inside the compression cell and the samples were ready for the analysis.

5.3.3- Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-CG-MS)

Pyrolysis–gas chromatography–mass spectrometry was carried out with an integrated system composed of a CDS Pyroprobe 1000 heated filament pyrolyser (Analytical Inc., New York, USA), and an Agilent Technologies (Palo Alto, Ca., USA) 6890N gas chromatograph coupled with an Agilent Technologies 5973N mass spectrometer and equipped with a pyrolysis injection system. An HP-5MS capillary column (5 % phenyl methylpolysiloxane; 30 m, 0.25 mm i.d., 0.25 µm) was used.

In-situ thermally assisted pyrolysis-silylation GC-MS using HMDS was performed with a temperature of pyrolysis of 650 or 700 ºC, for 10 seconds using a precalibrated Pt coil-type pyrolyser (CDS Pyprobe).

The pyrolyser interface and the inlet were set at 250 ºC. Samples were injected in split mode (split ratio 1:40). The GC temperature was initially 50 ºC for 2 min, and then programmed at 5° min^{-1} to 100 ºC, then at 15º min^{-1} to 295 º°C, held for 10 min. The electronic pressure control was set to the constant flow mode with vacuum compensation. Helium gas flow was set at 1.2 mL min^{-1}

Ions were generated by electron-impact (EI) ionisation (electron energy 70 eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was scanned from m/z =20 to m/z =800, with a cycle time of one second. Agilent Chemstation software G1701CA MSD was used for GC–MS control, peak integration, and mass spectra evaluation. Tuning and calibration of the mass spectrometer was checked using perfluorotributylamine (PFTBA). EI mass spectra were acquired in the total-ion monitoring mode and Peak area (TIC) data were used to obtain values of peak area percentage. The temperatures of the interface and the source were 28 0ºC and 150 ºC, respectively.

Compounds were identified by use of the NIST and Wiley Library of Mass Spectra and a library created by the authors for acrylic compounds.

5.3.4- Scanning Electron Microcope with Energy Dispersion X-ray fluorescence analysis (SEM-EDX)

Scanning electron microscopy–energy-dispersive X-ray microanalysis Surfaces and cross sections of the film specimens were monitored using a Jeol® JSM 6300 scanning electron microscope operating with a Link-Oxford-Isis X-ray microanalysis system. The analytical conditions were 10-kV accelerating voltage and 2×10^{-9} A beam current. Samples were gold-coated to eliminate charging effects.

5.3.5- Stress-strain tests

The stress-strain tests were performed with tensile testers in a controlled environment. The equipment consisted of a methacrylate box that acts as a climatic chamber where relative humidity (% RH) can be kept constant with trays of buffered silica gel, and ambient temperature (T) swings avoided. The specimens were mounted in the testing gages and conditioned in the chamber for 48 h at 50 (±0.5)% RH and 23 (±0.5)ºC prior to testing. The tests were run under the same environmental conditions. The average sample size was 5 mm (width) × 0.10-0.15 mm (thickness) x 15 mm (length).

The stress-strain tests performed for all acrylic paints, media and PVAc media consisted of strain applications every 30 seconds of stress-relaxation. The strain applications consisted of 0.5 strain increments in the knobs, which is equivalent to a 5% in length application for 15 mm length specimens. The chosen strain rate leads to relatively fast stress-strain tests of 600% length of the test sample per hour. More details on the development of these test protocols is included in Appendix D.

A different test protocol was chosen for testing the Flashe® paint samples, due to their reduced flexibility. The tests were performed at slower strain rates of 0.05 increments every 30 seconds of stress relaxation. Three replicas were tested for confirming the consistency of the results obtained.

5.4- Artificial ageing tests

The aging trials were performed with two aging regimes: simulated daylight and UV light aging. The specifications of each artificial ageing regime are described as follows.

5.4.1- Simulated daylight aging conditions

Daylight aging was carried out in an ATLAS Ci4000 Weather-O-meter with a Xenon Arc Lamp Type S-filter, which significantly reduces radiation below 300 nm, simulating natural daylight. Test conditions were 1.1 W/m^2 in the visible range at 420 nm (115000 Lux) and, at 300-400 nm, 56 W/m^2. The average temperature for 400 hours aging test was 26ºC and for 800 hours was 27 ºC. Relative

Humidity (%RH) was 35-40 %. Black panels temperature was 42 ºC, black standard temperature was 52 ºC

At the previously described ageing conditions, and assuming the reciprocity law following the Bunsen and Roscoe's classical model[15], 400 hours and 800 hours represent 102 and 204 years, respectively, according to Whitmore and Colaluca[16], or 74 and 153 according to Learner[17].

5.4.2- UV light aging conditions

A bank of three QUVA-351 nm fluorescente tubes that simulate high energetic visible wavelenghts (peak at 351 nm) and UV radiation entering through a widow glass were used to perform the UV ageing trials. The samples were placed inside a wooden box at 200 mm from the light source. The light measured in the surface of the samples was 804 lux for the visible range, and 612 W/m^2 for UV range. Temperature was average 34ºC, and %RH aproximately 15-20%. The test samples were aged for 400, 800 and 1200 hours. A selection of samples was further aged for 2500 hours.

In order to separate the possible effects caused by the temperature inside the chamber from the effects of light, a set of test specimens was introduced in the UV-light aging box and covered from exposure to light. Thus, the specimens received a mild thermal aging in the dark for a total of 1200 hours at average temperature of 34ºC and 15-20%RH.

5.5- Cleaning tests

Cleaning tests consisted of solubility tests, immersion tests, swabbing and cleaning tests with gels and emulsions. These trials were performed on rectangular samples separated from their Mylar® support. The dimensions of the films were 30 mm x 50 mm and weighted approximately 0.4-0.5 g (depending on Pigment Volume Concentration[18] (PVC) and pigment specific gravity).

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[15] The Bunsen-Roscoe law (BRL) of reciprocity states that a certain effect is directly proportional to the total energy dose irrespective of the administered regime.[1] Dose is the product of intensity and the duration of exposure and thus the time required to deliver a certain dose is influenced by the intensity of the source and whether the exposure is continuous or fractionated.

[16] According to Whitmore [1], the total exposure to light in a museum, refered as "museum year" is:
~3000 hours x 150 lux = 450000 lux hours = 450 Klux hours.

[17] According to Learner [2], the total exposure to light in a museum, refered as "museum year" is:
~3000 hours x 200 lux = 600000 lux hours = 600 Klux hours.

[18] Pigment Volume Concentration is an expression that relates the amount of pigment with the amount of binding medium present in a coating. It is expressed in percentage (%) and is defined as:

$$\% \text{PVC} = 100 * \text{Volume}_{\text{pigment}} / (\text{Volume}_{\text{pigment}} + \text{Volume}_{\text{non-volatile binder}})$$

5.5.1- Solubility tests

The tests performed for determining the solubility of acrylic and PVAc in organic solvents consisted of a solubility test proposed by Paolo Cremonesi [3]. It consists of a series of mixtures of ligroin and acetone, ligroin and ethanol, and acetone and ethanol (LA-LE-AE). By mixing these solvents in different proportions a wide range of polarity values can be covered in the TEAS chart, and it is possible to cover much more area of the solubility triangle than, for example, the Feller's solubility test [3]. Another advantage of this test is that the three solvents used are less toxic and can be stored for more amount of time when compared to Feller's test.

The proportions of these solvents and the resulting polarities are shown in table 5.3, and the range of polarities covered in the TEAS chart present in figure 5.1.

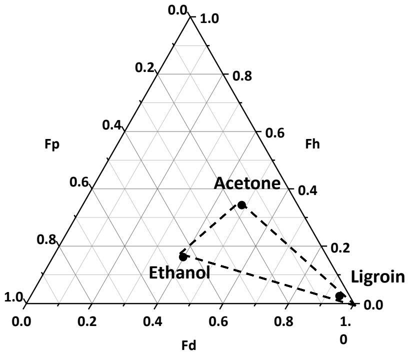

Figure 5.1: the polarity values of the LA-LE-AE mixtures from the solubility test cover an area of interest for the solubility of cultural materials in the TEAS chart.

Mixture abbreviation	% volume			solubility parameters		
	ligroin	acetone	ethanol	Fd	Fp	Fh
L	100	0	-	97	2	1
LA1	90	10	-	92	5	3
LA2	80	20	-	87	8	5
LA3	70	30	-	82	11	7
LA4	60	40	-	77	14	9
LA5	50	50	-	72	17	11
LA6	40	60	-	67	20	13
LA7	30	70	-	62	23	15
LA8	20	80	-	57	26	17
LA9	10	90	-	52	29	19
A	0	100	-	47	32	21
LE	90	-	10	91	4	5
LE	80	-	20	85	5	10
LE	70	-	30	79	7	14
LE	60	-	40	73	8	19
LE	50	-	50	67	10	23
LE	40	-	60	60	12	28
LE	30	-	70	54	13	33
LE	20	-	80	48	15	37
LE	10	-	90	42	16	42
E	0	-	100	36	18	46
AE1	0	75	25	44	29	27
AE2	0	50	50	42	25	33
AE3	0	25	75	39	21	40

Table 5.2: summary table of the preparation of the LA-LE-EA solubility tests. The polarity values obtained from each mixture are shown in the right of the table.

5.5.2- Immersion tests

Acrylic and PVAc tests specimens with dimensions of approximately 20 mm x 50 mm were immersed in 40 ml of deionized water or solvents (ethanol, acetone, white spirit, ligroin) for 20 minutes or 12 hours. For obtaining absorption and drying curves for the 20 minutes immersion tests, the specimens were immersed in water/solvent and weighted periodically every five minutes. The resulting data is plotted in a % weight vs time scale.

Prior to mechanical or chemical characterization, the test specimens subjected to immersions were kept at laboratory conditions from one to three months. An aliquot of the liquid extract obtained during immersion was preserved and another aliquot was dried at 40ºC in a laboratory oven and then analyzed.

5.5.3- Swabbing tests

Acrylic and PVAc tests specimens with dimensions of approximately 20 mm x 50 mm were swab rolled with sterilised laboratory cotton swabs. The swabs were immersed in deionised water and excess of water was removed with laboratory paper. The paint films were gently swabbed for approximately 30 times per minute (covering all surface and edges). The swabbs were changed about every minute. For weight measurements, the samples were dried out of excess of water with a laboratory paper and weighted directly.

5.5.4- Gels and emulsion cleaning methods

Four gellifying agents, Vanzan® NF-C, Klucel® G, Carbopol® Ultrez 21 and Agar-agar® were used to prepare aqueous gels.

The Vanzan® NF-C (a xanthan gum) water based gel was prepared by mixing 2 g of Vanzan® in 100 ml deionised water.

The Klucel G® (hydroxypropylcellulose) water based gel was prepared by mixing 4 g of Klucel G® in 100 ml deionised water.

Carbopol® Ultrez 21 (polyacrylic acid) water based gel was prepared by slowly adding 2 g of the polyacrylic acid in 100 ml deionized water (no stirring). After the product is hydrated (about five minutes) a NaOH 1M alkaline solution is used to neutralize the acid and form a gel. The addition of NaOH was added until the Carbopol® gel was of pH=6. The changes in pH were controlled by pH stripes.

The gels were applied with a brush on top of the test samples. A silicone coated Mylar® sheet was put on top of the applied gel to control evaporation of water.

Two Agar-agar® (an agarose polysaccharide) gels were prepared for this study. One gel was prepared by adding 1 g of agarose in 100 ml water, and another 2 g in 100 ml water. The solutions were then heated to 90 ºC and lef to cool down in a plain container. The resulting gels were rigid, especially the second one. The excess of water was dryed with laboratory paper from the surface of the gels and then they were deposed on the surface of the test specimens.

A Water-in-Oil emulsion system (W/O) was also tested. It was prepared by mixing firstly 10 ml water with 4 ml Brij 30 (nonionic polyoxyethylene surfactant) and mixed with a battery stirrer (an electric stirrer should not be used for safety reasons). After a dense white foam was prepared, 90 ml ligroin was slowly added and stirred until a buttery consistency was achieved. The emulsion was applied with a brush on the surface of the test samples with a silicone coated Mylar® sheet on top to avoid evaporation of solvents.

5.5.5- References

[1] Whitmore PM, Colaluca VG (1995) Stud Conserv 40:51–64

[2] Learner T, Chiantore O, Scalarone D (2002) In: Preprints ICOM ommittee for Conservation 13th Triennial Meeting. James & James, London: 911–919

[3] Cremonesi P (2004) L’uso dei solventi organici nella pulitura di opere policrome. Il Prato. Saonara, Seconda edizione

PART IV

6-Results and Discussion

6.1- Characterisation of acrylic and PVAc test specimens

6.2- The effects of light in modern acrylic and PVAc dispersion paints and binding media: Daylight and UV light aging

6.3- The effects of cleaning treatments in acrylic and PVAc films

6.1- Characterization of acrylic and PVAc test specimens

6.1- Characterization of acrylic and PVAc test specimens

The following section of this work is focused on the chemical and mechanical characterization of acrylic and PVAc products prepared as thin films over mylar sheets.

The chemical composition has been characterized by means of Fourier Transformed Infrared Spectroscopy-Attenuated Total Reflection (FTIR-ATR) and Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS). In situ thermally asisted Pyrolysis-Silylation-Gas Chromatography-Mas Spectrometry (Py-Silylation-GC-MS) (an analytical method consisting of Hexamethyldisilazane (HMDS) as a derivatizing reagent for Py-GC-MS) has been used for enhancing the resolution of the analyses and complement results obtained by means of conventional Py-GC-MS[19].

The mechanical properties of acrylic and PVAc test specimens were determined by stress-strain tests at fast loading rates and semi-equilibrium conditions (30 seconds relaxation)[20]. These are test conditions that avoid time dependent effects, as discussed in the introduction of this work. The tests were conducted at fast strains rates in order to achieve sample's failure, and thus determine the ultimate strain and stresses. In many cases, this was not possible due to the flexibility of acrylics that were superior to the maximum distance between gages (strains above 500%).

Studying the composition and mechanical properties of a large matrix of samples was important to determine the characteristics of the different films according to the type of binding medium and pigments/fillers. Also, it allowed narrowing the test matrix for the aging trials and cleaning tests that compose the following chapters of this work.

The results are divided into the two families of products tested: acrylics and poly(vinylacetates), and representative results are discussed.

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[19] The adaptation of this method to the study of additives present in PVAc paints is shown in Appendix E.

[20] More information on the adaptation of this method to the study of acrylic and PVAc test specimens is presented in Appendix D.

6.1.1- Acrylics

6.1.1.1- FTIR-ATR

A summary of the main absorptions that can be used to identify BA-MMA, EA-MMA and styrene-acrylic copolymers is presented in Table 6.1.1 is presented [1-4]. This table is included early in this text to serve as a guide to the identification of the main polymer aborptions present in the acrylic samples.

Band assignment	**Wavenumber region**	**p(nBA-MMA)**	**p(EA-MMA)**	**p(styrene-*acrylic*)**
C-H[a] and –C=C-[b] stretching	(3100-2800 cm^{-1})	-	-	3084[b]
		-	-	3063[b]
		-	-	3030[b]
		-	2985[a]	
		2960[a]	2954[a]	
		2938[a] (shoulder)	2910[a]	
		2878[a]	2878[a]	
		2850[a] (shoulder)	-	
C=O carbonyl stretching	(1750-1700 cm^{-1})	1730	1730	
Aromatic “ring breathing”	(1650-1450 cm^{-1})			1604
				1496
		-	-	1456
C-H bending	(1500-1300 cm^{-1})	1466 (shoulder)	1465 (shoulder)	
		1452	1449	
		1387	1383	
		1361	-	
		1344	-	
C-O and C-C stretching	(1250-900 cm^{-1})	-	1297	
		1240	1239	
		1170	1178	
		1150 (shoulder)	1162	
		-	1118	
		1067	-	
		1027	1029	
		992	-	
		963	-	
		947	-	
Aromating ring C-H rocking	(900-600 cm^{-1})	-	-	761
		-	-	702
C-H rocking	(900-600 cm^{-1})	-	854	
		844	-	
		756	761	

Table 6.1.1: IR characteristic absorptions of BA-MMA, EA-MMA and acrylic-styrene, commonly used as binding media in acrylic dispersion paints.

In Figure 6.1.1 are shown two FTIR-ATR spectra from Liquitex® gloss medium and varnish obtained 2 weeks and 4 months after its casting. Two diagnostic peaks are readilly identified. A strong and sharp absorption at 1730 cm^{-1} corresponds to the stretching vibration of the carbonyl group (–C=O), which is followed with a strong absorption at 1145 cm^{-1} with a shoulder at 1160 cm^{-1} from the streching vibration of the ester groups (-C-C(=O)-O-). Both peaks are characteristic of acrylics [1-4].

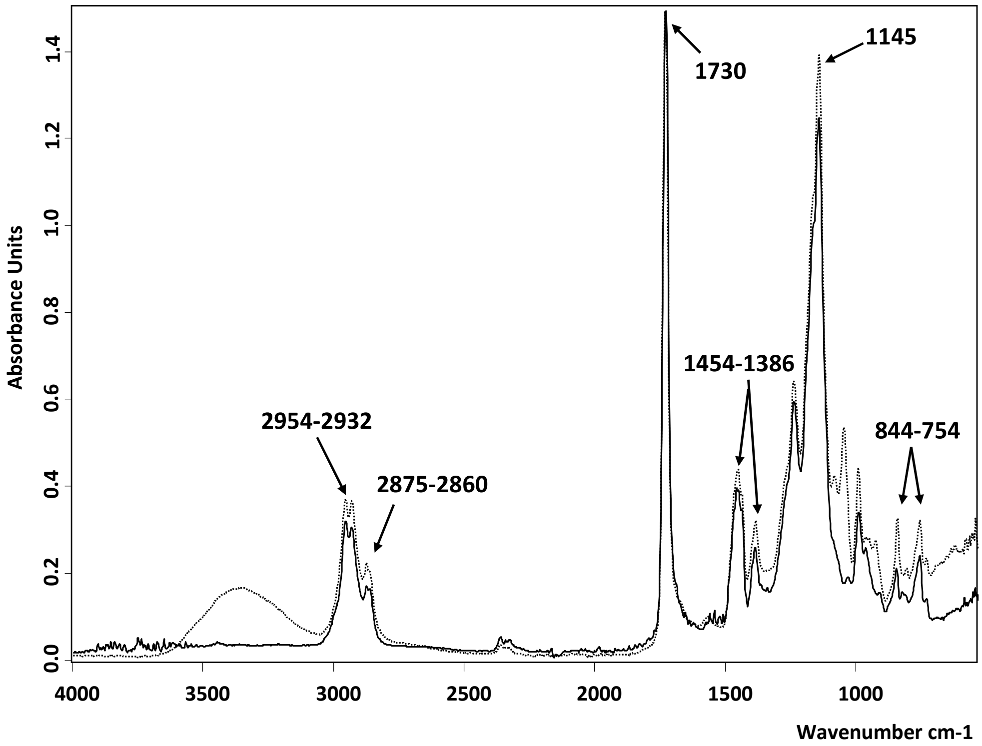

Figure 6.1.1: FTIR-ATR spectrum of Liquitex® gloss medium and varnish 2 weeks after casting (dotted line) and 4 months natural aging (solid line). The reader is reffered to the text for identification of the absorptions pointed out.

Differences in the –CH_3 and –CH_2 stretching region (3100-2800 cm^{-1}) can be used to determine the overall nature of the resins present in acrylic dispersion polymers[21] [1-2]. Thus, the presence of a strong peak at 2960 cm^{-1}, along with a second less strong peak at 2877 cm^{-1} can be ascribed to a p(nBA-MMA).

In the Liquitex® gloss medium and varnish spectra, in Figure 6.1.1, are pointed out peaks at 2954 cm^{-1}, 2932 cm^{-1}, 2875 cm^{-1} and 2860 cm^{-1}. The peaks found at 2954 cm^{-1}, and 2875 cm^{-1} are indicators of a nBA-MMA copolymer. Nevertheless, the presence of other peaks at 2932 cm^{-1} and 2860 cm^{-1}, which appear with higher intensities than expected for a nBA-MMA copolymer, are indicators either of other co-monomers or additives. The analysis performed by Py-silylation-GC-MS described latter in this chapter reveals that this medium has a monomeric composition of BA-MMA with trace amounts of butyl methacrylate (BMA) units.

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[21] The presence of minor compounds may influence the accurate interpretation of these bands. For this reason the results are contrasted to those obtained by Py-silylation-GC-MS.

Bands at 1454 cm^{-1} and at 1386 cm^{-1} are ascribed to C-C streching vibrations. The presence of shoulders in these bands is associated to nBA-MMA copolymers. The weak absorptions at 844 cm^{-1} and 754 cm^{-1} are ascribed to C-H rocking.

It is interesting to note that both spectra correspond to the same acrylic product obtained at different drying stages (2 weeks and 4 months). The spectra corresponding to the freshly prepared sample presents a broad band at 3350 cm^{-1} corresponding to hydroxyl structures (-OH) associated streching vibrations [4]. Two other bands at 1082 cm^{-1} and 1045 cm^{-1} ascribed to –C-O- stretching vibrations from alcohols confirm this [5]. These bands have not been found in the spectra obtained for the 4 month old resin. These absorptions are associated to volatile additives present in the original formulation, that are expected to slowly disappear from the dried film, as reported by Mecklenburg *et al* [6].

In Figure 6.1.2 is shown the FTIR-ATR spectrum of Liquitex® zinc white. Overall, the absorption profile of the pigmented sample is similar to that of the Liquitex® gloss medium and varnish and is indicative of a BA-MMA type polymer. This is confirmed by Py-Silylation-GC-MS. The major difference between these spectra is related to the presence of a series of sharp peaks at 1469, 1346, 1110, 1064 and 965 cm^{-1} characteristic of a poly(ethylene oxide) (PEO) type additive[22] [7,8]. A strong absorption at 2886 cm^{-1} is characteristic of the CH_2 streching vibration of PEO products. For comparisong purposes, a spectrum of PEG 1500 (a pure PEO type compound) is included in the figure. Finally, a broad peak is found in the 600-500 cm^{-1} region and is attributed to the presence of the zinc white pigment.

In Liquitex® pigmented samples, no extenders have been detected by means of FTIR-ATR analysis.

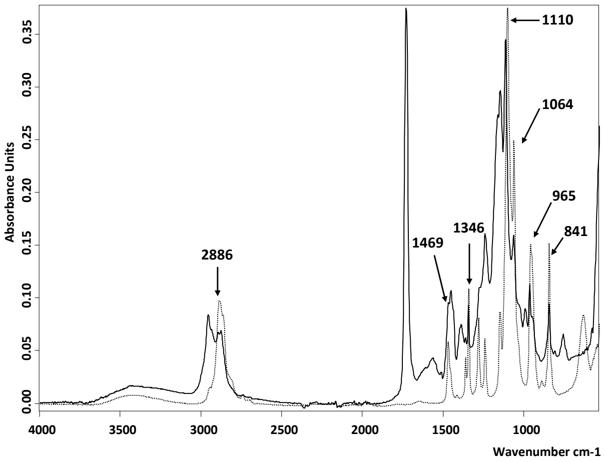

Figure 6.1.2: FTIR-ATR of Liquitex® zinc white paint samples. The peaks ascribed correspond to PEO type products. For comparison purposes, a reference PEG 1500 has been included in this figure (dotted line).

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[22] Poly(ethylene oxide) (PEO) is also commonly known as poly(ethylene glycol) (PEG). A PEO type chain can also be reffered to as poly(ethoxylated) chain.

Vallejo® colours are bound with a BA-MMA type resin identified by the characteristic absorptions at 2954 cm^{-1}, and 2875 cm^{-1} in the –CH region and the carbonyl and ester groups from acrylics. This was in good agreement with the analysis by means of Py-GC-MS.

The extenders present in these paints are not clearly visible, due to the high binder content. Nevertheless, naphthol red, titanium white and phthalocyanine blue show characteristic absorptions of silica at 1250-1100 cm^{-1} and 815 cm^{-1} (round absorption).

The spectra of Talens® gloss medium and Talens® gel medium are presented in Figure 6.1.3. The presence of sharp absorption bands ascribed to the carbonyl and ester groups of acrylic resins are present. An absorption band at 2983 cm^{-1} is ascribed to a EA-MMA resin type. However, the following peaks at 2987 cm^{-1} and 2878 cm^{-1}, are related to the presence of a BA-MMA type resin, as presented in table 6.1.1. The possible presence of these monomers is confirmed by the broadening of the peaks ascribed to the C-C stretching and C-H rocking region. These results are in good agreement with the results obtained by Py-silylation-GC-MS, which disclose a monomeric composition of EA-MMA-nBA-(BMA). A sharp peak at 1110 cm^{-1} along with an increase in absorption at 2886 cm^{-1} is present in both compounds and has been attributed to a PEO type compound.

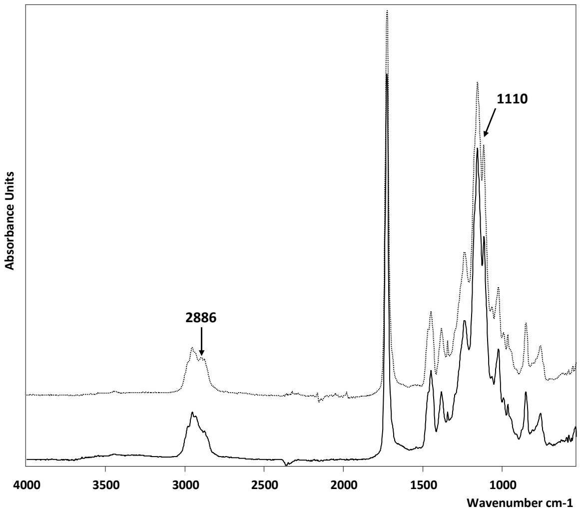

Figure 6.1.3: FTIR-ATR spectrum of both Talens® gloss medium (solid line) and gel medium (dotted line).

All Talens® colours prepared in this study exhibited similar binding medium profiles to that of the medium, except for white zinc, titanium white and phthalocyanine blue. In these colours, the peak at 2983 cm^{-1} is not present (see Figure 6.1.4). Also, a doublet at 1161 cm^{-1} and 1146 cm^{-1} together with a strong absorption at 1068 cm^{-1} can be associated to the presence of a BA type monomer, from a BA-MMA type polymer. This is confirmed by Py-GC-MS.

All paint samples exhibit a broad increase in the absorption range from 1500 cm^{-1} to 1400 cm^{-1} and two sharp absorptions at 877 cm^{-1} and 712 cm^{-1} associated to a calcium carbonate extender [1,2,5]. This is in good agreement with previous studies by Ormsby et al [9].

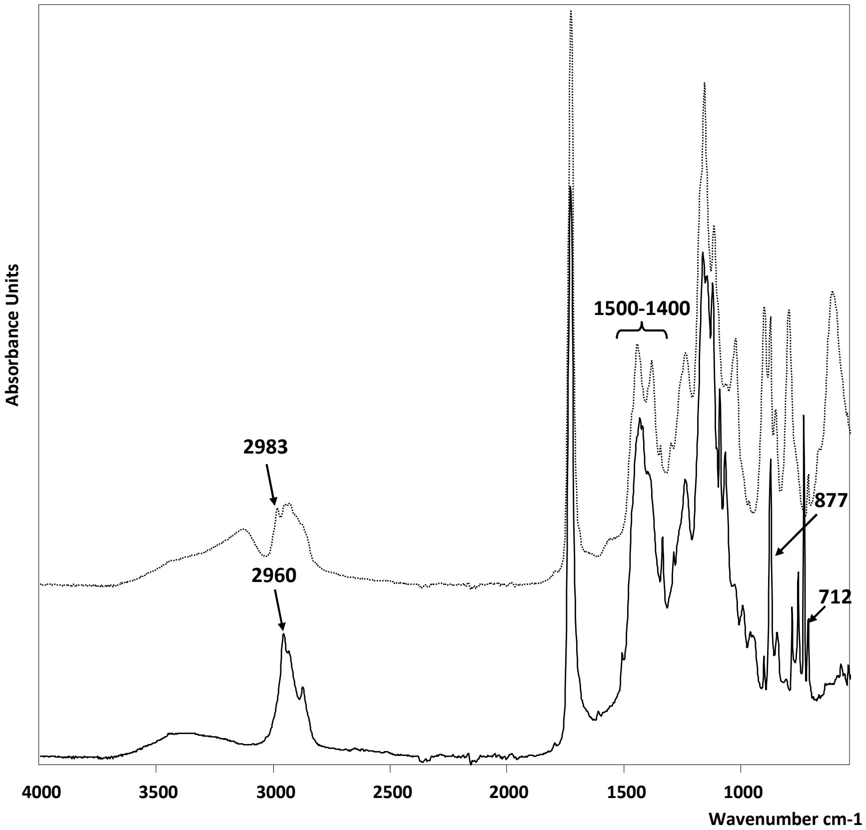

Figure 6.1.4: FTIR-ATR spectra of raw sienna (dotted line) and phthalocyanine blue (solid line). The absorptions pointed out in the figures are commented in the text.

Pébéo® colours show different spectra from those acrylics previously studied. In Figure 6.1.5 is shown the FTIR-ATR spectra of naphthol red. The absorptions at 1728 cm^{-1} and 1160-1145 cm^{-1} are characteristic of acrylic resins. Nevertheless, the presence of two intense peaks at 761 cm^{-1} and 702 cm^{-1}, acompanied by small absorptions in the range between 3100 cm^{-1} and 3010 cm^{-1} are clear indicators of aromatic rings ascribed to styrene. These features are ascribed to a styrene-acrylic type binding medium.

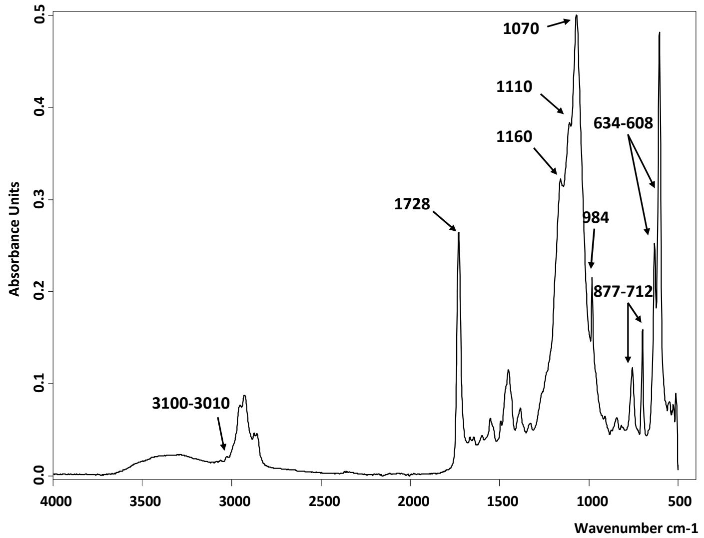

Figure 6.1.5: FTIR-ATR spectra of Pébéo® naphthol red sample. The absorptions pointed out are ascribed to the styrene monomer, acrylic monomer and barium sulphate.

Calcium carbonate extenders (broad absorption in the 1500-1400 cm^{-1} region and two sharp peaks at 877 cm^{-1}, 712 cm^{-1}) were detected in titanium white, phthalocyanine blue, red ochre, mars black, cadmium yellow (hue) and ceruleum blue from Pébéo®. On the other hand, barium sulphate (broad absorption in the 1250-950 cm^{-1} region with peaks at 1170, 1110, 1064, 984 cm^{-1}, and a characteristic doublet at 634-608 cm^{-1}) was found in mars black and naphtol crimsom. Phthalocyanine blue and mars black contains both types of extenders.

6.1.1.2- Py-GC-MS and Py-Silylation-GC-MS

In this study, a number of acrylic paints have been investigated by Py-GC-MS and by means of Py-silylation-GC-MS. These paints included Liquitex® burnt umber, phthalocyanine blue, naphthol red, Talens® gloss medium, gel medium and raw sienna, Vallejo® naphthol red and Pébéo® pthalocyanine blue and naphtol crimson.

In the analyses performed with conventional Py-CG-MS and with the derivatizing reagent Hexamethyldisilazane (HMDS), the monomeric fraction found was similar, and is summarized in table 6.1.2. The use of HMDS was intended to react with the polar groups of minor compounds present in the micro-samples and, thus, the monomeric fraction produced during pyrolysis was not affected. In table 6.1.3 is a summary of polar compounds detected by means of Py-silylation-GC-MS, that will be detailed later in this section.

brand	sample	monomeric composition
Liquitex® heavy body	burnt umber	BA-MMA –(BMA)
	cadmium yellow	BA-MMA -(BMA)
	phthalocyanine blue	BA-MMA -(BMA)
	titanium white	BA-MMA -(BMA)
	naphthol red	BA-MMA -(BMA)
	gloss medium	BA-MMA -(BMA)
Royal Talens® (Amsterdam)	gloss medium	EA-MMA-BA-(BMA)
	gel medium	EA-MMA-BA-(BMA)
	raw sienna	EA-MMA
	titanium white	BA-MMA-(BMA)
Vallejo®	naphthol red	BA-MMA-(BMA)
Pébéo®	naphthol crimsom	Styrene-2EHA-MMA
	titanium white	Styrene-2EHA-MMA

Table 6.1.2: monomeric composition found in the several dispersion acrylic paints tested, for both conventional Py-CG-MS and with HMDS.

brand	sample	polar compounds of interest
Liquitex® heavy body	burnt umber	PEO type compounds
	cadmium yellow	PEO type compounds, octylphenol ethoxylate surfactant
	phthalocyanine blue	PEO type compounds, octylphenol ethoxylate surfactant
Royal Talens® (Amsterdam)	gloss medium	PEO type compounds
	gel medium	PEO type compounds
	raw sienna	PEO type compounds
Vallejo®	naphthol red	PEO type compounds
Pébéo®	naphthol crimsom	PEO type compounds
	titanium white	PEO type compounds

Table 6.1.3: summary of the minor polar compounds detected in the analysis of the paint samples by means of Py-Silylation-GC-MS. In general, the pyrograms reveal the presence of PEO fragments, which are common in many types of additives [11 and references therein]. It was possible to detect an octylphenol ethoxylate surfactant in some Liquitex® samples.

In Figure 6.1.6 are shown two pyrograms corresponding to the anaylsis of burnt umber from Liquitex® by conventional pyrolysis and with HMDS. Overall, both pyrograms are dominated by the presence of the monomers methyl methacrylate (MMA), butyl acrylate (BA) and trace amounts of butyl methacrylate (BMA). At higher retention time, peaks corresponding to the sesquimer, dimmer and trimer fractions were also identified.

The analysis by Py-Silylation-CG-MS produced a higher number of peaks when compared to the analysis by conventional Py-GC-MS. This is related to the derivatization of minor polar compounds present in the micro-sample, and represents an interesting improvement in the general sensibility of the analysis. Thus, early in the pyrogram corresponding to the analysis with HMDS, there is a sharp peak ascribed to the trimethylsilylated form of methacrylic acid (TMSMA), which is normally undetected or appears as a fronting peak with conventional pyrolysis [10].

In the pyrogram is detected a peak corresponding to octylphenol in its derivatised form, with main ion fragments *m/z*=207 (TMS derivate) and 135. Other peaks with lower intensity may appear thoughout the pyrogram, presenting m/z =135. These are ascribed to the formation of octylphenol ethoxylated fragments, observed in the analysis of cadmium yellow paint sample. A more detailed analysis of an octylphenol ethoxylate type surfactant (Triton®X-100) is available in Appendix D.

Finally, throughout the entire pyrogram it is possible to identify several groups of peaks ascribed poly(ethylene oxide) in the derivatised form (PEO-TMS), in good agreement to studies performed by other authors [11 and references therein].

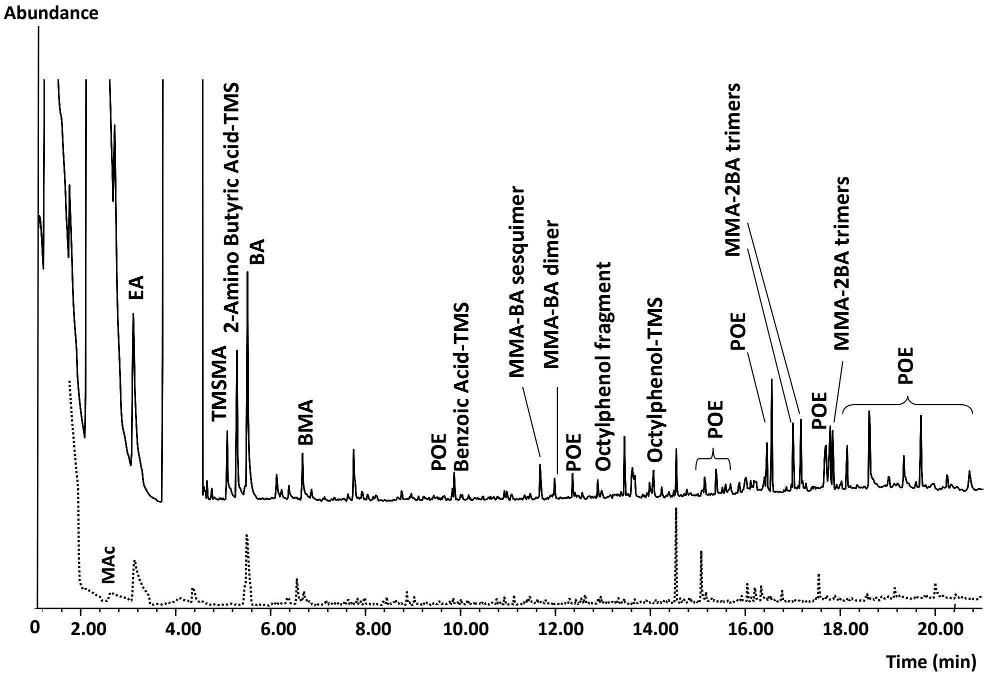

Figure 6.1.6: pyrograms of Liquitex® burnt umber. The analyses were perfomed by conventional Py-GC-MS (below) and by Py-Silylation-GC-MS (above). The appearence of several minor peaks are ascribed to polar compounds, such as PEO type fragments and also to an octylphenol type surfactant.

The analysis of naphtol red from Vallejo® acrylic brand reveals a monomeric profile of MMA, BA (and BMA), with the corresponding sesquimer, dimmer and trimer fraction [1,2,10]. The analysis of the paint sample with HMDS allowed furthermore the detection of several PEO type fragments throughout the pyrogram, similar to those found in the Liquitex® samples.

Talens® gloss medium, gel medium and raw sienna have been analysed by pyrolysis with HMDS, and the results have been summarized in table 6.1.2. The analysis of Talens® gloss medium, Talens® gel as well as titanium white reveals that they share similiar monomeric composition: EA, MMA and nBA (BMA). Whereas the paint sample raw sienna, from the same commercial brand, is an EA-MMA type polymer. The corresponding sesquimers, dimers and trimers have also been detected. A detailed description of these pyrolysis products can be found elsewhere and will not be discussed in this thesis [1,2,10,12].

6.1.1.3- Mechanical properties of acrylics

The characterization of the mechanical properties by means of stress-strain tests for a wide range of colours from distinct brands has been performed. This allows getting an insight on the Young's modulus and elongation to brake at environmental conditions (21-23ºC, 50-55% RH).

In Figure 6.1.7 are shown the stress-strain curves obtained for a number of Liquitex® paint films tested at 21ºC, 50% RH. Each colour, within the same commercial brand, presents a distinct mechanical behaviour, which has been observed for all acrylic brands tested. Overall, the samples showed higher flexibility and elongation at brake when compared to an oil paint film found in a traditional painting [13-15]. The Yield point of acrylics is also higher than the limit of 0.5 % elongation, which has been reported by Mecklenburg as the general limit for elastic recovery for materials present in traditional artworks [10,11,15]. For example, the Liquitex® acrylic specimens can withstand an average deformation of 15% without experiencing permanent deformation, which is fairly higher when compared to other materials such as oils, alkyds and hide glues [10-11]. Most acrylic formulations with inorganic pigments formed stiffer paint films with lower elongation at brake than those formulated with organic synthetic pigments. This implies that the colours prepared with organic synthetic pigments are softer at normal room temperature and consequently more susceptible to dirt picking and sticky, when compared to those containing inorganic pigments. Some of the pigmented specimens, such as naphthol red, phthalocyanine blue and, especially, hansa clair, were particularly soft materials exhibiting similar stiffness to that of Liquitex® gloss medium and varnish (also showin in Figure 6.1.7). This is related to the presence of additives in the bulk film that act as plasticizers as well as low pigment concentrations.

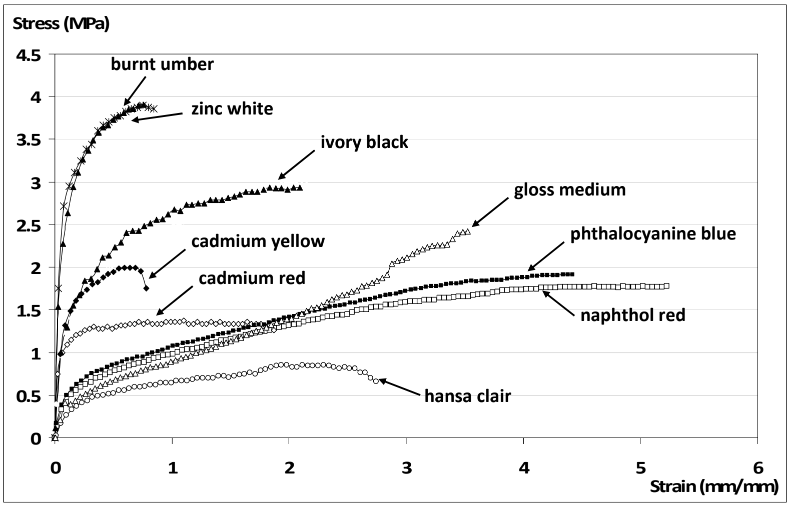

Figure 6.1.7: the results obtained from stress-strain tests performed for a series of Liquitex® specimens (21 ºC, 50 % RH). The results evidence the differences in the mechanical properties that these films may show within the same commercial brand. All specimens exhibit a strain to failure above 50 % elongation and, generally, paints formulated with inorganic pigments showed higher stiffness than those formulated with organic synthetic pigments.

The mecanical properties of Talens® specimens showed similarity in the overall trend of the mechanical properties: the films containing inorganic pigment showed higher stiffness and less flexibility. Contrary to Liquitex® samples, though, the Talens® gloss and gel media showed lower strength than the paint samples.

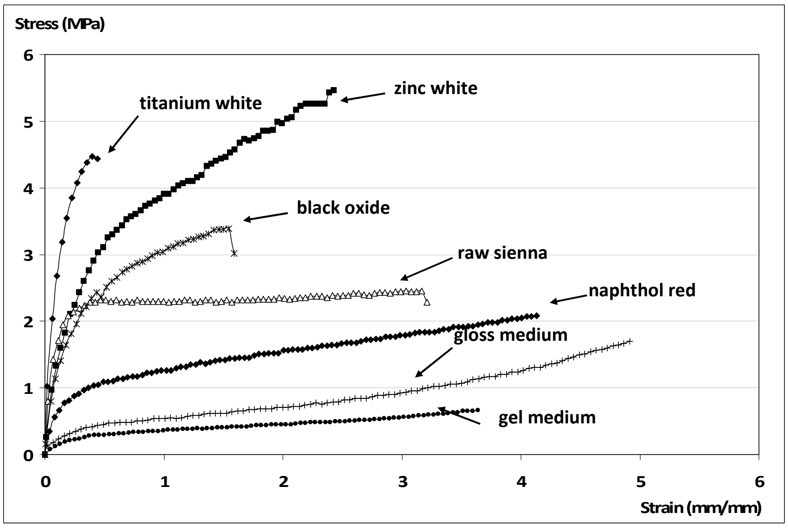

Figure 6.1.8: stress-strain curves obtained from a series of Talens® samples (22 ºC, 50 % RH). The results show similar trends to those of Liquitex® and, thus, paints formulated with inorganic pigments showed higher stiffness and less flexibility than those formulated with organic synthetic pigments.

The mechanical properties obtained for Pébéo® specimens are shown in Figure 6.1.9. These materials present less elongation at brake when compared to the previous acrylic brands tested. Some paint samples behaved has brittle materials such as cadmium yellow (HUE), and mars black. This last one was very fragile and impossible to test. The interesting point in this brand is that there is no general trend in the mechanical properties depending on the pigment type, as observed in the previous brands.

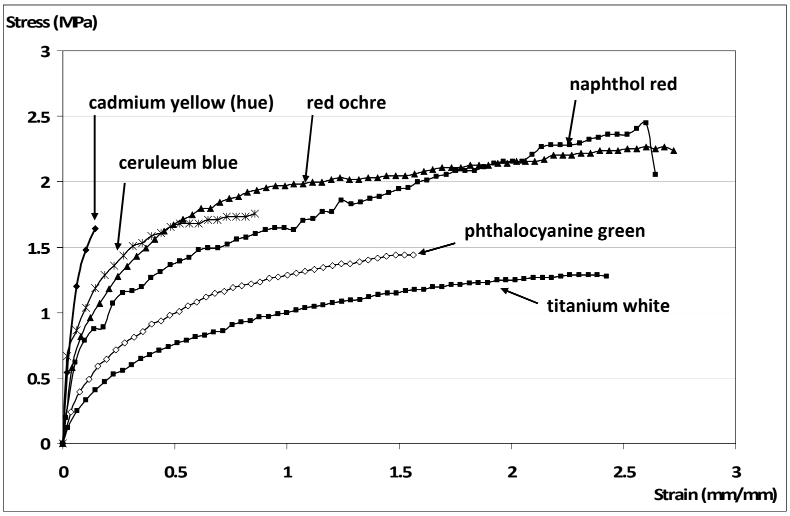

Figure 6.1.9: the mechanical properties of Pébéo® paint samples (24 ºC, 50 % RH). In the case of this paint brand there was no clear correlation between mechanical properties of the paint and the pigment nature. This appears to be also correlated to the high content of fillers that have been detected by FTIR-ATR.

6.1.2.- Poly(vinylacetates)

6.1.2.1- FTIR-ATR

In Figure 6.1.10 are two FTIR-ATR spectra from Flashe® burnt sienna, a PVAc-VeoVa copolymer (see analysis of Flashe® paints by means of Py-silylation-GC-MS), and Mowilith® 50 (a PVAc homopolymer included for comparison purposes). The PVAc-VeoVa resin presented peaks at 1737 cm^{-1} and 1232 cm^{-1} corresponding to the carbonyl and ester stretching vibrations. The homopolymer, on the other hand, presented the carbonyl band at a slightly lower frequency (1732 cm^{-1}). In the PVAc-VeoVa product, the carbonyl absorption was less intense than that of the ester, whereas in the homopolymer it was the opposite.

Another considerable difference in these two products was found in the C-H stretching region (3000 cm^{-1} to 2800 cm^{-1}). The homopolymer presents weak C-H stretching vibrations with peaks at 2970 cm^{-1}, 2926 cm^{-1} and 2860 cm^{-1}, whereas the PVAc-VeoVa shows stronger absorptions at 2961 cm^{-1}, 2926 cm^{-1}, and 2874 cm^{-1} with a shoulder at 2860 cm^{-1}. This is ascribed to the presence of the VeoVa fraction.

In the fingerprint region, both spectra present characteristic absorptions at 1370 cm^{-1} from C-H bending and 1020 cm^{-1} and 946 cm^{-1}, from the C-C stretching vibrations. Mowilith® 50 presents an absorption at 1434 cm^{-1} from C-H bending which is not detected in the Flashe® sample, due to overlapping from a strong and broad absorption in the 1500-1300 cm^{-1} region of a calcium carbonate extender. This absorption is accompanied by sharp absorptions at 872 cm^{-1} and 712 cm^{-1}, and smaller, but sharp peaks at 1796 cm^{-1} and 2514 cm^{-1} which are typical for this compound.

In addition to this, a broad band present in the 660 cm^{-1} to 500 cm^{-1} range is an indicator of iron absorption and has been ascribed to an iron oxide, and possibly not an earth colour, as declared by the manufacturer, since no absorption corresponding to silica and clayed materials at 1100-1000 cm^{-1} has been detected.

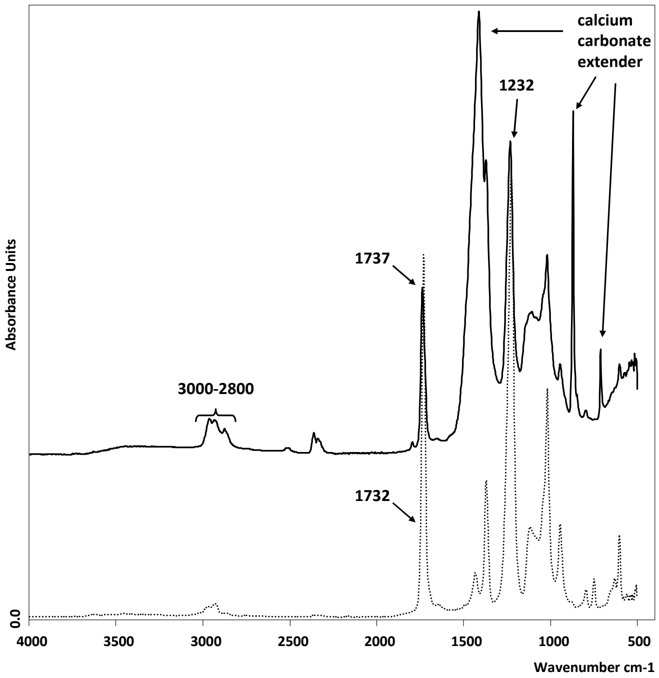

Figure 6.1.10: FTIR-ATR spectrum of Flashe® burnt umber paint films (above). Also included is the spectrum of a Mowilith® 50, a reference PVAc homopolymer material.

The spectra of Conrayt®, Vinavil® 59 and Mowilith® DMC2 show similar absorption profiles to that discussed for Mowilith® 50. This included an intense carbonyl peak at 1732 cm^{-1} accompanied by a less intense ester peak at 1230 cm^{-1}. Smaller absorptions at 1434 cm^{-1}, 1370 cm^{-1} are due to the bending vibrations of C-H bonds, and absorptions in the 1120 cm^{-1} - 1020 cm^{-1} region were ascribed to the C-C streching vibrations of the backbone of the polymer. Similarly to the reference resin, Conrayt® presents small and broad bands in the range of 3000 cm^{-1} - 2800 cm^{-1}, from C-H streching vibrations. A small peak at 1066 cm^{-1} was related to the presence of an unknown additive.

Mowilith® DMC2 is a PVAc-Butylmaleate type resin and shows some distinct features in the absorption profile [16]:

- An increase in the C-H stretching vibrations in the 3000-2800 cm^{-1} range, with characteristic butyl ester peaks at 2962 cm^{-1}, 2938 cm^{-1} and 2877 cm^{-1}, similar to those observed in BA-MMA type resins.
- Considerable absorptions at 1465 cm^{-1} and 1166 cm^{-1} were also ascribed to the co-monomer C-H and C-C absorptions.
- Finally, it was also interesting to note that the intensity of the ester absorption was higher in Mowilith® DMC2 than in the PVAc homopolymer reference material.

6.1.2.2- Py-GC-MS and Py-Silylation-GC-MS

A similar procedure used for the analysis of acrylic paints by means of Py-Silylation-GC-MS has been applied to the study of PVAc artists' dispersion paints (Flashe®). The selection of colours tested included armour green, oriental red, burnt umber, raw umber and white. The results obtained in the analyses of these samples are summarized in table 6.1.4.

Compounds Identified	***m/z* ion fragments**	**Flashe® Oriental Red**	**Flashe® Armour Green**	**Flashe® Raw Umber**	**Flashe® Burnt Umber**	**Flashe® White**
ethanoic acid-TMS	117, 75, 45	V	V	V	V	V
2-methoxyethanol -TMS	133, 103, 89, 73, 59, 45	-	V	V	-	-
2-TMS-oxy-ethanol	119, 103, 75, 73, 58, 45	V	-	-	V	-
propanoic acid-2-methyl-TMS	145, 117, 75, 73, 58, 45	V	-	V	V	-
methacrylic acid-TMS	158, 143, 73, 69, 41	V	V	V	V	-
styrene	104, 78, 51, 39, 27	-	V	-	V	V
phenoxy-TMS	166, 151, 77, 43	-	-	-	V	-
propanoic acid 2-oxy-TMS	234, 191, 147, 117, 73, 45	V	V	V	V	V
ethanoic acid 2-oxy-TMS	220 205, 147, 73	V	V	V	V	V
benzoic acid-TMS	194, 179, 135, 105, 77, 51	V	V	V	V	V
VeoVa	see Table 2	V	V	V	V	V
butanedioic acid- TMS	261, 147, 73, 55, 45	-	-	-	V	V
pentanedioic acid- TMS	189, 142, 115, 87, 57, 43	-	V	-	-	V
pigment traces		V (PR112: 2,3,4-trichloro Benzenamine) 195, 160, 124, 97, 62, 28)	-	-	-	-
bis(2-butoxyethyl) phthalate	366, 223, 149, 56	-	V	-	-	-
diethylene glycol dibenzoate	149, 105, 77, 51	-	V	-	-	-
diglycol benzoate,	163, 105, 77	-	V	-	-	-
isopropyl phenyl diphenyl phosphate	368, 251, 118, 77	V	V	-	-	-
PEG-TMS	45, 73, 101-103, 116-117, 145, 161 (...)	V	V	V	V	V

Table 6.1.4: main compounds found in the Py-Silylation-GC-MS analyses of Flashe® paint films.

A Flashe® armour green pyrogram is presented in Figure 6.1.11.

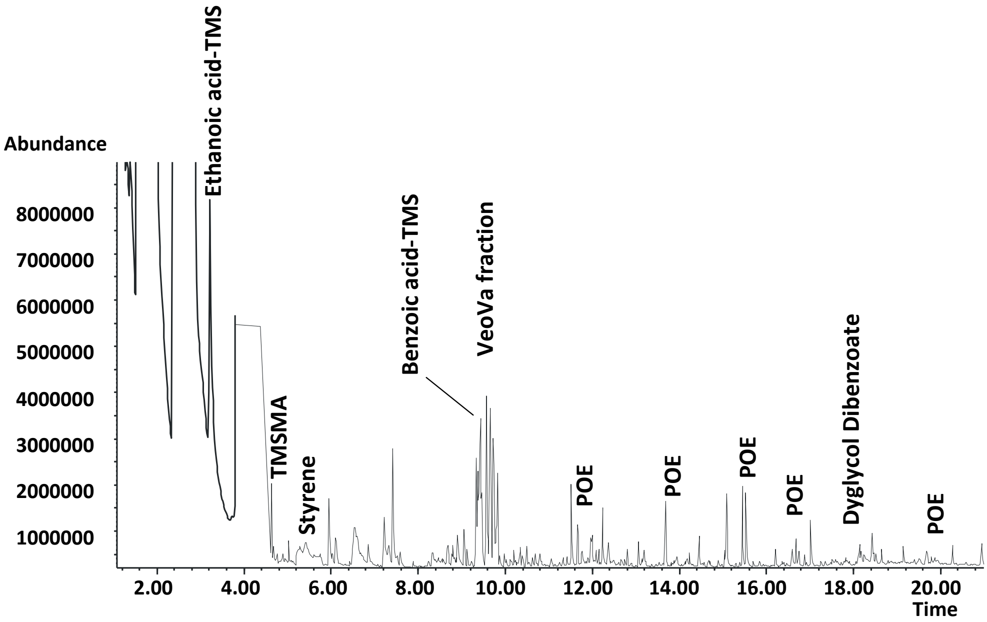

Figure 6.1.11: A pyrogram of Flashe® armour green obtained by means of Py-Sylilation-GC-MS.

A pyrogram of a PVAc based polymer shows two characteristic peaks corresponding to ethanoic acid (acetic acid) and benzene. Ethanoic acid is a product of side group elimination and benzene is the result of the brakedown and rearrangement of the resulting polyene chain [2,16]. In the Flashe® pyrogram is found a strong peak corresponding to ethanoic acid in its derivatised form, whereas benzene is hindered by the presence of HMDS (derivating reagent). According to the literature, there is evidence of the formation of benzene later in the pyrogram, due to combination and condensation reactions that occur during pyrolysis that form compounds such as 1,4-dihydronaphthalene, naphthalene and butyl benzoate [16]. Nevertheless in the commercial products studied here, and despite being PVAc based paints, such compounds were not detected.

Further analysis of the pyrogram reveals the presence of methacrylic acid (TMSMA) which is not detected with direct pyrolysis. This represents an improvement of the analysis achieved with the proposed method. Additionally, a series of peaks corresponding to PEO in their derivatised form could also be identified. These compounds have not been identified by means of direct pyrolysis.

The set of peaks that appear between 9.3-9.9 min in the pyrogram of the studied PVAc paints are associated to the presence of versatates used as internal plastizicer. Vinyl versatates, also named VeoVa monomers (Shell®), are understood to consist of several isomers of highly branched C_9 and C_{10} vinyl esters [16]. They copolymerize with vinyl acetate by addition polymerization. Peak distribution corresponding to the VeoVa fraction that appears in the pyrogram of oriental red for flashe PVAc paint using on line trimethylsilylation with HMDS is shown in detail, in Figure 6.1.12.

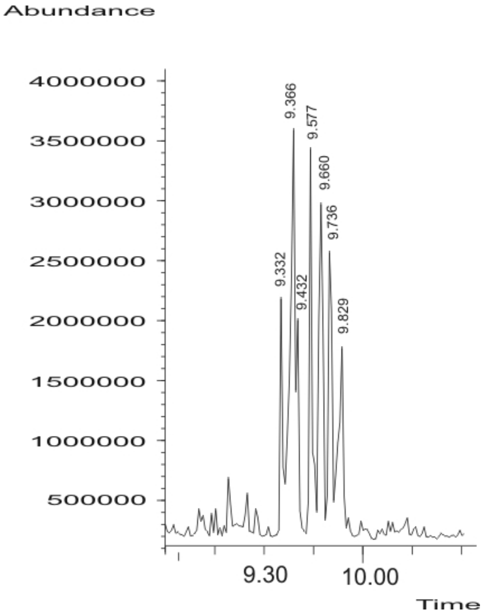

Figure 6.1.12: detail of the pyrogram of Flashe® oriental red corresponding to the VeoVa fraction.

The similarity in the retention time of these compounds suggests that their structures are quite related. m/z values of the main ion fragments from their mass spectra are summarized in table 6.1.5 together with the retention time of the different compounds.

Peak	**VeoVa fraction** **Assignment**	**M$_w$**	**t$_r$ (min)**	**Mass spectra data (70 eV)** **Characteristic ions: m/z**
1	Unidentified decanoic acid, TMS ester	244	9.34	229, 202, 188, 173, 159, 143, 126, 117, 99, 85, **73**, 71, 57, 43
2	Unidentified decanoic acid, TMS ester	244	9.43	229, 174, 159, 143, 126, 117, 85, **73**, 71, 57, 43
3	Unidentified decanoic acid, TMS ester	244	9.57	229, 202, 188, 174, 159, 143, 126, 117, 85, **73**, 71, 57, 43,29
4	Unidentified decanoic acid, TMS ester	244	9.66	229, 202, 188, 173, 159, 143, 126, 117, 85, **73**, 71, 57, 43
5	Unidentified decanoic acid, TMS ester	244	9.74	229, 174, 160, 143, 126, 117, 85, **73**, 71, 57, 43
6	Unidentified decanoic acid, TMS ester	244	9.83	229, 174, 159, 143, 126, 117, 85, 84, **73**, 71, 57, 43

Table 6.1.5: m/z values of the characteristic ions found in the mass spectra of the TMS derivatives of the main compounds included in the VeoVa fraction appearing in the pyrogram of oriental red PVAc paint

The mass spectra of the peaks in this region are very similar. They are dominated by *m/z= 7*3 ascribed to the fragment ion $[TMS]^+$, which indicates that these compounds have been satisfactorily trimethylsilylated by HMDS. The presence of a characteristic ion fragment at *m/z= 229* in the mass spectra of the main compounds appearing in the VeoVa fraction, which is ascribed to the loss of a methyl group from the TMS derivatives of the compounds, enables the identification of the group of compounds as isomers of the decanoic acid ($C_{13}H_{28}O_2Si$). The production on pyrolysis of C_{10} fatty acids is presumably taking place by a side group elimination mechanism similar to that of ethanoic acid from the PVAc polymer, and the identification of these compounds is in good agreement to that previously found by Learner in Emultex VV536 PVA emulsions using direct Py-GC-MS [17]. The rest of peaks that appear in the mass spectra of VeoVa compounds series exhibit low intensity when compared to the base peak.

6.1.2.3- Mechanical properties of PVAc products

Flashe® paint films exhibit very different mechanical properties when compared to acrylics. In fact, the samples exhibited such poor cohesion that the films showed early failure during the tensile tests. The test protocol for these samples shows slower strain rates (ten times less than for acrylics). For the other PVAc materials, the stress-strain test protocol was the same as for acrylics.

Figure 6.1.13 shows the stress-strain curves obtained for a series of Flashe® paint films (tested at 23ºC, 55% RH). These materials are weak and have low flexibility. In fact some of the films prepared were very brittle and it was impossible to separate them from the Mylar® support. The strain to failure of these materials was difficult to determine, since the samples do not exhibit a clean brake, but rather different failure points throughout the film. This is visible in the stress-strain curves, as the strength of the films starts decreasing with the strain application.

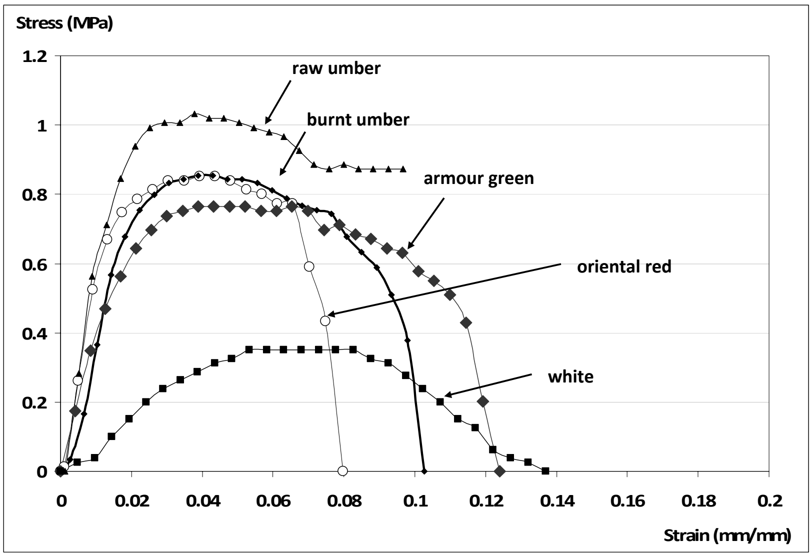

Figure 6.1.13: the mechanical properties of a series of Flashe paint films. These samples show low cohesion and start failing soon after the test starts.

The stress-strain curves obtained for Mowilith® DMC2, Vinavil® 59 and Conrayt® are shown in Figure 6.1.14. These materials are considerably flexible, especially Mowilith® DMC2 that did not fail during the test (the test stopped at 1000% deformation).

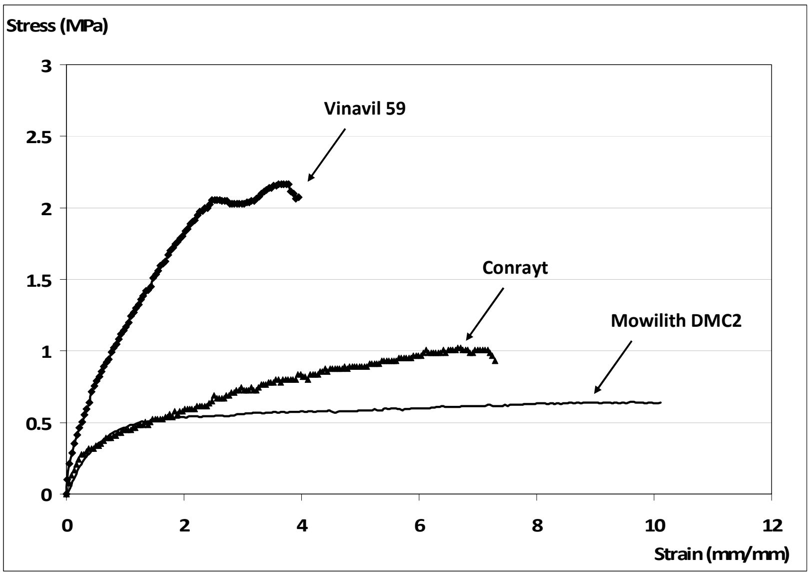

Figure 6.1.14: mechanical properties of three PVAc type products, Mowilith® DMC2, Conrayt® and Vinavil® 59. It is interesting to notice the different range of properties these products show, making them useful for distinct applications.

6.1.3- Conclusions

A combination of analytical techniques has been applied in the characterization of chemical and physical properties of a series of acrylics and PVAcs. The main focus of this work is the characterization of the resins present in the samples. However, the presence of some pigments and extenders has also been described in the text. The results are summarized according as follows.

Four acrylic paint brands were tested in this work: Liquitex®, Vallejo®, Talens® and Pébéo®. All paint samples are classified by the manufacturer as acrylic products. The chemical analysis of these paint revealed:

- Liquitex® and Vallejo® are BA-MMA-(BMA) type resins.
- Talens® media EA-MMA-BA type polymers, whereas colours revealed two distinct compositions: EA-MMA or BA-MMA.
- Pébéo® paints contain Styrene-2EHA-MMA type resin.

Four PVAc products were analysed including Flashe® paint samples and Conrayt®, Vinavil® 59 and Mowilith® DMC2 pure resins. The chemical analysis revealed:

- Flashe® paint samples are PVA-VeoVa product.
- Conrayt® and Vinavil® 59 are PVAc resins.
- Mowilith® DMC2 is a VAc-dibutyl maleate resin.

The use of HMDS for performing Py-silylation-GC-MS improved the general resolution of polar compounds in Py-GC-MS analysis. Some minor compounds (or additives) such as PEO-type fragments were detected in all samples, as well as octylphenol type surfactants in the case of Liquitex® samples. This is an improvement regarding the conventional analysis.

The characterization of the mechanical properties of these films showed that acrylics and PVAc media are higly flexible materials and at normal conditions, these are not expected to show mechanical failure. On the other hand, the softness of these materials indicates that they are prone to dirt pick-up and embebment. Within the same commercial brand acrylics can show different mechanical behaviour. In general, acrylic paint films inorganic pigments are stiffer that organic synthetic colours, and this may be related to the presence of additives that act as plasticizers in the films as well as PVC.

On the contrary, Flashe® paints (and also some Pébéo® samples) present low flexibility and strength, when compared to acrylics. Many behaved actually as brittle materials. These paints are much more prone to suffer damage due to stresses indiced during handling and transportation than the previous brands. The changes in the chemical composition and mechanical properties of these samples with aging and cleaning treatments will be studied in the following chapters.

6.1.4- References

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6.2- The effects of light in modern acrylic and PVAc dispersion paints and binding media: Daylight and UV light aging

6.2- The effects of light in modern acrylic and PVAc dispersion paints and binding media: Daylight and UV light aging

The following sections present and discuss the aging behaviour of a series of acrylic and PVAc products exposed to artificial daylight and UV light. At this time there will be a discussion and a general review on the theories regarding the aging of acrylic and PVAc polymers. Lastly there is a summary of the literature review concerning the aging characteristics of these materials.

6.2.1- General aspects in the aging of polymers

The degradation of polymers can be caused by the presence of external energy and reactive chemical species trough different mechanisms. A general description of these processes will be presented in this chapter. Overall, degradation takes place through two main mechanims [1,2]:

1. Absorption of ultraviolet radiation (UV) and/or thermal energy. The degradation processes are initiated by the rupture of weak bonds and followed by the formation of new bonds altering the original polymer structure. These processes are named *photolysis* and *thermolysis*, respectively.

2. Initiation of degradation by the presence of oxygen and water (atmospheric pollutants contribute also to degradation). These agents can alter the processes previously described and lead to the formation of new types of chemical groups. Such processes are named *photo-oxydation* and are also enhanced by temperature.

In the degradation mechanisms of polymers there are two main trends: bond-beaking and/or bond-making. The bond-brakeing processes lower the average molecular weight of the polymer chains (these include *depolymerization* and *random scission*) and/or separate pendant groups and cause emission of volatile small molecules (named *elimination*). Alternatively the bond-making processes result in material with increased molecular weight (reactions that are known as *cross-linking*) [1,2].

6.2.1.1- Thermolysis and photolysis

The degradation reactions that occur exclusively under the thermal regime are known as *thermolysis*. For the polymers studied in this thesis, these reactions can be considered unimportant since they are not generally observed under 100ºC[23]. Nonetheless, the degradation processes associated to the thermal effect are more likely to be elimination and depolymerization [1].

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[23] Some polymers such as poly(vinyl chloride) (PVC) suffer thermolysis below 100ºC by elimination mechanisms of HCl from the side-group decomposition [1].

Photolysis, on the other hand, concerns the degradation process that a material undergoes when exposed to a specific wavelength:

> *"The key principle of photochemical phenomena is the Grotthus-Draper Law. This states that only radiation that is absorbed by a substance may cause a chemical reaction. This, of course, is axiomatic: light must be absorbed, or taken up, so to speak, by a substance in order to act upon it* [2]*."*

Generally, polymers do not absorb much light energy at wavelengths above 290 nm, which indicates that degradation reactions involving bond brakeing and bond making that were above mentioned must be started by some particular groups that are sensitive to light. These are called *chromophores*, and can come from impurities, additives, etc. If an absorbing chromophore group is present, i.e. carbonyl, hydroperoxydes, imino, aromatic groups and C=C bonds, metallic impurities, degradation may occur [1]. The presence of chomophores is very important and has been shown that, even at low concentrations, can effectively catalyse the degradation processes [2]. The main energy-induced degradation processes are represented in figure 6.2.1.

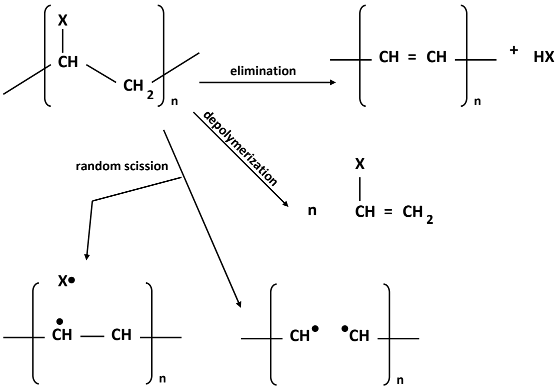

Figure 6.2.1: several pathways of energy induced degradation processes of polymers (adapted from [1]).

6.2.1.2- Photo-oxydation

The most common types of degradation mechanisms in polymers are those comprising oxygen and light (and/or thermal effects). If trace amounts of free radicals or atoms that can abstract a hydrogen atom are present in the polymer, the formation of radicals can occur as follows:

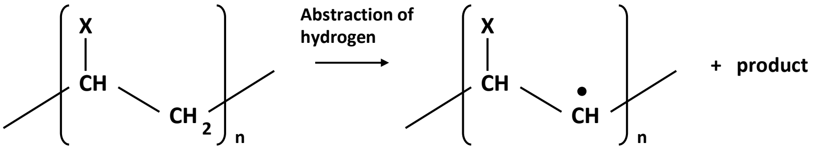

Figure 6.2.2: radical formation by means of a species capable of abstracting a hydrogen atom. This can comprise traces of free radical molecules, metallic ions, etc.

The presence of atmospheric oxygen can lead, at this point, to the formation of hydroperoxides, generally represented by the following equations:

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet$$

Figure 6.2.3: schematic representation of the formation of peroxides (above) and hydroperoxydes (below) species in polymers. R represents a general polymer chain. This step does not involve light or temperature.

These first two processes shown in figures 6.2.2-6.2.3 give rise to a complex series of reactions associated to the degradation of polymers. These reactions start with the formation of a radical which can either combine with other radical species or auto-oxidize. The combination with other radicals gives cross-linking. Auto-oxidation leads to the formation of oxygenated functional groups such as carbonyl, alcohols, ethers, and hydroperoxides. It can also lead to chain scissions (lower molecular weight products), occasional cross-linking between chains (ether or peroxide) and emission of small molecules (CO, CO_2, H_2O, H_2O_2, carboxylic acids and ketones). A diagram of these reactions is illustrated in figure 6.2.4 [1,2].

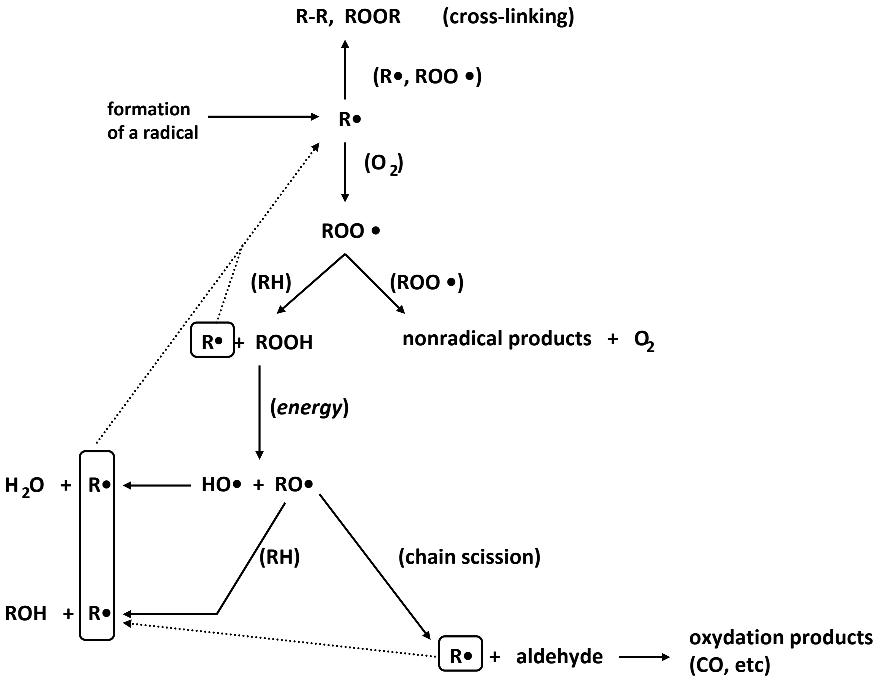

Figure 6.2.4: free-radical chain-oxidation sequence for polymers with hydrogen atoms suceptible of abstraction. Adapted from [1].

6.2.1.3- Hydrolysis

Functional groups such as esters, amides and acetals can be attacked by water. The presence of hydrolyzable bonds in the backbone of the polymer may lead to depolymerization and release of hydrolyzed monomers from the polymer. When these bonds are attached to the side of the backbone chain, the polymer remains intact but small molecules are released.

6.2.1.4- The aging characteristics of solution acrylic polymers

Chiantore *et al* published a series of studies on the thermal and photo-oxidation aging behaviour of acrylic polymers cast from solutions in solvents [3,4]. The study was focused on understanding the stability of acrylate and methacrylate type of acrylic resins, and revealed the following trends:

1. With thermal aging at 135 and 150ºC, the susceptibility of acrylic polymers was influenced by the nature of the alkyl side group. Oxidative decomposition of the side group was observed, especially on longer esters (eg. butyl side groups). The presence of more stable co-monomers (shorter side chains) slowed down this process. Moreover, resins with longer alkyl side groups also underwent extensive cross-linking, together with fragmentation and weight loss. When monomers contained smaller alkyl chains, molecular weight changes were found indicating that chain scission reactions prevailed. This was observed by size-exclusion-chromatography (SEC). Another important conclusion reached by the authors was that polymers with labile tertiary atoms on the alkyd side chain exhibited higher reactivity and promoted oxidation reactions and formation of anhydride structures, visible with FTIR spectroscopy.

   The resins studied in this work comprised Paraloid® B44 (EA-MMA), B82 (EA-MMA), B72 (MA-EMA-BMA), B66 (MMA-BMA) and B67 (isoBMA), as well as PMMA, PEMA and PBMA. The thermal treatments did not produce detectable degradation at 110ºC during the 200 hours aging trial, only consumption of chromophore species (impurities) present in the polymer. Degradation started occurring at 135ºC, with all Paraloid® resins exhibiting weight loss in the order of 5%. The PMMA, PEMA and PBMA accused 5, 15 and 9% weight loss respectively. PB67 and PBMA were the only resins that became more insoluble with thermal aging. Thus for B66 cross linking reactions were the main degradation reactions, whereas B82 and B72 showed chain scission. B44 and B48 showed an initial step of cross linking reactions but, in a second aging step, chain scissions prevailed. B67, PEMA and PBMA showed both types of degradation (similarly to photo-oxidation results). Finally PBMA became an insoluble gel.

2. The photo-oxidation studies carried out at wavelengths > 295 nm, that contain high energy (tests conducted at 45ºC) revealed that the alkyl side group is also a determinant factor in the aging trends. Thus, for both acrylate and methacrylate resins with short alkyl side groups, chain scissions prevail over cross-linking, with no insoluble fraction being formed. Acrylates showed more reactivity towards oxidation when compared to methacrylates. For longer alkyl side groups (such as pBMA) the polymers show fast and extensive crosslinking in a first step, as well as fragmentation in a later step.

   The resins studied in this work comprised PMMA, PEA, PEMA and PBMA. For PMMA resins there was a increasing weight loss during the aging trial that reached 27% the polymer’s weight. No cross-linking reactions were detected and the degradation pathways consisted exclusively of chain scissions. PEA, on the other hand, did not suffer weight loss or gel formation. The degrdation pathways detected were, in a first step a bimodal fragmentation pattern consisting of chain scissions and cross linking. In a second step, chain scission prevailed. For PEMA, no insoluble fraction was detected or weight loss. However, cross linking and chain scission reactions compete in the degradation of the polymer (chain scissions are more important). For PBMA, a fast gel growth was detected with aging time. 14% of the polymer was a gel at 300 hours and, consecutively, 58% at 900 hours and 70% at 1500 hours. 2% weight loss was detected in the aging of these films. At the end of the trial, PBMA turned into an almost insoluble polymer.

6.2.1.5- The aging characteristics of dispersion acrylic polymers

Acrylic dispersion products used in paint systems are known to be fairly resistant to weathering. This has become clear in several aging studies performed for both unpigmented media and paint systems of interest for conservation [5-13]. This is because they are normally based in emulsions designed to be used as outdoor protective coatings, comprising EA-MMA and BA-MMA copolymers. Nowadays, BA-MMA copolymers are included in the majority of polymer compositions in acrylic paint formulations [7,8]. Other copolymers based on styrene and acrylic copolymers, and PVAc with internal or external plasticising are generally considered less durable in comparison to pure acrylic products. The aging properties of waterborne resins and paints are complex processes that are still far from being fully understood. This is mainly related to the complex formulations these products present in the dispersion form.

The following section presents a short review of the aging studies performed on acrylics and PVAc products that may interest the conservator and conservation scientist. Inevitably, due to the importance these products have achieved in the market, the majority of the studies mainly comprise acrylic EA-MMA and BA-MMA type resins. An effort has also been made to gather information from the industry to complete the *corpus* of knowledge for other dispersion products (PVAc and styrene-acrylic).

The first authors to establish a complete aging protocol of an acrylic dispersion medium used in artists' materials were possibly Whitmore and Colaluca, which studied the aging behaviour of a Liquitex® gloss medium under different sources of UV radiation (UV-A and UV-B regimes), thermal aging and dark natural aging [5]. The acrylic product showed high stability under the artificial light aging regimes. The studied samples indicated a slight loss of tensile strength and increased in solubility, suggesting chain scissions reactions as the main degradation process. This was consistent for both UV light aging regimes. Comparatively, the samples aged under the UV-B light regime evidenced faster degradation processes when compared to UV-A light. Under dark aging, these products developed yellowing and exhibited increased stiffness and insolubility. Such alterations have been ascribed to cross-linking reaction [5]. Also determined in this study is the stabilization of the mechanical properties that are accompanied by the decrease in solubility of the product during natural and dark aging. This correlates well to the film formation processes that occur in the early drying stages of these materials. It is also interesting to mention that the Liquitex® gloss medium was shown to be a EA-MMA co-polymer, which contrasts to the Liquitex® gloss medium studied in the work presented here, which is characterized as a BA-MMA. This is a good example of the changes that formulations may occur over time.

In a more recent study, Smith has shown that a BA-MMA formulation (Rhoplex® AC-235) also presents high wheathering resistance to light with wavelegth higher than 300 nm. The author shows that this product, in the long term, exhibits prevailing cross-linking reactions, even though these did not affect the overall tackiness or Tg of the product [9].

Lazzari *et al.* recently published an ageing study of commercial acrylic dispersions comprising EA-MMA and BA-MMA products, subjected to a Xenon-Arc filtered to wavelengths below 295 nm (experimental temperature was of 45 ºC) [12]. The results of this study are very relevant since they combine chemical and mechanical characterization of the samples during several exposures to radiation. The overall results indicate that both dispersions were less resistant to photoaging when compared to the homologous solution polymers, and this has been attributed to the presence of additives that may influence the aging reactions. Several conclusions were reached by the authors concerning the monomeric composition: first, all dispersion products showed an initial presence of insoluble fraction before aging, which was determined by SEC. This fraction increases with aging, especially in BA-MMA polymers, which is related to the oxidation of BA units (long alkyl chains) with cross-linking. At the same time, the analysis of the soluble fraction shows that low molecular weight products from chain scission reactions are also being produced, with negligeble formation of volatile compounds.

Overall, the oxidation reactions observed by FTIR spectroscopy are associated to the presence of the acrylate monomer, since they are preferable sites for oxidation. Unstable secondary peroxides that decay via cross-linking were seen in BA-MMA polymers and are in good agreement with results obtained by other authors [14,15]. Also very interesting in this study is the analysis of the Tg and mechanical properties of these products. The data shows that, even thought these aging processes are occuring in the films, the Tg is mildly affected by aging, which has been explained by the presence of competing cross-linking and chain scission reactions. However, the results obtained from stress-strain curves showed that the specimens exhibit an increase in Young's Modulus (stiffness) and decrease in strength for both types of polymers. This does not fully correlate with the results obtained by Whitmore and Colaluca [5,12].

Cocca et al [16] presented an interesting study on the durability to light aging (wavelengths longer than 300 nm) of EA-MMA dispersion products. The results presented by the authors showed that products that present similar polymeric composition can show sometimes contradictory chemical and mechanical aging behaviour trends. In the case of this study some EA-MMA products exhibited cross-linking behaviour and other predominantly chain-scission trends.

Early studies by Allen *et al* summarize the thermal and light aging trends of BA-MMA dispersion products with different monomeric ratios [14-15].

First, during thermal degradation, MMA homopolymer show an unzipping reaction (inverse of polymerization). This reaction is blocked by the presence of a comonomer such as BA, reducing the length of the fragments produced. BA homopolymers do not undergo unzipping. Rather they promote competing reactions of cross-linking and also chain scission.

With photo-oxidation (conditions of the experimental tests were with wavelengths longer than 300 nm and 50 ºC), it has been shown that BA-MMA promotes the formation of short-chain fragments, which increase with the amount of acrylate content via intermolecular reactions as shown in Figure 6.2.5. All copolymers with different BA:MMA ratios showed photolysis of the ester groups, shown in Figure 6.2.6.

An interesting result was obtained by measuring the amount of hydroperoxide concentration in the polymers. First, it was shown that the small amount of initiators present from the polymerization process readily decomposed and did not influence the overall peroxide formation. Second, the increasing amount of MMA showed the most formation of hydroperoxides. This was also related to the stability of such hydroperoxides. Thus, whereas the oxidation of tertiary carbon atoms present in the back chain of the polymer produces stable hydroperoxides in MMA, these were very unstable in BA enriched polymers. Also, BA units suffer photo-oxidation on the ester groups. The decomposition of peroxides is followed by the formation of further oxidation species such as ketones (lactones) and aldehydes [14,15,17]. The general photo-oxidation and photolysis of these polymers are illustrated in Figure 6.2.5 and Figure 6.2.6 [13,14,16], and are similar to those proposed by Lazarri *et al* [12].

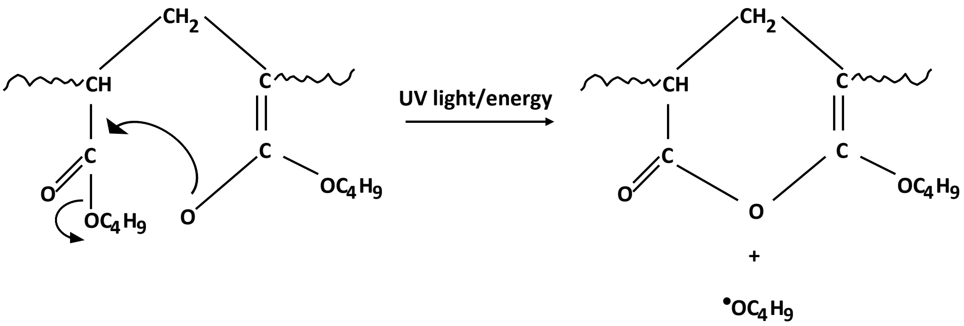

Figure 6.2.5: intra-molecular chain transfer process that involves terminal C=C carbon bonds. The formation of such products can be identified with FTIR absorptions at 1640 cm^{-1} [14,15,17].

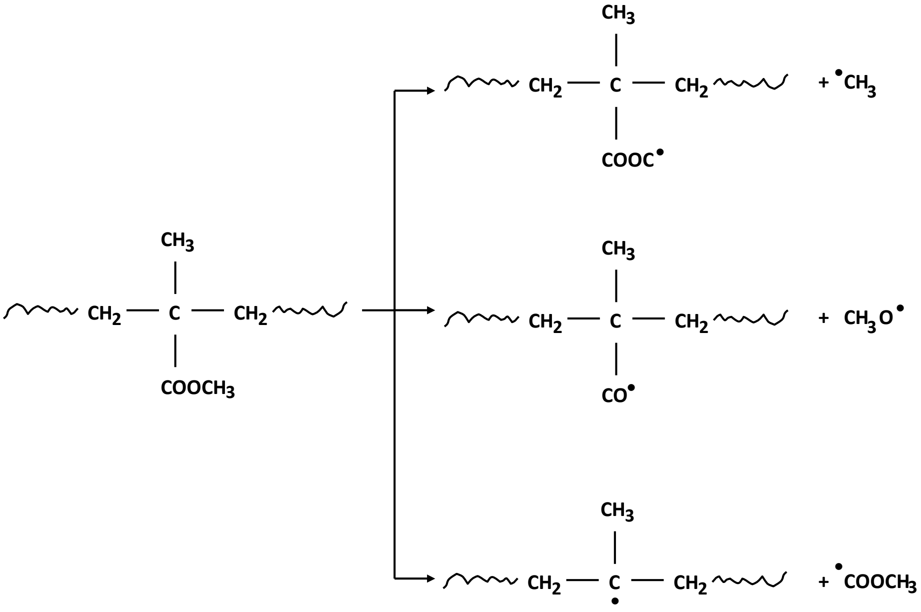

Figure 6.2.6: photolysis of the ester group represented for a MMA type polymer. These reactions have also been found in acrylates and are responsible for absorptions in FTIR at 1763, 1772 and 1793 cm^{-1}, attributed to peresters and peracids [12,14,16].

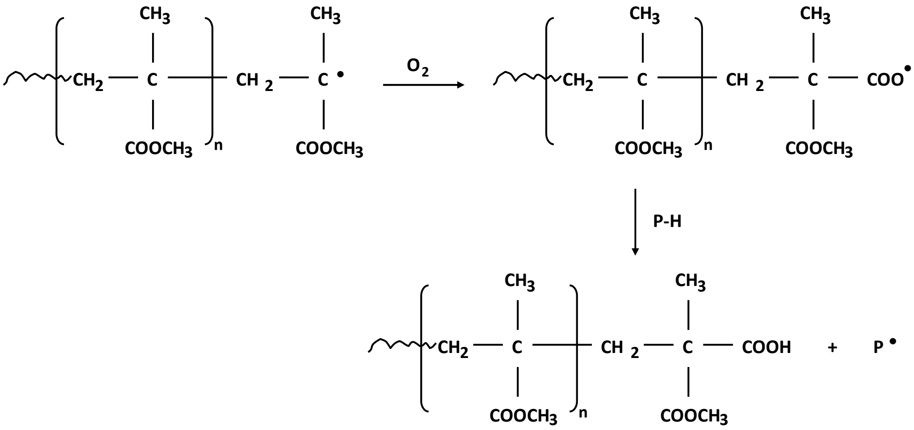

Figure 6.2.7: formation of end-chain hydroperoxides in MMA, according to Allen *et al* [12,14,16]. Such oxidation species are relatively stable.

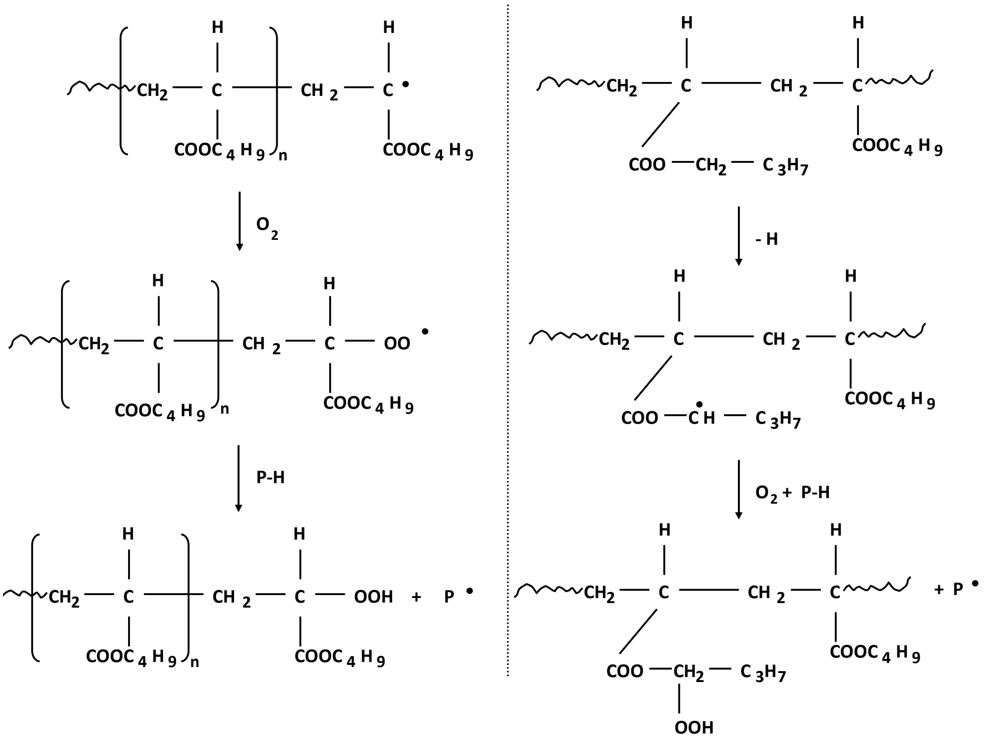

Figure 6.2.8: formation of hydroperoxides in BA according to Allen *et al* [12,14,16]. These oxidation species are unstable and tend to decompose rapidly. (Left) The formation of hydroperoxides in the main backbone chain. (Right) Mechanism of formation of hydroperoxides in the ester side groups.

A study on the aging of acrylic dispersion paints with EA-MMA and BA-MMA formulations has been published by Learner *et al* [7] and Scalarone and Chiantore [8]. Two aging regimes were used, one including a cut off radiation below 400 nm (indoor light exposure at ~30ºC, 30-40 %RH) and another with a cut off of wavelengths below 295 nm (UV light aging). These studies showed very interesting results. First, it was shown that EA-MMA and BA-MMA dispersion paints were very stable to both aging regimes. This means resistance to yellowing and no changes observable with FTIR spectroscopy. The only changes observed were in solubility of the films and determined by SEC analysis in the soluble fraction of the paint films (thus, direct measurements of the polymer itself were not carried out).

Acrylic dispersions have a high insoluble polymeric fraction after drying. Insolubility was found to increase in BA-MMA paint samples, but the trend was not consistent in the EA-MMA type, which showed opposite trends within the same paint brand (either increase solubility or insolubility). It was also shown that, in prsence of UV light component, some pigments can act as catalysts of photo-oxydation processes. This was observed for Cobalt Blue pigment in a BA-MMA formulation. The trends expected for EA-MMA are, as mentioned before, to suffer chain-scission reactions, rather than cross-linking. Another interesting result showed that the surfactants tend to disappear with aging by photodegradation. But only with stronger radiation was the surfactant fully eliminated from the bulk film. It became clear that mechanical tests of the specimens were needed in order to assess the physical effects of these aging programes.

6.2.1.6- The aging characteristics of dispersion styrene-acrylic polymers

In the study by Learner, Scalarone and Chiantore [7-8] a styrene-BMA-2EHA was included in the yellowing measurements during heat aging at 60 ºC. This paint sample exhibited a slightly higher sensitivity to yellowing when compared to pure acrylic ones. A more comprehensive study on the aging of styrene-acrylic paint samples has been published recently by Papliaka *et al* [18]. The aging regimes tested by the authors comprised heat and moisture (90 ºC, 60 %RH) and UV light in the 300-400 nm region, with peak at 350 nm (UV component simulating daylight filtered through a window glass). The temperatures of this aging program rose from 50 ºC to 90 ºC. The results obtained by FTIR spectroscopy on the aging of the styrene-acrylic polymers revealed the following trends:

1. The thermal and moisture aging induced minor structural modifications attributed to the BMA and 2EHA, rather than styrene. These experience oxidation on the side groups, form hydroperoxides and undergo scission, followed by the formation of carboxylic acid groups and anhydrides. This is in good correlation with the theory cited previously in this work [3,4]. Oxidation in the tertiary carbon of the ester group of

2EHA was also observed with the consequent decomposition. Side group elimination was also proposed by the authors in the long chain alkyl groups.

2. The UV light aging results indicated the formation of lactones from the photo-oxidation of the long alkyl side groups, as well as the ester loss. Moreover, with UV light aging, the decreasing of the bands associated to the styrene ring reveal ring that opening-ring reactions are promoted by UV energy.

The aging characteristics of styrene based polymers can be very complex, and a detailed description on possible degradation chemical species has been described by Holland *et al* [19]. Nevertheless, it is interesting to regard that the generally acepted view of degradation of styrene units is related either to the presence of impurities in the backbone chain or to the presence of macroradicals[24] in the tertiary carbon atom in the back bone chain. These lead to oxidation and peroxide decomposition by photolysis as shown in Figure 6.2.9. The decomposition of the aromatic species has been also described in this study, but it has been associated to UV aging regimes with wavelengths below 300 nm. The reader is referred to this study for further details [19].

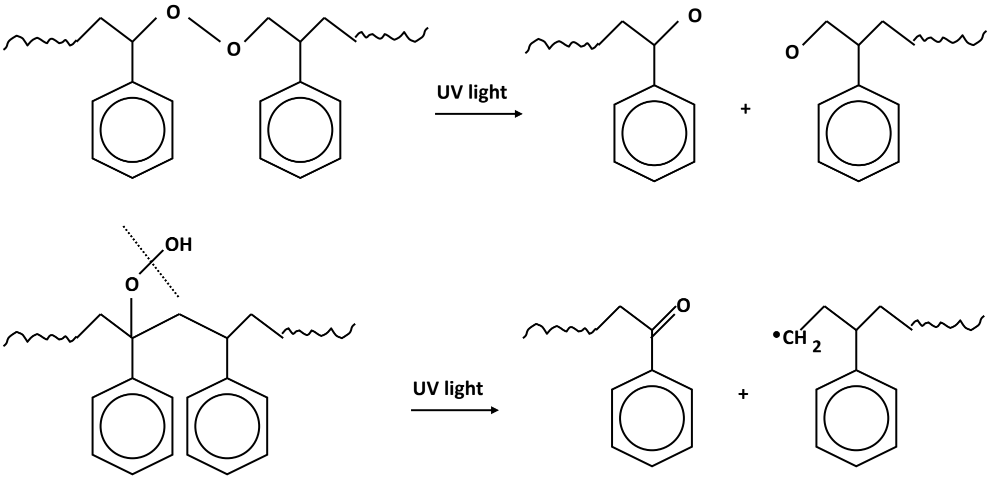

Figure 6.2.9: proposed intial steps of photodegradation/photo-oxydation of poly(styrene) proposed by Holland *et al* [19]. The resulting products can undergo further degradation mechanisms that can involve formation of acetophenone, muconaldehyde, in-chain ketones, end-chain aldehydes and keto-lactone type groups.

6.2.1.7- The aging characteristics of dispersion PVAc polymers

Studies on the aging characteristics of PVAc dispersion products used in paint are less common that those exhisting for acrylics. PVAc polymers subjected to thermal degradation at 100 ºC are known to

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[24] A macroradical is a macromolecule that is also a free radical. A free radical is a molecule with an unpaired electron. In this context a macroradical reffers to a polymer fragment (macromolecule) that has an unpaired electron.

liberate acetic acid via elimination reactions and formation of a doble bond [1,11]. Under UV light exposure with wavelengths under 295 nm radiation, these polymers undergo chain-scissions and release of volatile compounds such as acetic acid, methane, carbon monoxide and carbon dioxide, by Norrish type mechanisms, as presented in Figure 6.2.10 [1,19,20].

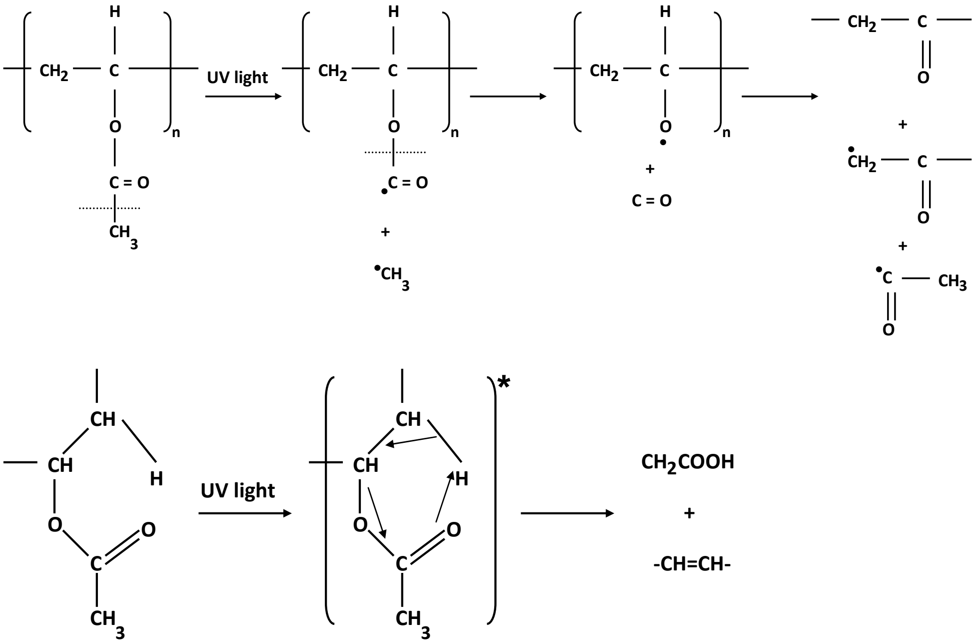

Figure 6.2.10: (Above) Norrish type I reaction, with the production of several volatile products in the intermediate steps. (Below) Norrish type II reaction with liberation of acetic acid, adapted from [20].

An interesting study on the degradation of a PVAc based dispersion used by a Portuguese artist has been published recently by Ferreira *et al* [20]. In this study, the irradiation used was above 300 nm, with a Xenon-Arc lamp (24 ºC and 40 %RH). This study revealed that the PVAc based emulsion is very stable at such wavelengths and that the main degradation pathway is mainly due to chain scission and not side group elimination. Acetic acid elimination was not detected by FTIR, and combination with other characterization methods was not performed [20]. Acetic acid emissions have, nevertheless been observed by Down *et al* in the aging of PVAc products, especially in the early stages of curing [11]. But it is not clear in this study if the emission of volatiles was due to the presence of small molecules released from the dispersion in the first drying and curing stages, rather than from the degradation of the polymer itself. No significant yellowing was observed in the paint samples tested by Ferreira and, moreover, the presence of different pigments did not appear to influence significantly the degradation pathways.

In summary, all studies concerning the light aging characteristics of pure acrylic paint films suggest that these products will not suffer major changes in their chemical and mechanical behaviour with time. This is encouraging since they can actually benefit light exposure without suffering fast aging, considering that these materials may suffer discoloration in the dark [27]. The sum of the studies indicates that acrylics are durable materials, and that the main guidelines to safe care and handling of artworks with these materials will be the similar in the future to those regarded today. These include a special attention to Temperature drops below Tg that induce a brittle behaviour. Also, care for good ventilation due to dust accumulation, especially if temperature conditions are not adequate (higher than room temperatures) [25-26].

On the other hand, the studies conducted so far on paints containing PVAc and Styrene-acrylic also reveal good stability to light exposure. However, these materials show more degradation evidences under aging trials when compared to acrylics [11]. Data on the mechanical properties of such materials is scarce (especially on Styrene-acrylic paints) and may give a good insight in what the extention of degradation may be and help establishing conservation guidelines.

6.2.2- Study of the aging behaviour of acrylic and PVAc products subjected to simulated daylight

In view of testing the aging behaviour of acrylic dispersion paint samples, a range of colours from each acrylic brand considered in this study was subjected to two aging programs: a simulated daylight aging and a UV light aging regime[25]. Both accelerated aging programs corresponded to realistic aging conditions, with low temperatures and mild relative humidity. This was intended to simulated museum or gallery exposition conditions [28 JULIO DEL HOYO]. And, thus, avoid results that are derived from possible extreme aging conditions (high temperatures and UV-B light content), that originate degradation pathways that do not correspond to those developed in normal exposure conditions.

The aging trials consisted of a two step simulated daylight aging (Xenon-Arc lamp) program of 400 and 800 hours at 115000 Lux, 26-27 ºC. The UV component below 300 nm was controlled through a S-filter. Approximately, these conditions correspond to a 74 and 153 “museum years”. A similar set of samples was subjected to a multi-step UV light aging program. The aging steps consisted of 400, 800, 1200 hours exposure to 804 Lux for the visible range, and 612 W/m^2 for UV range, which simulate the UV content of sunlight filtered by a window glass (UV peak maximum at 351 nm). Some Liquitex® samples where further aged to 2500 hours. Since there was an important thermal component (~34 ºC), a similar set of samples was protected from light and introduced in the UV chamber, for receiving only the heat component produced by the lamps during the trial. These samples are referenced in the text as *thermal controls*, or thermally aged samples, and are used to distiguish the heat effect of light effect.

Changes in the chemical composition of the aged samples were studied by FTIR-ATR. In parallel their mechanical properties were determined. Due to the large test matrix of samples and conditions, only the representative cases are presented for each brand studied.

A summary of the aged paint samples according to brand and colour is presented in Table 6.2.1.

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[25] A more detailed description of the aging programs can be found in the experimental section of this work.

Brand	Daylight simulation	UV aging
Liquitex® heavy body	titanium white	titanium white*
	zinc white	zinc white*
	pthalocyanine blue	pthalocyanine blue
	naphthol red	naphthol red*
	burnt umber	burnt umber*
	gloss medium and varnish	gloss medium and varnish
Royal Talens®	titanium white	titanium white
	zinc white	zinc white
	naphthol red	naphthol red
	raw sienna	raw sienna
	gloss medium	gloss medium
	gel medium	gel medium
Vallejo®	titanium white	titanium white
	naphthol red	naphthol red
	pthalocyanine blue	pthalocyanine blue
	-	iron oxide
Pébéo®	titanium white	titanium white
	napthol crimson	napthol crimson
	red oxide	-
	phthalocyanine blue	phthalocyanine blue

Table 6.2.1: summary of the samples tested for the two aging programs: daylight UV light and simulated aging. The samples marked with an asterisc (*) have been subjected to 2500 hours of UV light aging.

6.2.2.1- FTIR-ATR study of acrylic products exposed to simulated daylight aging

a) Liquitex® Heavy Body

The 400 hours and 800 hours of simulated daylight aging of Liquitex® gloss medium are included in Figure 6.2.11 along with two control samples, one obtained in the first week of casting and the second prior to the aging trials after one year casting. The spectra show that during the drying process there is a decrease in the broad -OH band (peak at 3350 cm^{-1}) ascribed to the evaporation of water or compounds with terminal –OH groups, which is confirmed by the absorption at 1045 cm^{-1} between the recently cast film and the fully dried product.

In early studies, Whitmore *et al* characterized Liquitex® gloss medium films as EA-MMA polymers with high amounts of PEO type compounds [5]. In the case of the Liquitex® product studied here, the products were characterized as BA-MMA copolymer. This is another example of changes in formulation one can find with time within the same product label. No evidences of PEO type compounds have been detected by means of FTIR-ATR.

The study of the aged samples by FTIR-ATR reveal minimal spectral differences between the unaged (1 year drying) and 400 and 800 hours aged films, as evidenced in Figure 6.2.11.

Overall, the carbonyl absorption at 1728 cm^{-1} does not decrease, nor reflect broadening, with aging and only very moderate changes in the spectra are seen in the ester region at 1150 cm^{-1} as well as in the -OH region (broad band centered at 3350 cm^{-1}). These changes are ascribed to oxidation, even though to a very limited extent. Since the carbonyl peak appears to be unaffected, it is possible that these oxidation processes are related to polymer backbone rather than side group processes.

In general, the limited changes in the spectral profiles of the aged samples indicate photo-oxidation stability at the present artificial aging conditions. No additional peaks are detected after the aging trials, as expected for *stronger* aging regimes such as those used by other authors in the introduction of this chapter.

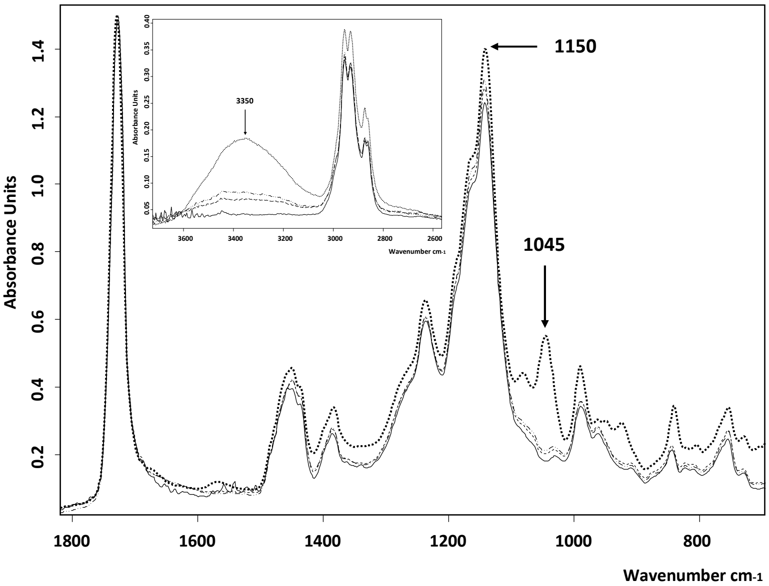

Figure 6.2.11: Liquitex® gloss medium FTIR-ATR spectra in the 1800-700 cm^{-1} region obtained from the curing and daylight simulated aging. The spectra correspond to: 2 weeks drying (dotted line), 1 year curing (solid line), 400 hours aging (dashed line) and 800 hours (dashed-dotted line). The last two spectra are superimposed due to similarity. The region corresponded to the –OH region.

The FTIR-ATR spectra of Liquitex® zinc white paint samples aged for 400 and 800 hours are shown in Figure 6.2.12. In the figure are pointed out bands ascribed to PEO-type compounds (main absorptions at 2886, 1341, 1111, 954, 843 cm^{-1}), more specifically a octylphenol polyethoxylate type surfactant, which has been characterized priorly in this work by Py-Silylation-CG-MS[26] and is

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[26] The reader is referred to the chapter dedicated to the characterization of the test samples studied in this work.

confirmed by the small sharp peak at 1514 cm^{-1} ascribed to aromatic ring absorptions. A list of studies on the analysis of PEO extracted additives from acrylic formulations have been gathered elsewhere by Bronwyn and Learner [1].

Also pointed out in the figure are the absorptions at 1565 cm^{-1} ascribed to metal-carboxylate complexes, most probably calcium-carboxylate formed from the combination of the calcium ions coming from calcite extender and acrylic or methacrylic acid present in the emulsion [21,30].

The FTIR-ATR spectra obtained for the aged samples indicate that the binding medium does not suffer detectable degradation, which is in good correlation to the results obtained for the gloss medium. On the other hand, the absorptions ascribed to PEO type additives show alteration, with a general tendency to decrease intensity. This is in good agreement with previous studies where these observations have been related to the degradation of both ethoxylated chain as well as hydrocarbon moiety [23]. It is interesting to notice though, that the peak at 1514 cm^{-1} related to the aromatic ring decreases intensity but is still present at 800 hours aging, which reflects higher stability of this moiety when compared to the etoxylated chain. This is in full agreement with studies performed by Hidaka *et al* that state the PEO chain degrades faster that the hydrocarbon moiety [24].

Moreover, the absorption related to the metal-carboxylates complexes also decreases, which shows that these species are affected by light. The aging patterns of the other Liquitex® pigmented samples showed a similar pattern. Absorption peak at 1565 cm^{-1} was also found in this sample despite the metal ions present here are different. This result sustains the hypothesis of formation of calcium-carboxylates from the combination of the extender and free acrylic and methacrylic acid. The presence of calcium carbonate in the studied samples was confirmed by parallel analyses performed with SEM-EDX, and the interactions of surfactants and ions have been reported previously [21,33-35].

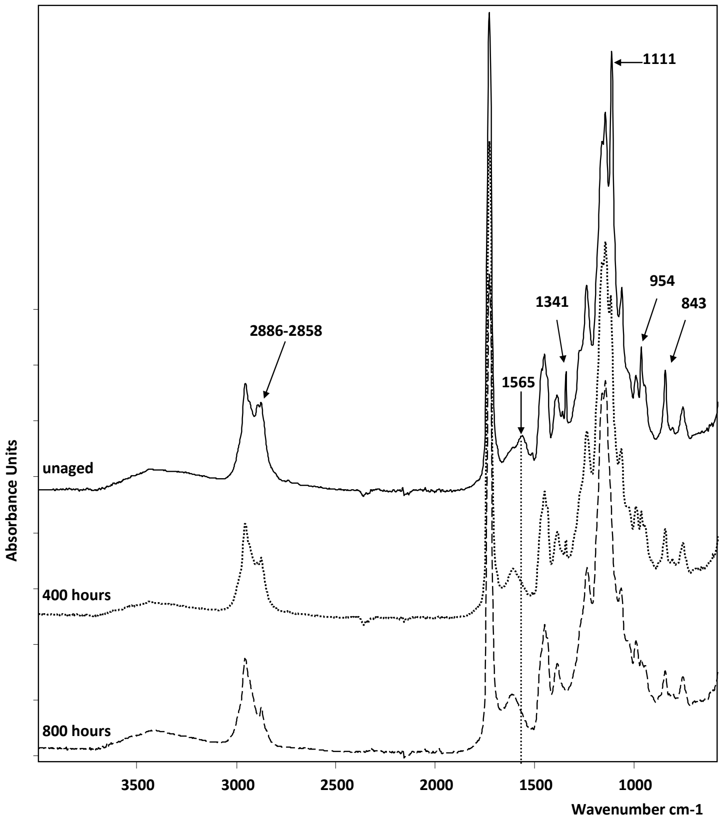


Figure 6.2.12: FTIR-ATR spectra of Liquitex® zinc white obtained after 400 and 800 hours of daylight simulated aging trials. The bands pointed out in the figure are related to the presence of a PEO type additive (octylphenol type surfactant). The figure shows the effects of the light aging trials in the degradation of this surfactant that leads to its disapearing from the surface.

b) Royal Talens® series

The FTIR-ATR spectra corresponding to the aging of Talens® gloss medium are shown in Figure 6.2.13. The aged samples showed yellowing and a gel consistency that render it impossible to separate them from the Mylar® support for mechanical testing.

The main degradation feature is the disappearing of the band at 1115 cm^{-1} and shoulder at 1096 cm^{-1}, ascribed to a PEO type compound. The decrease in the PEO absorptions is accompanied with the limited appearence of a series of new absorptions in the ~1650-1540 cm^{-1} at 400 hours of aging. The band at ~1650 can be associated with the formation of C=C double bonds, possibly formed during the decomposition of the PEO type products, and the other minor absorptions can be associated to the formation of carboxylic acids groups. These peaks were not observed at 800 hours of aging.

A limited decrease in the –CH region at 3000-2800 cm^{-1} after both 400 and 800 hours aging may correspond to degradation of polymeric chains to some extent.

If such degradation is accuring, chain-scission reactions should be more probable than cross-linking in EA-MMA type polymers [1], which is in good agreement with the overall gel-like consistency of the films. Additionally, there is no evidence of side group oxidation or elimination since the carbonyl (1725 cm^{-1}) and ester (1155 cm^{-1}) absorptions remain unaffected. This is generally expected for EA-MMA products, as described in the introduction of this chapter.

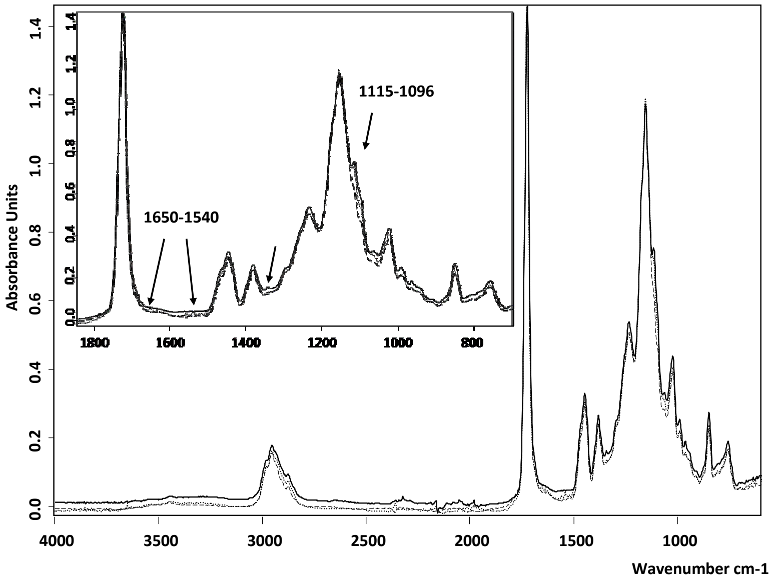


Figure 6.2.13: FTIR-ATR spectra of Talens® gloss medium (solid line), after 400 hours (dotted line) and 800 hours (dashed line) of simulated daylight aging regimes. Above is a magnification of the 1800-700 cm^{-1} region. The numbers labeled ascribed to surfactant degradation.

The aging of Talens® naphthol red is shown in Figure 6.2.14. The overall degradation features show similar trends to those seen in the pure medium. The bands corresponding to the polymer chains do not show evidence of degradation, and a decrease of the major surfactant absorptions at 1110 cm^{-1} and 2888 cm^{-1} is evident. The FTIR-ATR spectrum of the unaged sample clearly demonstrates that the surfactant content decreases consistently with the several aging steps. Also pointed out in the figure is the broadening in the 1700-1580 cm^{-1} region, which is atributed to oxidation products. It remains unclear if these oxidation products are related to the polymer itself or to additives.

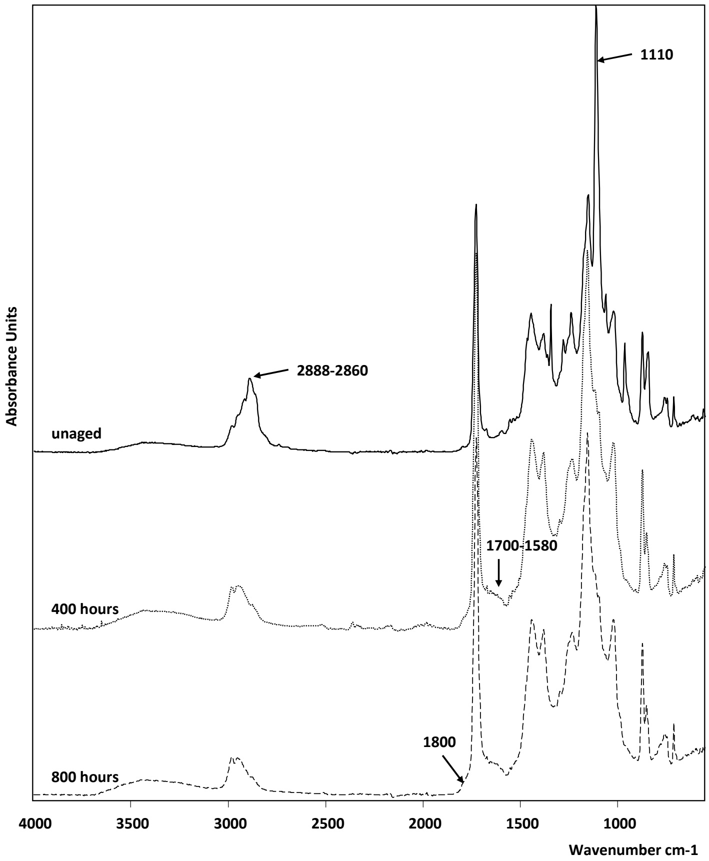


Figure 6.2.14: Talens® naphthol red FTIR-ATR spectra after 400 hours, 800 hours daylight simulated aging trials.

c) Vallejo® series

Vallejo® phthalocyanine blue FTIR-ATR spectra obtained after the aging trials are presented in Figure 6.2.15. For clarity reasons, the figure shows a magnification of the spectral region comprising the 1800 to 700 cm^{-1} range. The spectra illustrates a small but progressive decrease in the general polymer absorptions (decrease in carbonyl content and moderate increase in the ester absorption) which is in good agreement with the aging of BA-MMA, indicating that side group degradation reactions may be occuring [14,15,17]. These reactions are, for these samples, fairly limited.

In the unaged sample shown in Figure 6.2.15, there is an absorption band at 1560 cm^{-1} that has been associated previously to metal-carboxylate groups in Liquitex® samples. Interestingly, both Liquitex® and Vallejo® share similar composition (BA-MMA) and this result appear to suggest that similar additives, and extenders, form such complexes. With light aging, this peak tends to disappear, which is also consistent with the results obtained for the Liquitex® samples.

A broad band centered at 1613 cm^{-1} is formed with aging and is ascribed to the formation of oxidation species. However, the exact nature of this band has not been fully disclosed to date.

The results presented for phthalocyanine blue have been observed for all paint samples tested with the exception of titanium white. This paint sample did not show evidence of degradation, possibly due to its high PVC content that may act as a shield to light absorption.

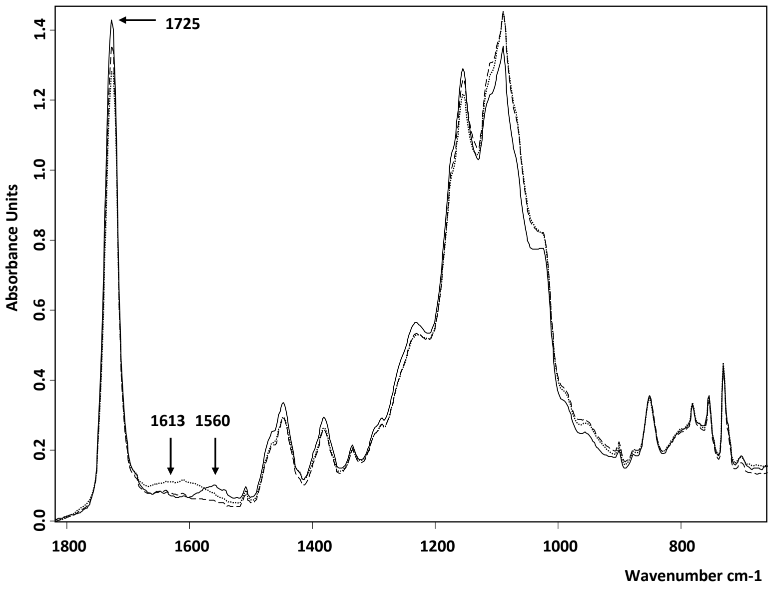


Figure 6.2.15: FTIR-ATR from Vallejo® phthalocyanine blue after 400 hours (dashed line) and 800 hours (dotted line) daylight simulated aging. See text for pointed absorption peaks.

d) Pébéo® series

The results obtained from the 800 hours simulated daylight aging conditions of Pébéo® red oxide are shown in Figure 6.2.16. The analysis of the –CH region indicates an overall decrease in these absorptions, especially those related to the CH_2 groups. The loss of matter rich in CH_2 groups is associated to the elimination of long alkyl side group chains. This hypothesis is further confirmed by a discrete decrease in the carbonyl absorption shown by the aged spectrum of the samples. On the contrary, the styrene moiety seems unchanged after the aging regime (styrene main absorptions are assigned in the spectrum). A slight decrease in the overall polymer absorptions in relation to the calcium carbonate extender may be related to a discrete loss of polymeric material at surface of the sample. Nevertheless, by FTIR-ATR, no strong degradation processes have been identified.

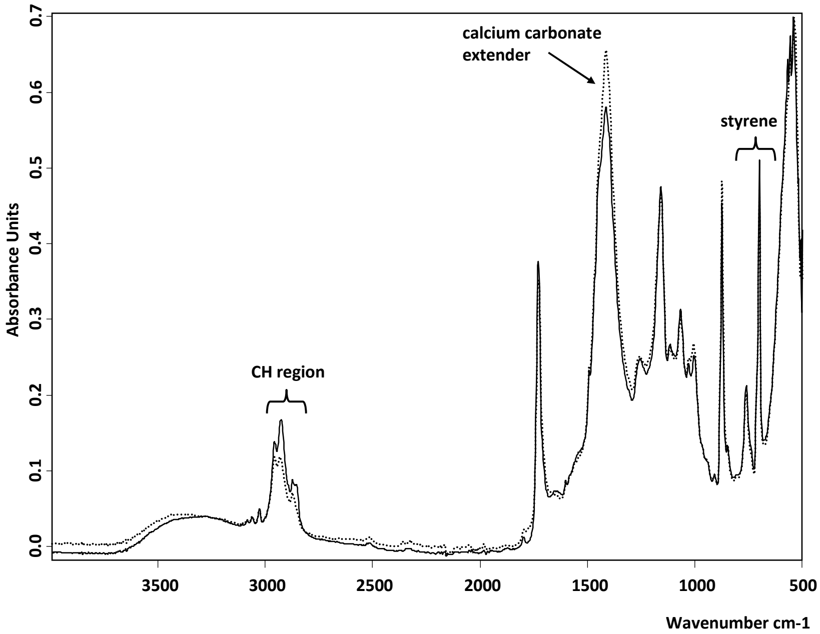


Figure 6.2.16: Pébéo® FTIR-ATR spectrum of red oxide subjeted to simulated daylight aging. The dotted line corresponds to the 800 hours aged sample, the solid line corresponds to the unaged control sample.

6.2.2.2- Study of the mechanical properties of acrylic products exposed to simulated daylight aging

a) Liquitex® Heavy Body series

The results of the mechanical testing of Liquitex® heavy body paint films subjected to a 400 hours and 800 hours daylight aging program are presented in this section. The test matrix included titanium white, zinc white, burnt umber, phthalocyanine blue, naphtol red and Liquitex® acrylic gloss medium.

In Figure 6.2.17 are shown the mechanical properties of a reference sample of Liquitex® gloss medium (~4 years old) and a sample aged for 800 hours. Both samples revealed similar mechanical behaviour (stiffness and flexibility) that reflect the high stability of the product. This is in fairly good agreement with the data obtained by FTIR-ATR that showed no evidence of polymer degradation.

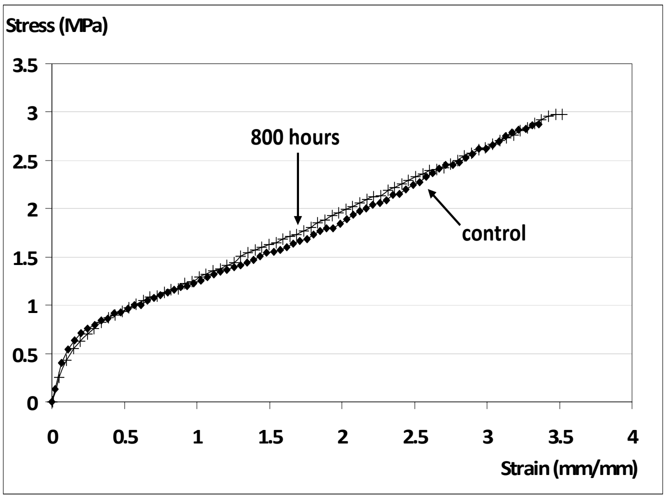


Figure 6.2.17: the mechanical properties obtained for Liquitex® gloss medium (BA-MMA). Results are shown for control and 800 hours of aging. The samples show high stability to degradation under the aging conditions.

Unexpectedly, the aged Liquitex® pigmented films revealed differences in the mechanical behaviour when compared to the binding medium. An illustrative example of the general mechanical behaviour trends showed by the aged Liquitex® paint samples is shown in Figure 6.2.18, for a naphthol red (see Appendix B.2 for results concerning other pigments). The paint films showed a progressive decrease in stiffness (Young's Modulus) with increasing light exposure and did not show loss in extension to failure (elongation up to 500%).

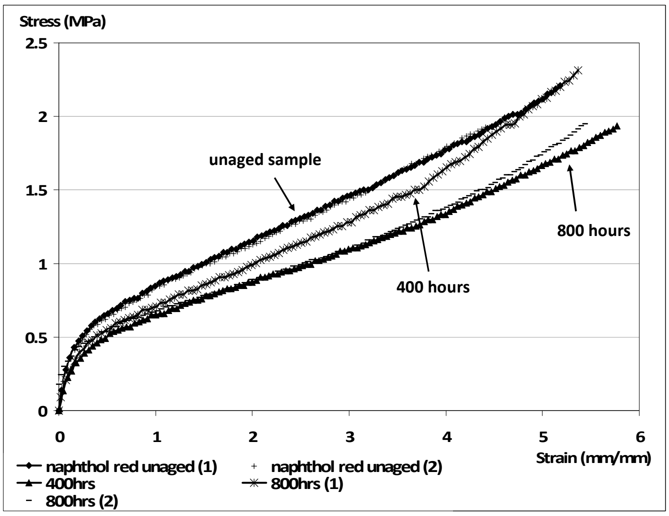


Figure 6.2.18: the mechanical properties of Liquitex® naphthol red paint films after the daylight simulated aging trials. A decrease in the stiffness of the paint samples is readily visible. In this graphic are included repetitions of each sample to show the consistency of the results obtained.

The decrease in Young's Modulus can be tentatively ascribed to two main degradation mechanisms: one process can readily be associated to the degradation of the polymer, specifically to chain-scission reactions, that may lower the molecular weight of the polymer chains and, consequently, lowering the Modulus. This should also be accompanied with a decrease in flexibility. There was no clear indication of such processes with FTIR-ATR analysis. Another point to discuss at this time is that the pure binding medium (with same polymeric composition) did not evidence such degradation, which leads to think that the increase in flexibility may be related to the presence of additives.

A second possible degradation pathway may be related, thus, to the additives. In that case, the fragmentation of the additive chains leads to smaller molecular weight molecules that can act as plasticizers inside the bulk film and aid the overall loss in mechanical strength observed with aging. The degradation and elimination of additives with light aging can also contribute to a further coalesced film that could explain the increase in elongation of these paint samples. Such degradation processes of the PEO additives have been generally observed by FTIR-ATR analysis and have been studied by other authors [7,8,21,24]. These results are in good agreement with those obtained for the UV light aging program, which will be discussed later in this chapter.

b) Royal Talens® series

Talens® test samples aged under the simulated daylight regime consisted of titanium white, zinc white, naphthol red, and gloss and gel media. After the aging trials, Talens® gloss and gel media were impossible to separate from the polyester sheet and the characterization of the mechanical properties could not be carried out. For the rest of the test samples, no problems occurred during the separation of the film from the support.

The mechanical properties of Talens® raw sienna aged samples are presented in Figure 6.2.19. The mechanical properties shown by these samples are in very good agreement with the results described by FTIR-ATR. First, the samples showed an overall mechanical stability at these aging conditions. Second, a slight loss in tensile strength is observable, especially in the first 400 hours of aging, which appears to be related to the degradation of the additives and the formation of small fragments that may act as plasticizers for the film. With further degradation, at 800 hours, these compounds tend to keep degrading and eventually disappear, which is reflected in the mechanical properties with a slight increase in stiffness.

Overall, all Talens® samples showed a similar trend in the mechanical properties, with apparently minor changes in the mechanical properties after 800 hours aging (approximately 100 years aging at museum conditions).

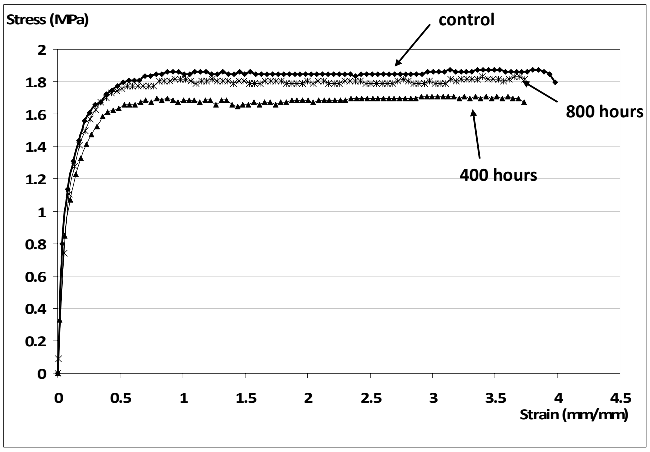


Figure 6.2.19: mechanical properties obtained for Talens® raw sienna paint samples subjected to 400 and 800 hours of simulated daylight aging.

c) Vallejo® series

The effects of the aging on Vallejo® series show trends similar to thoseobserved for the Liquitex® brand. This is interesting since these brands share the same polymeric composition (both BA-MMA). The samples show a steady decrease in strength with aging, but the films remain flexible. For this brand, the samples elongated from 600-700 % at room temperature. An example of this is presented in Figure 6.2.20, for phthalocyanine blue. It is interesting to notice that the strength to failure, or ultimate strength, is higher than that presented by the control sample, and the overall shape of the stress-strain curves are also different. As discussed previously for the aging of Liquitex® paint samples, the loss in stiffness is ascribed to possible changes in the polymer as well as additives. Some degradation of the polymeric matrix of Vallejo® paint samples has been detected by FTIR-ATR analyses; however, the degradation occurs to low extent to clearly determine the nature of the degradation pathways. In view of the mechanical results it is fair to propose, if there is polymeric degradation, that the main competing processes are chain-scissions.

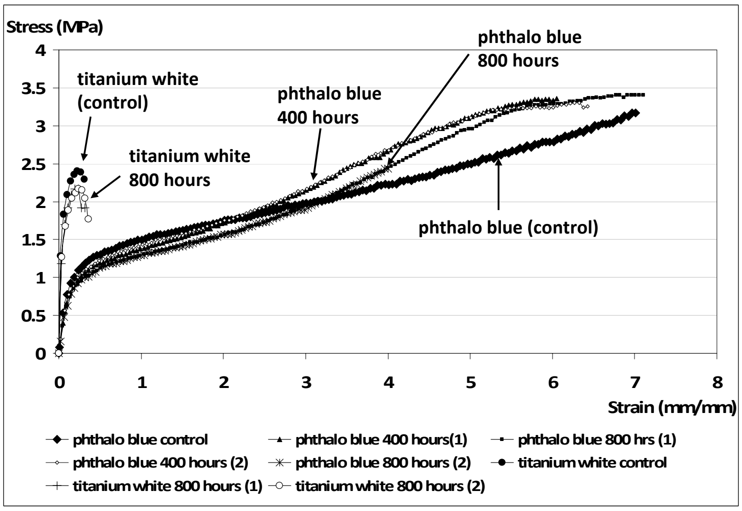


Figure 6.2.20: mechanical data obtained for Vallejo® titanium white and phthalocyanine blue. It is important to notice that, even though phthalocyanine blue samples exhibit higher ultimate strength with aging, the Young's Modulus decrease with aging.

In the figure have also been included the stress-strain curves of titanium white. This sample presents high PVC and therefore the samples were fairly less flexible, when compared to phthalocyanine blue. The mechanical properties of titanium white after 800 hours indicate that the average Modulus also decreases slightly, as the samples maintain similar flexibility to that presented by the control sample. In contrast to the results shown by pthalocyanine blue and naphtol red samples, there was no increase in the ultimate strength values.

d) Pébéo® series

Pébéo® paint samples revealed a different aging behaviour when compared to the previous samples. The data obtained from the stress-strain tests indicate that the samples tend to increase stiffness and loose flexibility (suffer embrittlement), which is generally consistent with chain-scission and side group elimination processes. Figure 6.2.21 shows the mechanical properties of naphthol crimson and titanium white aged samples. The mechanical properties shown by these films are in fairly good agreement with the data obtained by FTIR-ATR that showed overall degradation of the polymeric chains in the –CH region, with possible loss of side groups from the bulky side groups, showed by the decrease of the carbonyl content. Even though they show limited degradation, these samples seem to degrade faster than pure acrylics. This trend is in good agreement with previous studies [14-18].

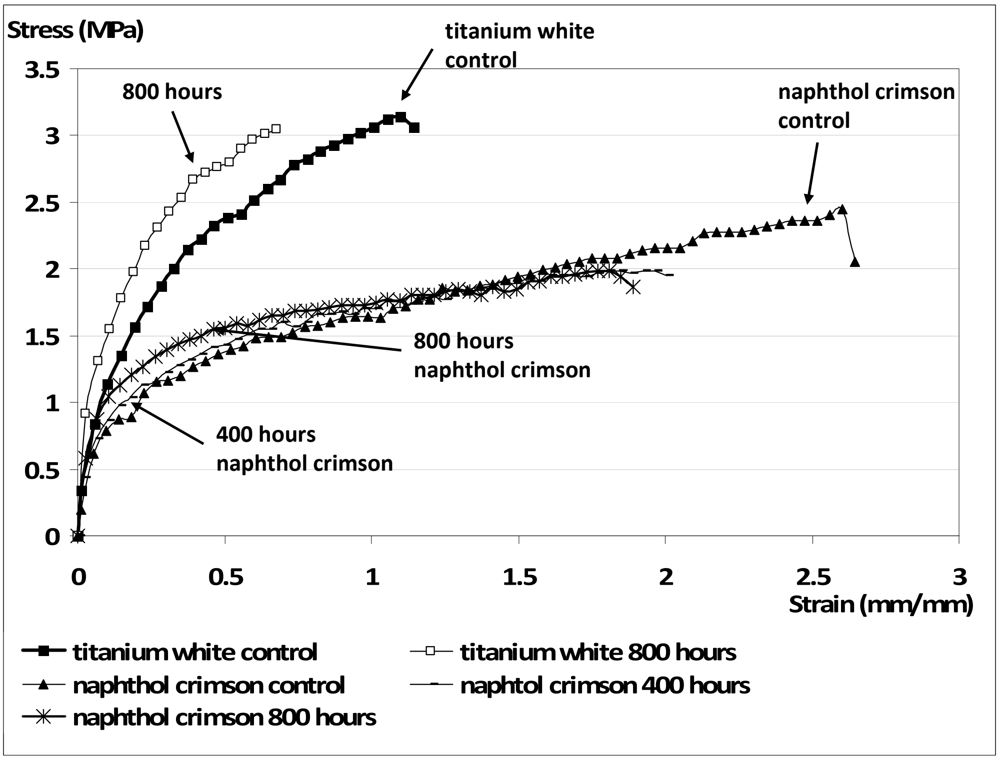


Figure 6.2.21: mechanical data obtained for Pébéo® naphthol crimson and titanium white. The samples tested showed increase in stiffness and fail sooner. This is related to the degradation of styrene-acrylic type polymers.

6.2.3- Study of the aging behaviour of acrylic products subjected to UV light artificial aging programs

6.2.3.1- FTIR-ATR study of acrylic products exposed to UV light aging

a) Liquitex® Heavy Body series

A set of Liquitex® test specimens consisting of gloss medium and varnish, titanium white, zinc white, burnt umber, phthalocyanine blue and naphthol red was subjected to a multi-step UV light aging program, consisting of 400 hours, 800 hours and 1200 hours light exposure. Titanium white, zinc white, burnt umber and napthol red received an additional aging step of 2500 hours. Taking into account that the temperature inside the aging chamber was relatively elevated (average 36 ºC), a similar set of samples was protected from the light source and aged at for 1200 hours, exclusively receiving heat. For comparison purposes, and to discard possible temperature effects but not UV light effects, the results are also included in this section. The samples that were exposed to heat are reffered to as "thermal controls" in the text.

The results obtained for the UV light aging of Liquitex® naphtol red are presented in Figure 6.2.22. The results clearly show similar trends to those seen with the daylight simulated aging trials: the overall polymer absorptions do not show degradation, whereas the absorptions corresponding to PEO type additives decrease in intensity. This suggests that the major degradation pathways seen at these conditions are possibly not occuring to the polymer itself but to the additives. Furthermore, the FTIR-ATR aquired for the thermal control samples show that the surface is enriched in surfactant when compared to the reference, unaged sample. This indicates that temperature is a very important factor in additive migration/exudation, whereas intense UV light exposure promotes photo-degradation of the additives, which is in good agreement with previous studies [12,31].

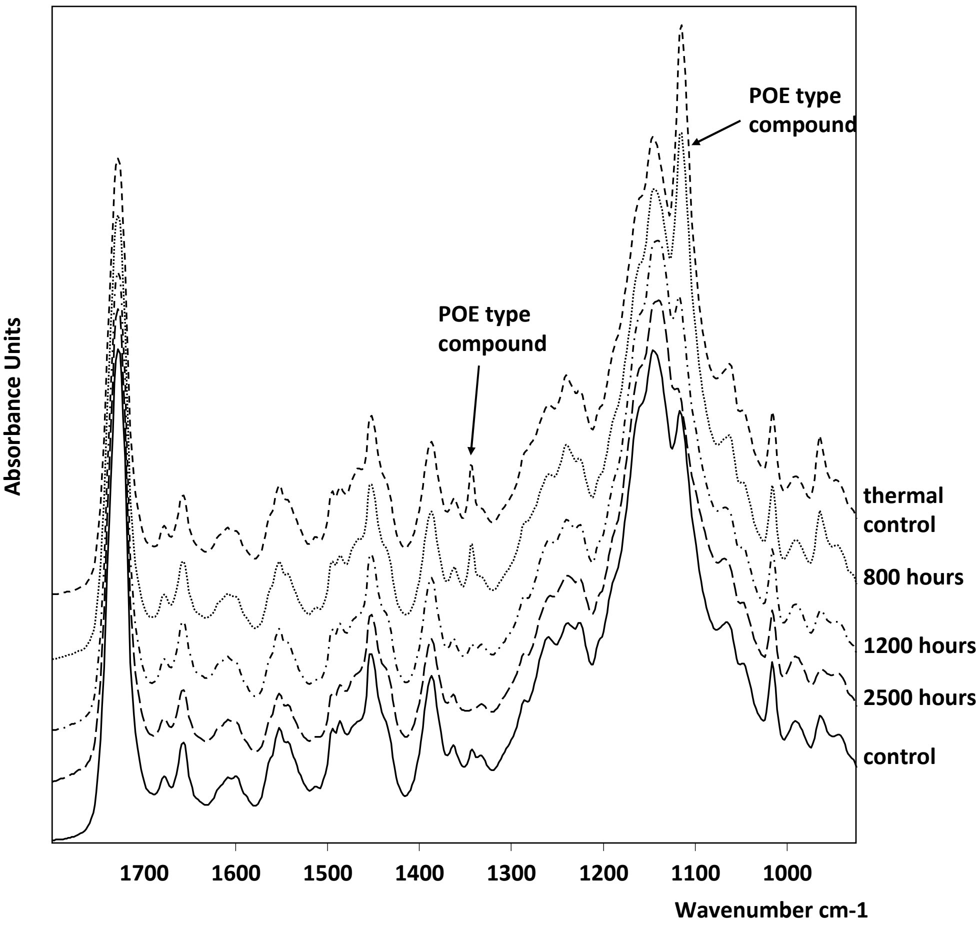


Figure 6.2.22: FTIR-ATR spectra of Liquitex® naphthol red after the UV aging trials (range 1800-800 cm^{-1}). The samples included here received 800, 1200 and 2500 hours of light exposure. Additional control and thermal control samples have been included. The results show the photo-degradation of the surfactant at the surface of the samples with increasing exposure. The comparison between the thermal control and the unaged control sample shows that temperatures above normal environmental conditions (eg. 37ºC) can lead to major surfactant exudation.

The FTIR-ATR spectra obtained for Liquitex® burnt umber are presented in Figure 6.2.23 and also show a very consistent degradation patterns with the daylight aging trials. The spectra shown here comprise the reference sample, thermal control and aged sample for 2500 hours. Similarly to the daylight trials, absorption at 1560 cm^{-1} ascribed to carboxylate-metal complexes is present. This band is not present in the light aged samples (disappears after the first 400 hours of aging) but is present in the thermal control. This demonstrates that these complexes are photo-sensitive.

In general, there is a limited decrease in the general polymer absorptions and the carbonyl-ester ratio also suffers a change after the aging regimes. A new carbonyl species appears centered at 1780 cm^{-1} and is associated to the photo-oxidation of the BA side groups, as discussed in the introduction of this chapter [15]. An increase in the absorption around 1640 cm^{-1} may be related to the formation of terminal C=C double bonds [14].

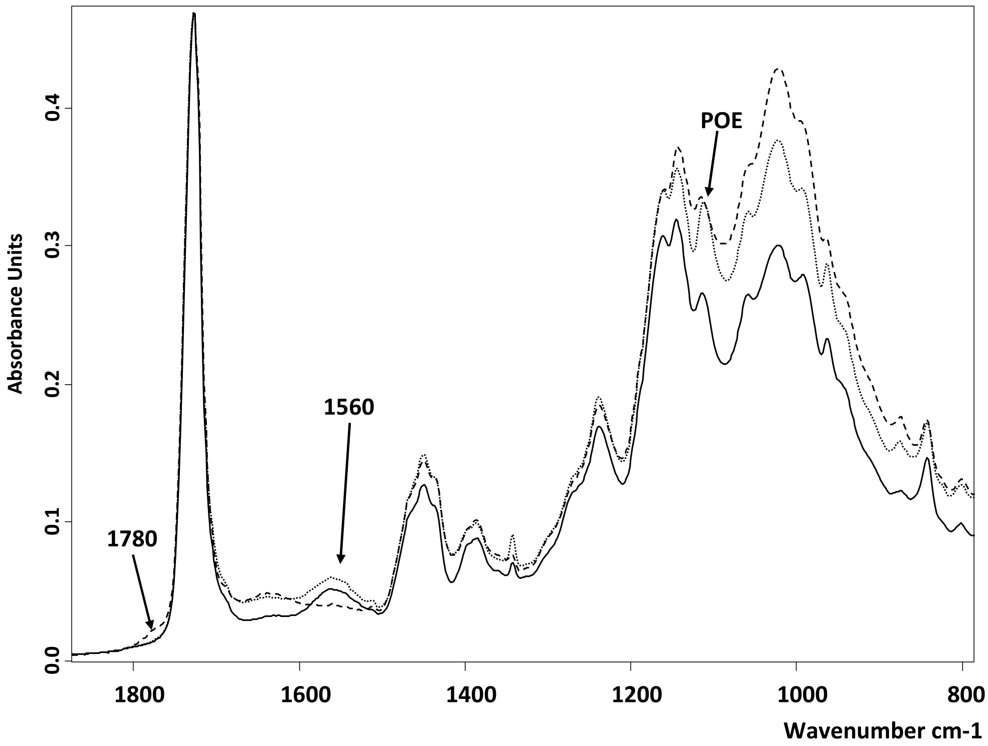


Figure 6.2.23: FTIR-ATR spectra on Liquitex® burnt umber. Samples shown comprise reference sample (solid line), thermal control (dotted line) and 2500 hours UV aged sample (dashed line). The other UV aging steps were not included in this figure for clarity reasons. They shown similar trends to that shown for naphthol red.

The rest of the Liquitex® samples showed similar behaviour. Interestingly, and consistent with the daylight aging trials results the binding medium did not show degradation of the polymeric chains, which reveal high photo-stability at this irradiation conditions. Since both binding medium and paint sample share BA-MMA polymeric content, these results suggest that the main degradation pathways may be related to additives used to produce the paint, rather than the polymer itself.

b) Royal Talens® series

The results obtained for the Talens® unpigmented and pigmented products are discussed in the following section. The test matrix consisted of gloss medium, gel medium, titanium white, zinc white, naphthol red and raw sienna. In general, the results obtained are in good agreement to those discussed for the daylight aging programs of the same brand. The only contrasting results were obtained for the Talens® gloss medium.

The FTIR-ATR spectra obtained for Talens® gloss medium aged up to 1200 hours are shown in Figure 6.2.24. The figure shows a complex aging behaviour, with the appearence of several new absorptions in the 800 and 1200 hours aging steps (bands pointed in the figure). These bands are associated to the migration of additives to the surface of the samples and consequent photo-degradation with light exposure. The absorptions at 3350, 1590 cm^{-1} are associated to the formation carboxylic acid, hydroxyl and/or peroxide moieties, and at 1154-1025 cm^{-1} to different ester type compounds. These absorptions can come from many different oxidation compounds in agreement with both EA-MMA degradation [14,15], as well as PEO type surfactant degradation studied by Scalarone *et al* [22,31].

Macroscopically, the samples showed yellowing to some extent and changed consistency to a gel like form, as observed with the simulated daylight aging trials. Interestingly, the FTIR-ATR anaylisis of the gel medium did not show similar results, even though the samples visually appeared much more affected by aging. In the case of the gel medium, the spectra revealed the degradation pathways of the PEO type compounds with the disapearence of the absorption at 1115 and 1343 cm^{-1}. This is in agreement with the results obtained from the daylight aging trials.

Finally, the results obtained from the mechanical properties of these two materials show larger changes in the the gel medium when compared to the gloss medium. It becomes clear that the aging study of these types of products exclusively by FTIR-ATR may lead to misleading results.

The pigmented samples exhibit a decrease in the PEO content at the surface, and no evident degradation of the absorptions associated to the polymer chains is detected. This reveals an overall good stability of these paints, which is in agreement with the mechanical properties that will be described later in this chapter.

Talens® zinc white was the only sample that clearly exhibited visual changes and also in the FTIR-ATR spectra. Macroscopically, the samples yellowed progressively with the aging trials, and this can be associated to the appearence of new absorptions around the carbonyl region that can be associated to oxidation products that can produce colour.

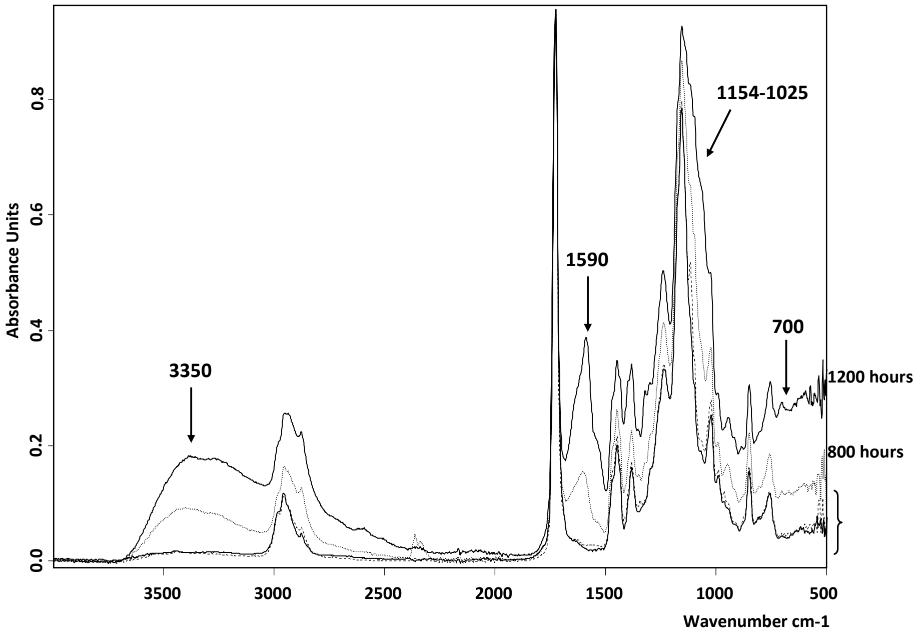


Figure 6.2.24: FTIR-ATR spectra of UV light aging trials of Talens® gloss medium. In the figure are comprised the results obtained for the reference, thermal control, 800 and 1200 hours of aging. It is worth underlining that both reference and thermal control spectra show similar plots.

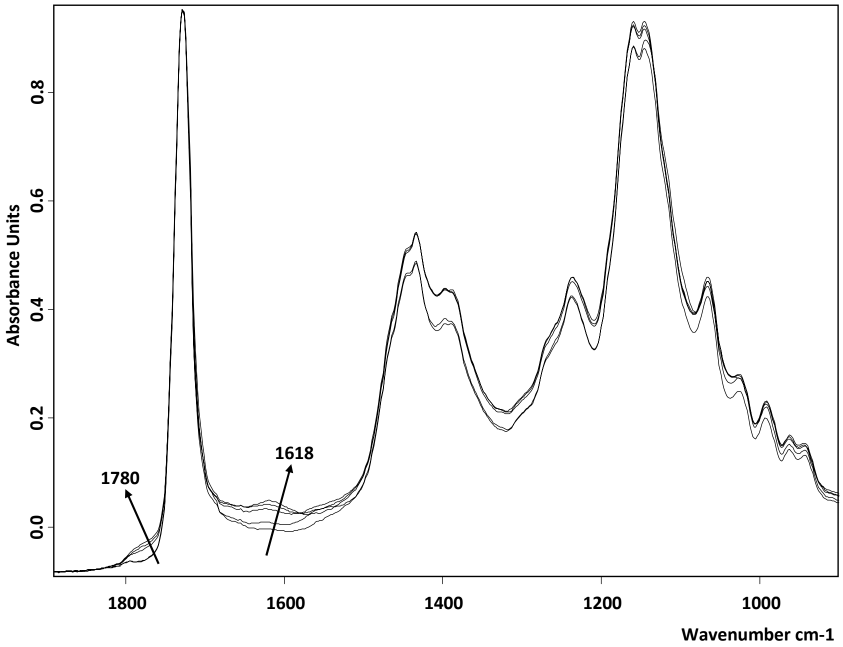


Figure 6.2.25: FTIR-ATR spectra of the UV light aging trials of Talens® zinc white. In the figure are signed the bands related to the appearence of oxidation species with aging. These absorptions are not present in the reference and thermal control samples, which indicates they are products of photo-degradation.

c) Vallejo® series

The Vallejo® samples aged under this regime consisted of titanium white, red oxide, phthalocyanine blue and naphthol red. The FTIR-ATR study of these samples revealed little spectral changes, and the trends were similar to those seen with the aging trials performed with the simulated daylight aging trial. The only exception to this is naphthol red that showed clear spectral changes as shown in Figure 6.2.26. The main features induced by the UV light exposure are the decrease in intensity and broadening of the carbonyl absorption centered at 1728 cm^{-1}, related to the photo-oxidation of the side groups in the acrylic monomers and formation of oxidized species [14,15,17]. The broadening of the carbonyl suggests the formation of peresters and peracids above 1728 cm^{-1}, as well as other carbonyl species below 1728 cm^{-1} [14,15,17]. Another prominent absorption appears at 1640 cm^{-1}, which has been related to the formation of double bonds [14,15,17]. The formation of peroxides is evidenced by the increase in the –OH absorption region seen in the figure. It is also observed a general decrease in the –CH skeletal absorptions and ester peaks signed in the figure, which is associated to a general polymer degradation [14,15,17].

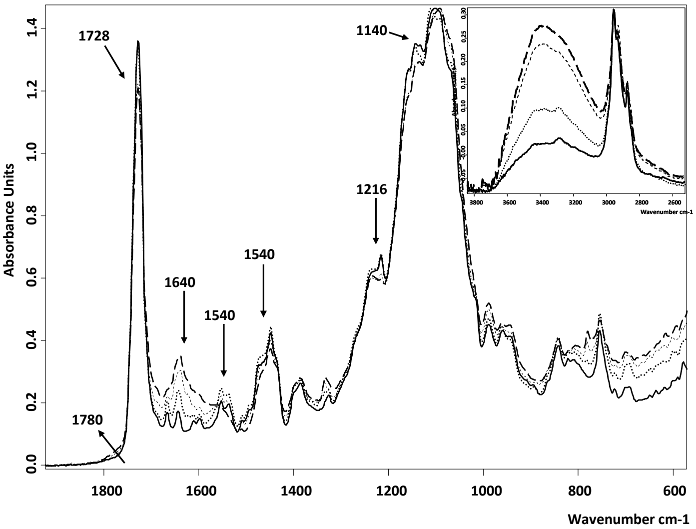


Figure 6.2.26: FTIR-ATR spectra of the UV light aging trials of Vallejo® naphthol red in the 1900-600 cm^{-1} region. Above in the right corner is a detail of the –OH region. The spectra correspond to unaged samples (solid line), thermal control (dotted line), 800 hours (dashed line), and 1200 hours (highlighted dashed lines). The sample aged for 400 hours has not beed included for clarity of the spectra. The absorptions signed in the figure are related to the degradation of the polymer matrix, as mentioned in the text.

d) Pébéo® series

The test matrix of Pébéo® UV light aged samples consisted of titanium white, naphthol crimsom and phthalocyanine blue. The results obtained from the aging trials of Pébéo® paint samples showed an overall aging trend similar to that of the simulated daylight aging conditions. Thus, no strong variation is detected in the FTIR-ATR spectra.

The exception to this is the naphthol crimson sample, which showed interesting changes in the absorption profiles with increasing UV light exposure. The results obtained for this sample are shown in Figure 6.2.27. There is a clear similarity to the data obtained from the simulated daylight aging trials. In general, there is a decrease of the –CH vibrations, visible at 3000-2800 and 1450 cm^{-1} and carbonyl absorption at 1728 cm^{-1}, attributed to the loss of the bulky alkyl side groups present in the binding medium [3,4,18,19]. It is interesting to notice that the absorption ascribed to the styrene ring vibrations does not show significant degradation, which means that these moieties are fairly stable in comparison to the acrylic ones at these aging conditions.

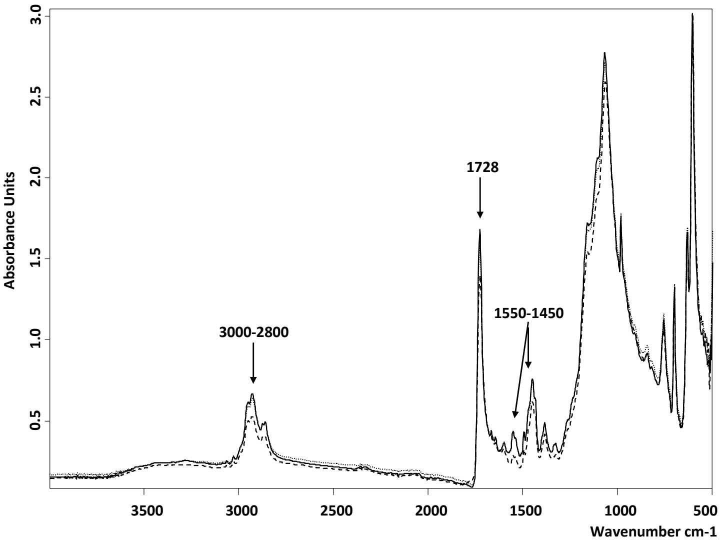


Figure 6.2.27: FTIR-ATR spectra of Pébéo® naphthol crimson after exposure to the UV light aging regime. The spectra shown here correspond to the unaged sample (solid line), thermal control (dotted line-overlayed by the control sample) and 1200 hours (dashed line). An overall decrease in the polymer absorptions and, in particular, in that corresponding to the carbonyl group, are ascribed to the photo-degradation of the long chain alkyl groups [3,4,18,19].

6.2.3.2- Study of the mechanical properties of acrylic products exposed to UV light aging

a) Liquitex® Heavy Body

The general trend seen in the mechanical properties of this series of aged films is similar to that discussed before with simulated daylight aging. Under the UV light aging, the Liquitex® samples tested loss mechanical strength and gained in flexibility. A clear example of this can be observed in Figure 6.8.28 where the mechanical properties of zinc white aged samples are presented along with the liquitex® gloss medium samples. Whereas the results obtained for the medium show high stability, consistent with the results obtained for the simulated daylight aging trials, the aging properties of the paint samples show different results. The response of the thermally aged sample marks a considerable difference from the samples aged under the UV light regime. The stiffness of the thermally aged sample is similar to that of the reference, even though an important increase in the elongation to brake properties can be observed. These changes may be related to film formation processes that are promoted by the effects of temperature. On the contrary, after UV light exposure, there is a decrease in the stiffness of the sample.

Taking into account that the polymer does not appear to be affected by the aging treatment, as suggested by the FTIR-ATR results described previously, it is possible that the plasticizing effect seen here are mainly due to the production fragments of additives that remain in the film. However, the idea of limited chain-scission reactions in the polymer chains it is not fully discarded.

Similar results were observed in titanium white samples, which exhibit loss of strength and increase in flexibility consistently at each aging step. The results are shown in Figure 6.2.28-29.

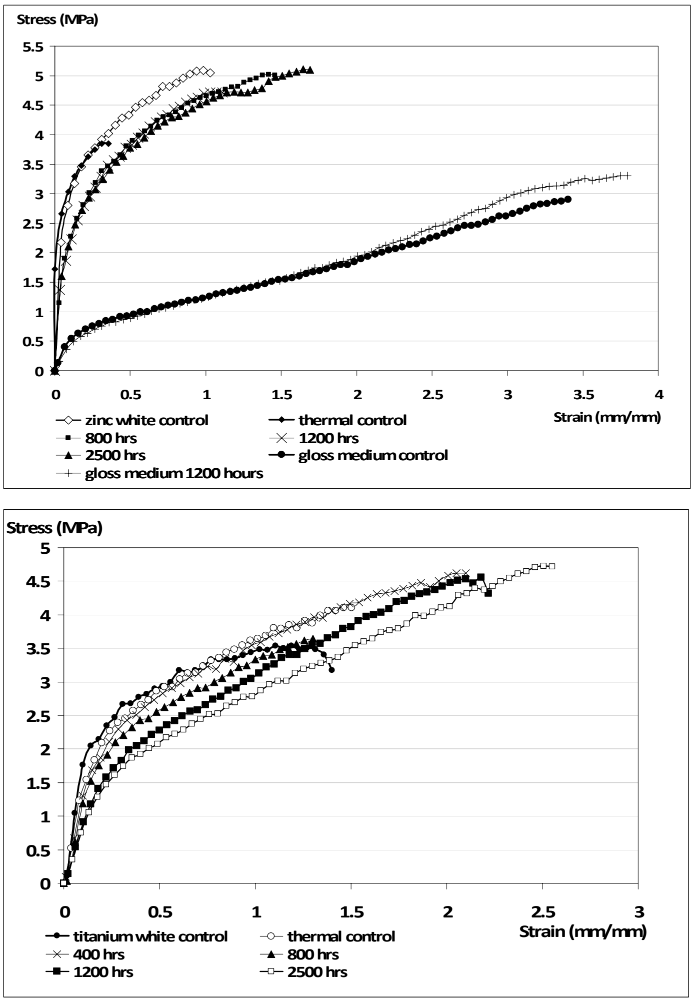


Figure 6.2.28-29: (Above) The mechanical properties of Liquitex® gloss medium and zinc white after different aging steps. (Below) Aging of titanium white samples after 400, 800, 1200, 2500 hours of UV light aging. The thermal control sample is also included.

b) Royal Talens® series

In Figure 6.2.30, are presented the results obtained for the aging of Talens® gloss medium and Talens® gel medium. Both unpigmented media show significant loss of strength after the first 400 hours of aging. In contrast, the reference samples exhibit a similar behavior to those thermally aged. After 400 hours aging, the gloss medium maintains the mechanical properties for the rest of the aging steps. In contrast, the gel medium further loses strength. This appears to be an indication of chain scission of the polymer molecules, even though no changes associated to such degradation processes have been observed in the FTIR-ATR spectra.

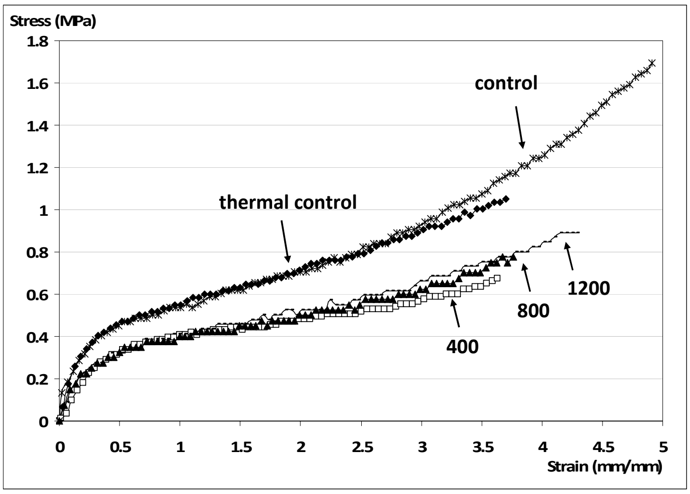


Figure 6.2.30: the mechanical properties of Talens® gloss medium after UV light aging trials. An important change in the initial properties is observed after 400 hours aging and is maintained after 800 and 1200 hours.

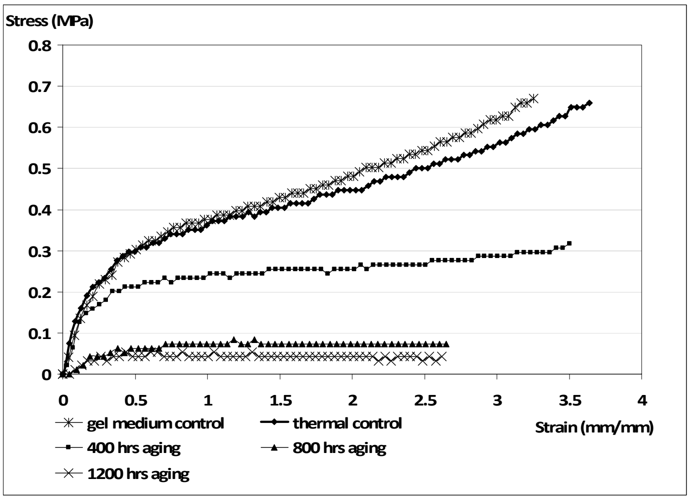


Figure 6.2.31: the mechanical properties of Talens® gel medium after UV light aging trials. An important change in the initial properties is observed with the aging steps of these samples. The thermal control is also included and shows that this alteration is associated mainly to the effects of the UV light component of the aging trial.

The stress strain curves of Talens® zinc white are presented in Figure 6.2.32, these samples are representative of the general behaviour experienced by the pigmented specimens tested. After aging, zinc white exhibited a lower modulus, when compared to the 4 year old reference sample, and maintained fairly the same elongation properties. The case of this sample is interesting, since the specimen yellowed progressivelly with the aging steps. Nevertheless, this yellowing effect was not translated into dramatic changes in the mechanical properties of the samples. Additionally, the thermal control sample did not experience any change in appearence, whereas the mechanical properties showed a similar trend to those samples that yellowed.

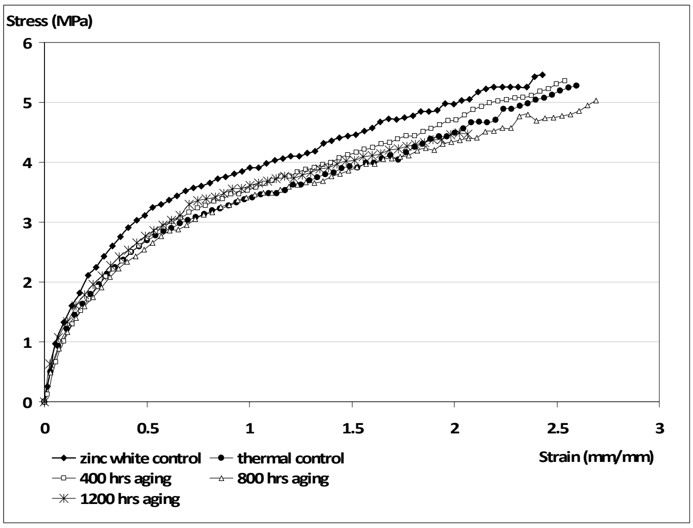


Figure 6.2.32: stress-strain curves obtained after the UV light aging of Talens® zinc white samples. The results show a very mild decrease in the stiffness of the paint for all samples, which can be related to film formation processes. However the samples exhibited a strong yellowing effect that was increased after each aging step.

c) Vallejo® series

Two Vallejo® samples, red oxide and naphthol red, are shown in Figure 6.2.33. Both samples maintained strength and flexibility after the aging trials. Visually, these samples did not show any change in colour. This is an interesting result since these paints share similar BA-MMA polymeric composition with the Liquitex® brand. But in comparision, these present higher mechanical stability. This may also be an indicator that, rather than only polymer content, other factors such as additives, PVC, or the type of pigment participate in the overall changes in the properties of these products.

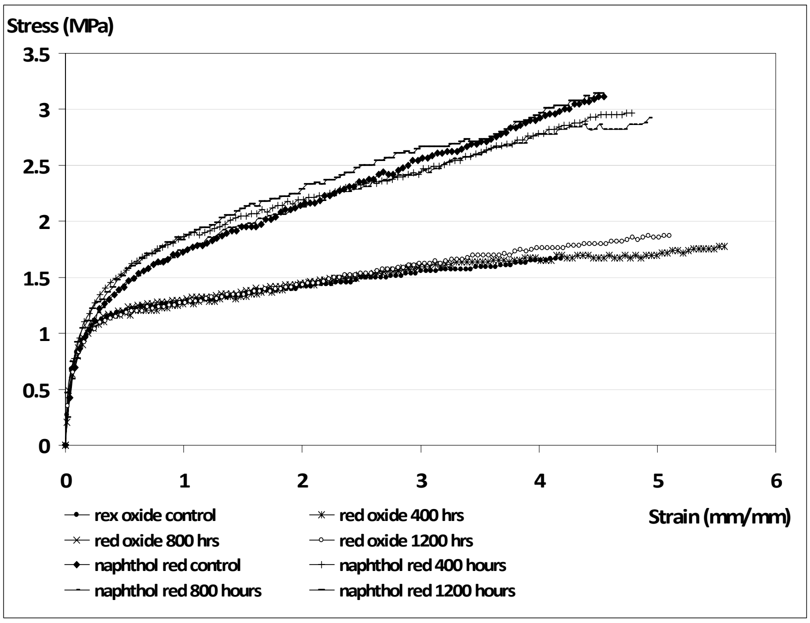


Figure 6.2.33: stress-strain curves obtained after the UV light aging of Vallejo® rex oxide and naphthol red samples. The results show that these samples show no appreciable degradation at these aging conditions.

d) Pébéo® series

The study of the mechanical properties of naphtol crimsom and titanium white, with styrene-acrylic based binding medium, are shown in Figure 6.2.34. The results clearly indicate that these products show a loss in tensile strength and stiffening effect with aging. This is most evident in the results obtained for naphthol crimsom paint films, which was the sample that showed more pronounced change in the FITR-ATR general absorption profiles. It is interesting to point out that the thermal control samples also show sign of alteration in the mechanical properties, which has not been observed for the other products tested in this work. This suggests that styrene-acrylic paints present a distinct aging behaviour to those presented by pure acrylics or even PVAc. As proposed in the FTIR-ATR study of the degradation of these paints, this effect may be due to the bulky side chains from the acrylic co-monomer, especially EHA units, which are prone to photo-oxidation or, as it seems, by thermal degradation. Light is, nevertheless, accelerating the degradation processes within the paint films, increasing Young’s Modulus beyond thermal degradation.

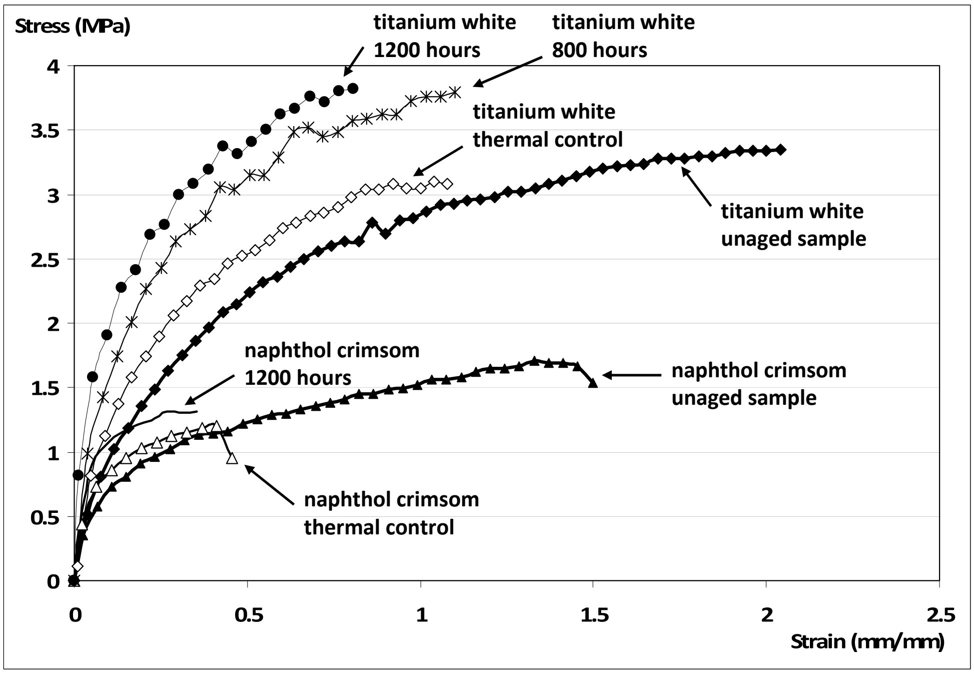


Figure 6.2.34: the mechanical properties of Pébéo® naphthol crimsom and titanium white paint aged samples. The figure shows that these products suffer degradation under thermal and UV light effects.

6.2.3- Study of the aging behaviour of PVAc products exposed to simulated daylight and UV-aging

A set of PVAc products was subjected to simulated daylight and UV light aging trials. The PVAc sample matrix is summarized in table 6.2.2 for both simulated daylight and UV light aging regimes. The results obtained by FTIR-ATR spectroscopy and mechanical tests in the characterization of the aging behaviour of these products are presented in the following section.

Brand	Daylight simulation	UV aging
Flashe®	oriental red	oriental red
	senegal yellow	senegal yellow
	green armour	green armour
	white	white
	burnt sienna	burnt sienna
Conrayt®	V	V
Mowilith® DMC2	V	V

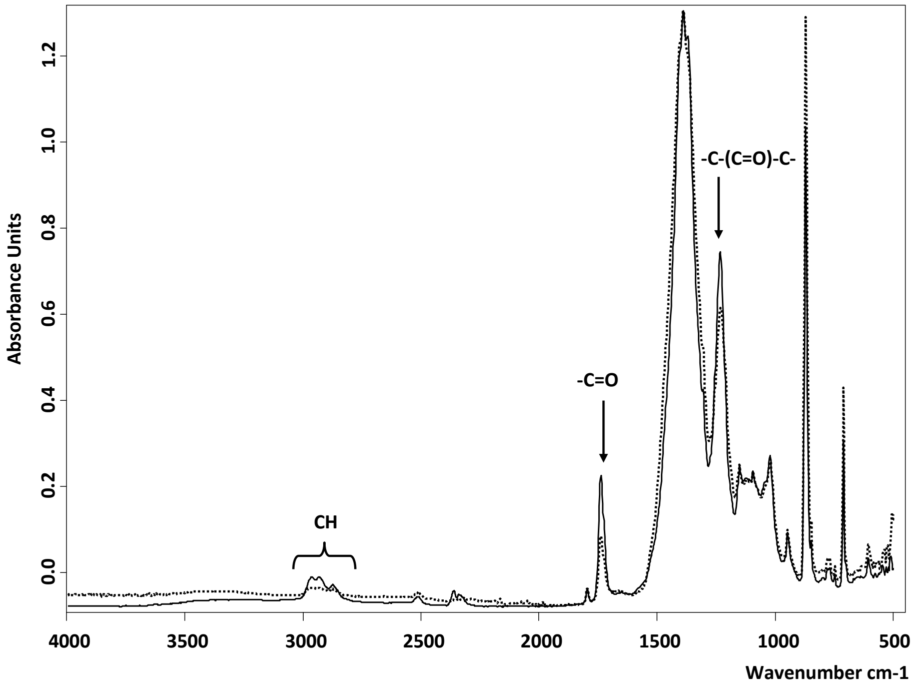
Table 6.2.2: summary of the PVAc samples tested for the two aging programs: daylight UV light and simulated aging.

6.2.3.1- FTIR-ATR study of PVAc products exposed to simulated daylight aging

a) Flashe® series

The FTIR-spectra of Flashe® armour green is presented in Figure 6.2.35 and burnt sienna in Figure 6.2.35. The degradation seen in these figures are representative for all paint samples aged. The main features of these Flashe® spectra concern the carbonyl band at 1740-1725 cm^{-1} ascribed to the presence of distinct carbonyl species from PVAc and VeoVa moieties. The intense and broad absorption at 1372-1390 cm^{-1} is related to the –CH_2 and –CH_3 of the backbone of the VeoVa structure [32]. A pure PVAc compound does not present bands with this intensity. The broad band at 1410 accompanied by sharp peaks at 871 and 712 cm^{-1} are clear markers of a calcium carbonate extender [32].

After the aging trials, and especially after 800 hours aging, the samples exhibited a clear degradation of the polymer chains which is reflected in the general decreasing intensity of the –CH absorptions in the 1372-1390 cm^{-1} region, which is confirmed by the decreasing of the homologous absorptions in the 3000-2800 cm^{-1} region. Furthermore, the decrease of these absorptions is accompanied by a decrease in the carbonyl peak, which is tentatively ascribed to the side group elimination of the versatate ester group and also acetate groups. These features are clearly visible in the burnt sienna sample.



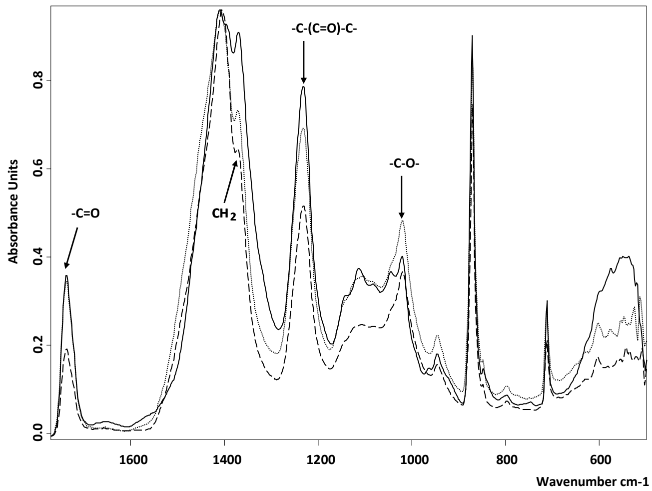


Figure 6.2.35-36: FTIR-ATR spectra after daylight simulated aging trials: (above) armour green; (below) detail of the FTIR-ART spectrum of burnt sienna in the 1800-500 cm^{-1} range.

b) Conrayt® series

The FTIR-ATR spectra corresponding to the aging of Conrayt® PVAc medium is shown in Figure 6.2.37. After aging, the aging features of the spectra seem to only concern the degradation of a dibutylphthalate (DBP) type plasticizer. It is worth mentioning that the absorptions that correspond to the polymeric chains did not accuse degradation in opposition to that seen previously in the Flashe® samples. Nevertheless, the samples did exhibit changes in their physical properties. In fact, after 800 hours of aging, the samples were not possible to detach from the Mylar® support, and the mechanical properties were only possible to measure for 400 hours, as described later in this chapter. Such alterations found no correlation to the FTIR-ATR analysis.

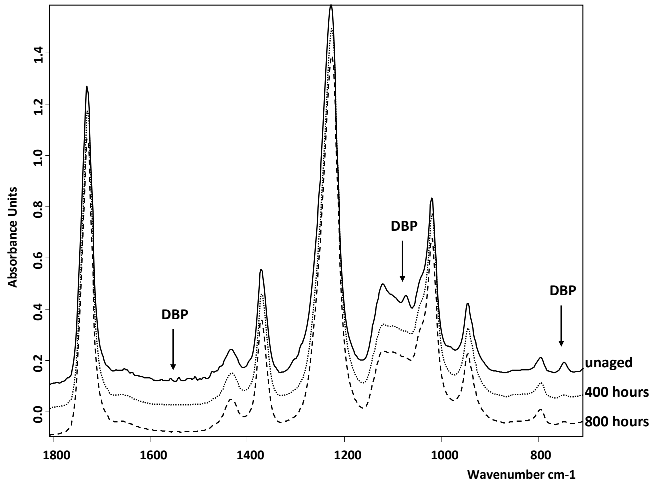


Figure 6.2.37: FTIR-ATR spectra of Conrayt® aged specimens at 400 hours and 800 hours with simulated daylight aging trials.

c) Mowilith® DMC2

The analysis of Mowilith® DMC2 aged samples by means of FTIR-ATR did not show any noticeable changes at any of the 400 and 800 hours aging steps. However, the samples exhibited yellowing and micro-craking and were impossible to separate from the Mylar® support after both aging steps. This is a clear indication that other analytical techniques must be employed in order to obtain a complete characterization of the aging of these specimens.

6.2.3.2- Study of the mechanical properties of PVAc products exposed to simulated daylight aging

a) Flashe® series

The Flashe® paint films aged under the simulated daylight regime consisted of oriental red, senegal yellow, green armour burnt sienna and white. Flashe® paint films are very heterogeneous and present high PVC, which leads to the formation of brittle films upon drying with heterogeneous mechanical properties.

After aging, the data obtained by FTIR-ATR indicates that few alterations of the polymer matrix occurs, this is in good agreement with the mechanical data shown for burnt sienna in Figure 6.2.38. Oriental red showed a different degradation pattern that is presented in Figure 6.2.39. The film loses strength and decreases Young's Modulus, consistent to chain-scission degradation reactions. The aged films also experienced higher deformation values before braking.

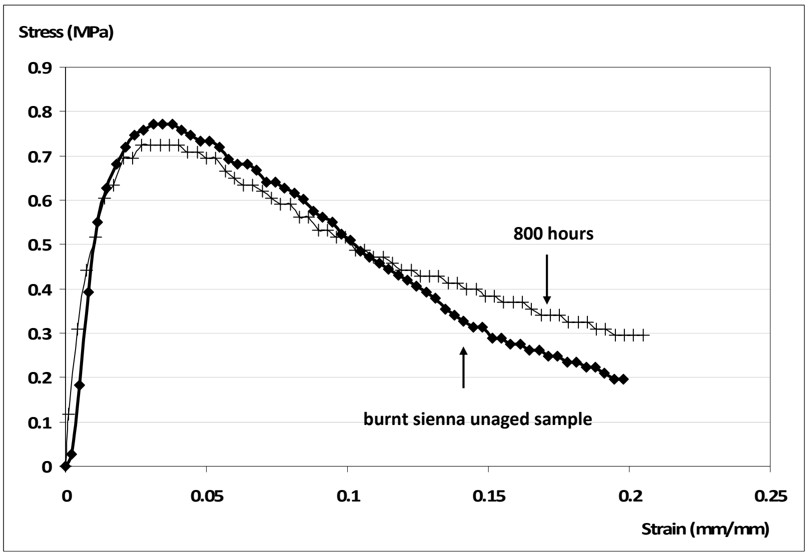


Figure 6.2.38: stress-strain data Flashe® burnt sienna aged specimens at 800 hours with simulated daylight aging trials. The data reveals limited alteration in the mechanical properties after aging, which may be due to the shielding effect promoted by the high PVC content of the paint film.

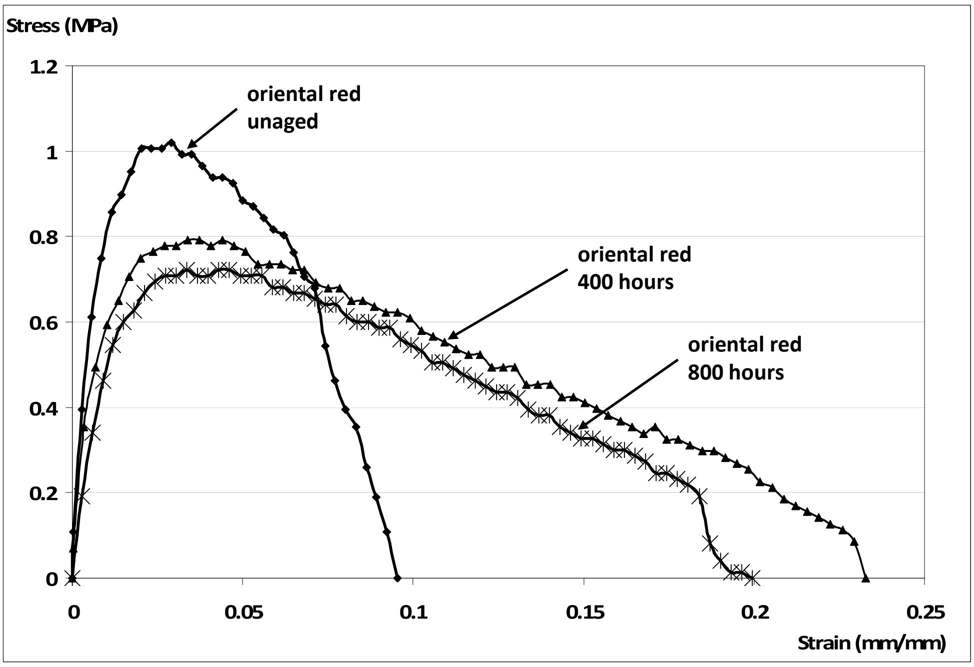


Figure 6.2.39: stress-strain data Flashe® oriental red aged specimens at 400 and 800 hours with simulated daylight aging trials. The data indicates a decrease in Modulus and strength, consistent with chain-scission reactions during aging.

The data obtained for Flashe® paint films is somewhat difficult to interpret due to the fragility of the films. Overall, after the aging trials these films showed similarity to the two cases presented here and more results are shown in Appendix B.2. The presence of high amounts of the calcium carbonate extender appears to confere a shielding effect on these paints, and no distinct degradation feature could be attributed to organic or inorganic pigments, which is in good agreement with previous studies [20].

b) Conrayt® series

As mentioned previously, Conrayt® specimens were strongly adhered to the mylar® support after 800 hours of simulated daylight aging and impossible to test. Thus only the specimens aged for 400 hours are shown in Figure 6.2.40. The stress-strain data reveals a clear loss in tensile strength and elongation properties that can be correlated to degradation of the main polymer chains, especially to chain scission reactions that may occur with photo-oxidation. Despite the evidence of changes in the mechanical properties, Conrayt® films were ductil after this aging step, with an elongation above 400 %.

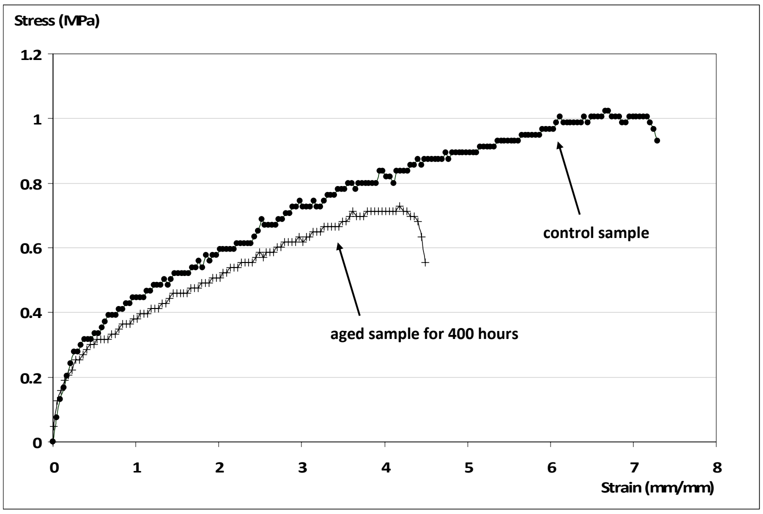


Figure 6.2.40: stress-strain data of Conrayt® aged specimens at 400 with simulated daylight aging trials. The samples aged for 800 hours were impossible to test since they were adhered to the support.

c) Mowilith® DMC2

After the 400 and 800 hours aging steps the Mowilith® DMC2 samples were strongly adhered to the support and it was impossible to obtain a free film for performing stress-strain tests. It is worth to notice that the samples were stiffer and exhibited micro-craking. When attempting to separate them from the support most broke inmediately. These observations lead to think of possible cross-linking reactions that may be promoted by the simulated daylight exposure. This is in good agreement with the results obtained for the UV light aging trials described in the following section of this work.

6.2.3.3- FTIR-ATR study of PVAc products exposed to UV-aging

The FTIR-ATR studies of the UV light aged PVAc based samples concerning Flashe®, Conrayt® and Mowilith® DMC2 did not bring forward further information on the degradation of the samples. The characterization of the mechanical properties of the aged specimens was of precious aid, since they helped identifying the general aging trends that are developed in these products during aging. These tests are a valuable tool, if not essential, for the study of the aging properties of such materials. The results are discussed in the following section.

6.2.3.4- Study of the mechanical properties of PVAc products exposed to UV-aging

a) Flashe® series

The mechanical properties studied for the Flashe® UV light aged films showed consistent results to those obtained for the simulated daylight aging tests. In general, the samples did not show pronounced change in their mechanical properties with aging, which has been tentatively related to shielding effect of the high PVC content films. An example of this is shown in Figure 6.2.41, for burnt sienna and is representative of the general results obtained for the other colours tested.

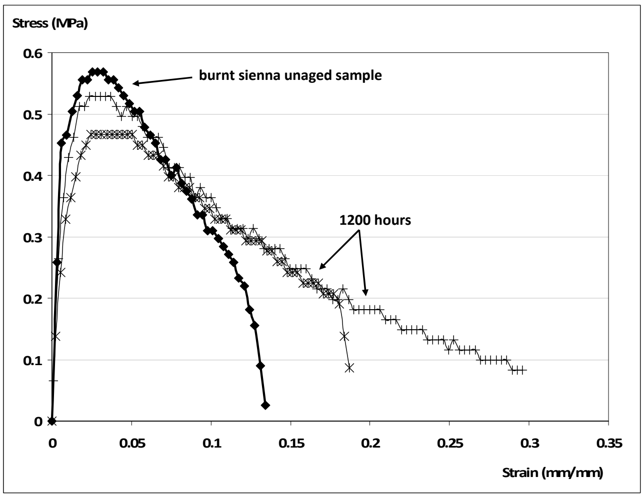


Figure 6.2.41: The mechanical properties of Flashe® burnt sienna samples aged for 1200 hours under the UV light aging regime. It is interesting to notice that the films show a discrete loss of strength consistent with chain scission reactions due to aging.

b) Conrayt® series

The mechanical properties obtained for Conrayt® aged samples are shown in Figure 6.2.42. Conrayt® suffers a progressive loss of mechanical strength with UV light exposure, which is an indicator that chain-scission reactions are the predominant degradation processes, even though not evident in the FTIR-ATR study of the samples. These results are in full agreement with those obtained for simulated daylight aging trials.

It is interesting to note that the stress-strain curve of thermal control sample shows a moderate increase in strength at high deformation values. This stiffening effect may be due to loss of plasticizer (DBP), which has been detected in the Conrayt® formulation by means of FTIR-ATR and Py-Silylation-GC-MS[27].

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[27] The reader is referred to the characterization of the test specimens chapter of this thesis for more information on the chemical composition of this product.

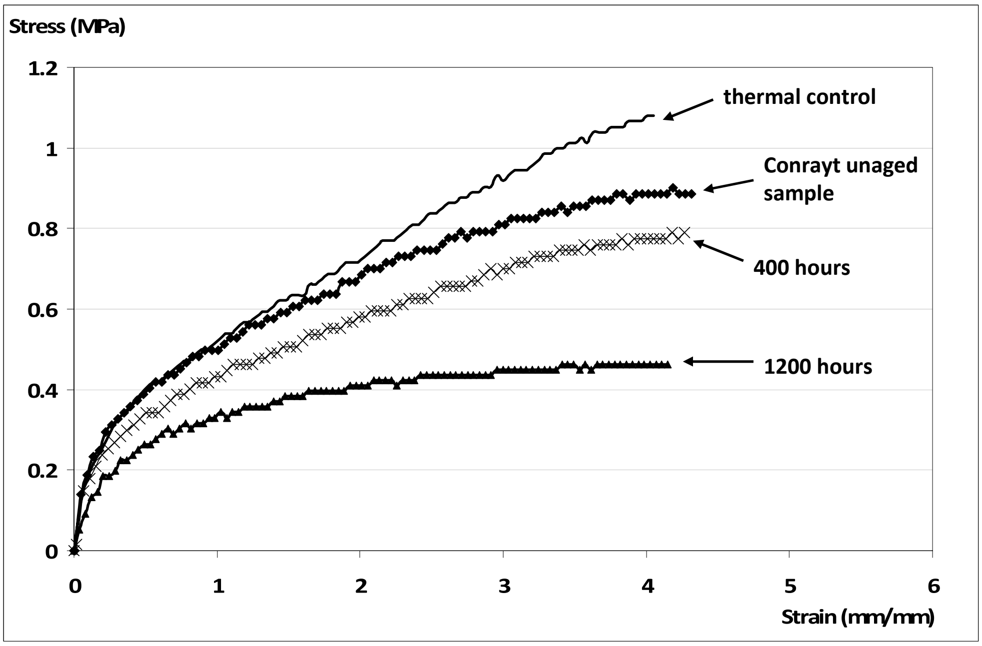

Figure 6.2.42: the aging behaviour of Conrayt® to UV light exposure (the films tested were not taken to failure). The results indicate an important loss in tensile strength, such as the samples tested for the simulated daylight aging tests. These results suggest that predominat chain-scission reactions are occuring during the aging of this PVAc product. This is also in good agreement with the results obtained for Flashe® paint films (a PVAc-VeoVa co-polymer).

d) Mowilith® DMC2 series

Interestingly, the results obtained for the aged samples of Mowilith® DMC2 are contrast to those of Conrayt®. The mechanical properties obtained for the aged samples are shown in Figure 6.2.43. The UV light exposure induced an increase in Young's Modulus (stiffness), and an increase in ultimate strength could be detected since the samples streched all up to 600% their original length. Some stiffening effect has also been seen in the thermal control samples, similarly to Conrayt®.

The contrasting aging trends evidenced by these products' mechanical properties seem to be related to the polymeric composition, i.e., Mowilith® DMC2 is a PVAc-Butylmaleate based co-polymer and Conrayt® a pure PVAc product (with DBP plasticizer). Thus, it is possible that the Butylmaleate units promote cross-linking reactions whereas PVAc polymers mainly suffer chain-scissions. It is also interesting to think that PVAc degradation may influence (possibly promote or accelerate) the rate of Butylmaleate unit cross-linking reactions. Further study on the aging of these co-polymers by means of other analytical techniques appears of interest.

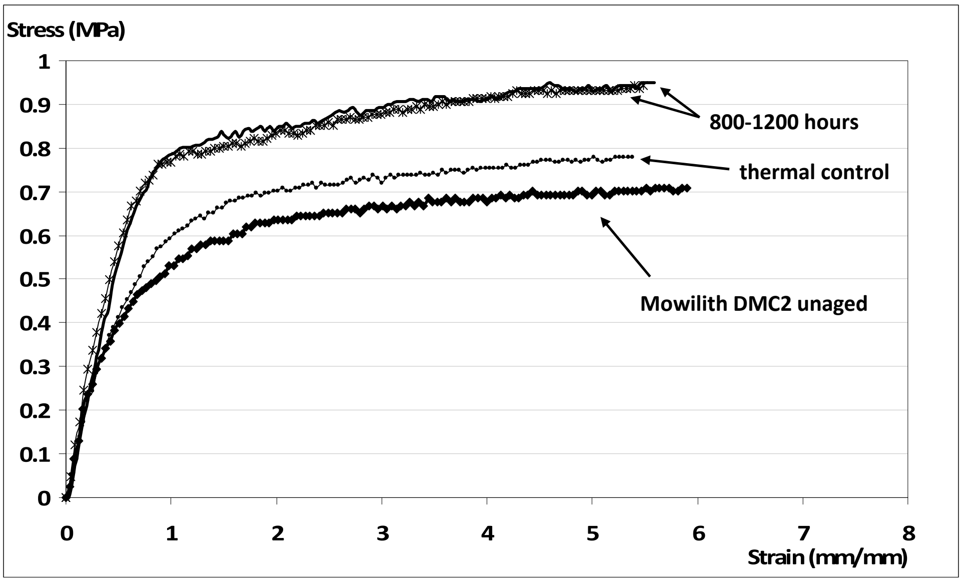

Figure 6.2.43: the mechanical properties of Mowilith® DMC2 samples after UV light aging. The trend of the data suggests that cross-linking reactions are occuring (predominantly) with light exposure.

6.2.4- Conclusions

In this chapter, acrylic and PVAc based formulations containing different chemical composition were subjected to two artificial aging programs: simulated daylight and UV light aging trials. These aging programs were selected for several reasons: First, they were conducted close to ambient temperatures and relative humidity and, thus simulated normal enviromental conditions. Second, the light sources were specifically chosen to simulate light (energy) exposure conditions of indoor and museum ilumination. Third, these lighting characteristics avoid undesirable results from non-representative degradation reactions that undergo under irradiation regimes that do not correspond to the realities we, in service to conservation, wish to study. The aged samples were studied by FTIR-ATR, and the mechanical properties were obtained by stress-strain tests. The results are summarized below.

The acrylic samples considered for the aging programs consisted of Liquitex® (BA-MMA), Talens® (EA-MMA or EA-MMA-BA), Vallejo® (BA-MMA) and Pébéo® (Sty-2EHA-MMA) paint samples and media. The results obtained for these products show that they were generally very resistant to the simulated daylight and UV light aging programes. However, they did show alteration to some extent. Mostly photo-degradation of additives was the feature common to all brands, whereas a few paint brands showed degradation associated to the polymer chains (binding medium). The studies of the chemical and physical properties of these products lead to the following conclusions:

a) Liquitex® gloss medium and varnish (a dispersion BA-MMA medium) did not show changes in mechanical properties with both aging trials. However, the samples showed some yellowing under the daylight aging regime, and this is an indicator of chemical changes. A previous study by Howells et al showed that yellowing of acrylic dispersions can be related to the presence of additives; in that case, a cellulose based thickener [6]. Such type of alterations could be associated to the yellowing effect seen in this medium. However, the analysis of the extracts perfomed later in this work does not reveal the presence of such type of compounds.

b) On the other hand, the pigmented Liquitex® samples (also BA-MMA products) showed some changes in the respective mechanical properties. The degradation trends consisted of loss of strength and decrease in Young's Modulus, which is a tipical consequence of chain-scission reactions. However, these degradation mechanisms were not detected by FTIR-ATR. This technique was very sensitive to the degradation of additives, mainly surfactants, on the surface of the samples. Taking into account the resistance to wheathering of the unpigmented Liquitex® binding medium, it is proposed that the changes in the mechanical properties (loss of strength and decrease in Young's Modulus) are associated to a complex process that may involve the plasticizement of the film due to the formation of small degraded additive fragments in the film.

c) The pigmented samples from Vallejo®, also a BA-MMA co-polymer, did not show evident changes in mechanical properties, indicating that they were resistant to the light aging regimes. Nevertheless, some samples showed changes in the absorption spectra that could not be correlated to the study of the mechanical properties. This suggests two possibilities: that the changes observed are occurring only in surface or with additives or that there are competing (at similar rate) cross-linking and chain-scission reactions suggested by FTIR-ATR.

d) EA-MMA-BA unpigmented binding media from Talens® showed changes in the mechanical properties which were not accompanied by evidence of spectral changes by FTIR-ATR. The mechanical tests suggest that the main degradation pathways followed by these products are chain-scissions, which are in good agreement with the literature [13-16]. The pigmented samples, on the contrary, were fairly more resistant to light degradation and few changes have been detected in this study. The trends in the data for the samples aged at these conditions also showed that chain-scissions may be the predominant aging steps, even though to a very limited extent.

e) Styrene-acrylic polymers from Pébéo® showed evident degradation which is in good agreement with the theory, that suggest that lower stability is expected from styrene-acrylic co-polymers when compared to pure acrylics. The main degradation is associated to side group elimination or chain-scissions. Interestingly, the UV light aging regime evidenced higher degradation when compared to the daylight aging trial.

The PVAc based products tested in this work consisted of a series of Flashe® paint samples (PVAc-VeoVa), Conrayt® (PVAc + DBP) and Mowilith® DMC2 (PVAc-Butylmaleate). The aging of these products showed the following trends:

a) The degradation mechanisms of Flashe® paint films indicate that chain-scissions are the most predominant processes prone to occur under these aging conditions. They were both identified by FTIR-ATR analysis and by the stress-strain curves obtained from the aged films.

b) Conrayt® samples aged under the daylight regime were possible to test for mechanical properties only after the first 400 hours aging step. After 800 hours the films adhered to the Mylar® support and could not be tested. With the UV light aging program there were no such problems and all films were tested. The results obtained here showed evidences of predominant chain-scission processes under these aging regimes, consistent for both aging trials. FTIR-ATR analysis was also useful for the detection of DBP plasticizer elimination under the daylight aging conditions.

c) The mechanical properties of Mowilith DMC2® were not possible to test after aging with the simulated daylight regime since the samples turned to a yellow product, adhered to the support. However, the samples aged under UV light were possible to test and showed that cross-linking reactions are possibly the most predominant aging features suffered by these films under these aging conditions.

In conclusion, it is worth remarking that the results obtained for both artificial aging conditions were in full agreement for all the test samples. Generally, the simulated daylight exposure caused more evident degradation than with the UV light aging conditions. This was a benefit as some samples (such as PVAc media) that were not possible to test for mechanical properties after daylight aging, were possible to test after the UV light aging.

Finally, it should be emphasized that the combination of mechanical tests by means of stress-strain tests and FTIR-ATR analyses have shown new results and have widened the knowledge on the aging of acrylic and PVAc based paints and media. In particular, the results shown by the combination of these analytical methods have shown clear degradation trends that had not been characterized for these materials yet. Research on the specific chemical details of the degradation pathways was out of the scope of this thesis and is encouraged to follow this study. In detriment of that, a general overview of the aging characteristics of these materials was preferred.

As expected, most pigmented films (i.e. paints) perfomed as “class A” materials, following Feller’s classification of materials [2]. This was not observed for all the unpigmented media that generally fell under the “class B” classification. Following these results, PVAc and styrene-acrylic films should be considered as different materials than pure acrylics in terms of susceptibility to degradation.

6.2.5- References

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6.3- The effects of cleaning treatments in acrylic and PVAc films

6.3- The effects of cleaning treatments in acrylic and PVAc films

The effects of water and solvents in the properties of acrylic and PVAc products have given rise to much debate in the last years. Recently, Ormsby and Learner have published a thorough review on the scientific research developed in the conservation field on the effects of wet surface treatments on acrylic emulsion paints [1].

In general, acrylic and PVAc films are affected by most solvents with exception of higly non-polar solvents such as iso-octane or mineral spirits [1-5]. And the conservator must be aware that the traditional cleaning approaches based in the use of organic solvents may be inadecuate [6]. At the moment of making a decision on what cleaning treatment should be carried out, the choices are pretty narrow: dry or mechanical methods [7] or wet cleaning methods based in water or highly non polar solvents [1,6].

The cleaning methods chosen for surface cleaning are dependent on the degree of bonding of dirt to the surface of the acrylic or PVAc paint layer [6,8]. If the paint exhibits soiling or embebed matter in the paint layer, it is probable that mechanical cleaning methods may not be fully satisfactory. It may become necessary the use of wet cleaning methods as a conservation cleaning treatment and, especially, the use of water based systems [1,6,8].

Aqueous cleaning systems comprise water as the solvent and other modifying agents such as surfactants, sequestring agents, buffered solutions, etc [9-13]. The effects of water based cleaning systems have been studied by many authors, and a detailed review on the scientific studies on this subjects can be found elsewhere [1].

In broad terms, water does not dissolve the main polymer chains of an acrylic or PVAc paint, however, it causes swelling of the paint film [1,2,5,15-20], which is attributed to the presence of water soluble additives. Whitmore et al [16] has shown that water can fastly penetrate into the paint layers and is capable of extracting additives, especially surfactants, from the surface or the bulk film [17]. The resulting films see their mechanical properties affected after these cleaning treatments, normally inducing some stiffening effect [1,6,18-25]. The latter studies suggest that smaller molecules such as surfactant act as plasticizers in the films.

The presence of surfactant at the surface of the acrylic films is associated with optical changes and loss of saturation of the colour [1,14,26]. The presence of these compounds has been monitored by SEM, AFM and FTIR-ATR (see Ormsby [1] and references therein). The studies reveal that surfactants may be present as different types of aggregates depending on the paint film, that are prone to be partially removed with swabbing tests and immersions [1,27]. Higly non polar solvents, on the other hand have shown to be less efective in the removal of these molecules, which, in its turn relates to few changes in the mechanical properties of the resulting films [19].

Many studies have dedicated efforts to the characterization of additives present in acrylic paint films [1-5,15,27-35] whereas, comparatively, there are much less studies on additives present in PVAc type products [2,19,36]. Overall, PEO type surfactants, especially Triton®X (405 and 305) are the most common compounds identified either in paint specimens [27-35] or real paintings [1,30,31].

The effects of cleaning by means of an aqueous treatment can be controlled by means of changing the activity of water. This is accomplished by modifying the ingredients present in the aqueous cleaning system. Recently, Wolbers has presented a work on the effects of pH and conductivity in the swelling behaviour of acrylic paint films, in good agreement with a previous report by Ormsby et al [1,10]. The authors states that swelling may vary according to the presence of ions in solution, and that this can be used for enhancing the cleaning effects of acrylic surfaces and minimize the damage caused during the intervention.

Rheological modifiers are also gaining importance in the conservation field. They can be added to a cleaning solution to increase its viscosity and, consequently, limit its penetration into the paint layers. These modifiers form what is commonly known as "gels" [10,13,37-39]. Though the use of gels in the cleaning of traditional painting systems is being studied and put into practice, it is fair to say that few studies have been dedicated to the effects or benefits of these agents in the cleaning of acrylic or PVAc paints [19].

There is much interest to widen the knowledge on the effects of either solvents or water based systems in the properties of acrylic films. The study on the effects of free water based treatments and comparison to gelled water based systems as been proposed as an objective for this work. Thus, in the following chapter, four main subjects will be studied and discussed:

1. A study on the solubility of acrylic and PVAc specimens in organic solvents. Study of the effects of a selection of organic solvents on acrylic and PVAc paints. This section is included to illustrate the narrow selection of organic solvents that the conservator may dispose for the surface cleaning of an acrylic or PVAc painting.
2. Study of the effects of free water cleaning treatments on acrylic and PVAc by subjecting test specimens to immersion and swabbing tests. Absorption of water, leaching of additives, mechanical properties and characterization of the surface morphology of the resulting films is considered here.
3. Characterization of the materials leached during the immersion tests by FTIR and Py-Silylation-GC-MS.
4. Study of the efficiency of water based gels as an alternative to free water cleaning is evaluated. The water based gels studied comprise Carbopol® Ultrez 21 (buffered with NaOH up to pH=6.5),

Klucel® G, Vanzan® NF-C and Agar-agar®. The possibility of using cleaning systems based on Water in Oil (W/O) emulsion systems is also evaluated[28].

Ultimately, the scope of this work is to gather information to serve a guiding tool for the painting conservator to know the following:

- Which range of solvents is dangerous for a surface cleaning of an acrylic or PVAc painting? What are the consequences of using these solvents?
- Is it possible to use water as a cleaning solvent for a surface cleaning treatment of an acrylic or PVAc painting? What are physical consequences of using water? What is removed from an acrylic or PVAc painting when water based cleaning treatment is used?
- Can alternative water based cleaning systems be used for cleaning acrylic or PVAc painting

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[28] Emulsion systems are not exclusively water based cleaning systems, since it contains water and a non-polar solvent. The reader is reffered to the experimental section for more details on the preparation of the emulsion systems.

6.3.1- The effects of cleaning treatments in acrylic products

6.3.1.1- The solubility range of acrylic paint films in the TEAs chart

The sensitivity of acrylics to organic solvents was determined by an experimental ligroin-acetone (LA), ligroin-ethanol (LE) and ethanol-acetone (EA) solubility test[29]. These solvents are mixed at different proportions to obtain a wide range of polarity values that cover most of the TEAs chart [20]. The acrylic films were swabbed for 10 seconds with the different mixtures and the polarity values at which the surface is affected are represented in the chart shown in Figure 6.3.1. All acrylic samples showed similar results irrespectively of the brand and pigments.

The acrylics were dissolved by all mixtures from the solubility test, except for ligroin (Fd=97) and the LA1 mixture (Fd=92). A painting conservator can readily recognize that possibility of using organic solvents for the surface cleaning of an acrylic painting is limited to the highly non-polar solvents, such as ligroin (Fd= 96), or iso-octane (Fd= 100), etc.

The solubility test was also performed in aged samples[30] in view of predicting possible changes in solubility that may occur in a painting with years of natural aging. Interestingly, mostly all aged acrylics grew more sensitive in the low polarity region. The exception to this was the Vallejo® brand which became less soluble in the low polarity region after aging[31].

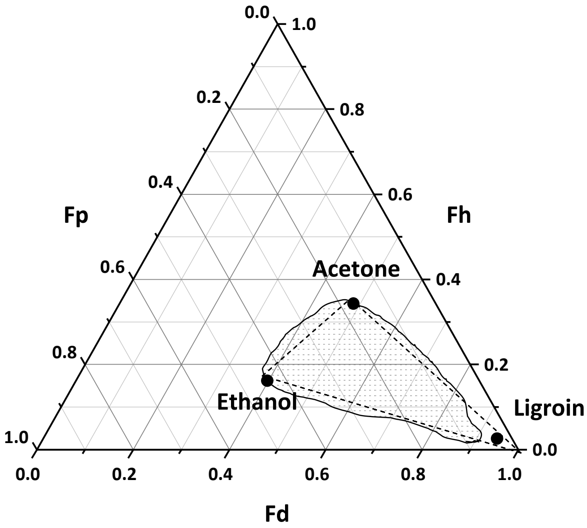

Figure 6.3.1: experimental solubility region of a Talens® gloss medium obtained with a standard LA, LE and AE solubility test (the polarites of the mixtures are delimited by the triangle composed of dashed lines). The acrylic medium is soluble solubility most solvent mixtures from the solubility test.

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[29] The reader is reffereed to the experimental section of this work concerning the preparation of the solubility test.

[30] The samples were aged for 1200 hours in the UV-light regime described in the experimental section.

[31] An increase in solubility is associated to chain-scission degradation reactions, which is in good correlation to the results described in the previous chapter. On the contrary, cross-linking reactions promote insolubility.

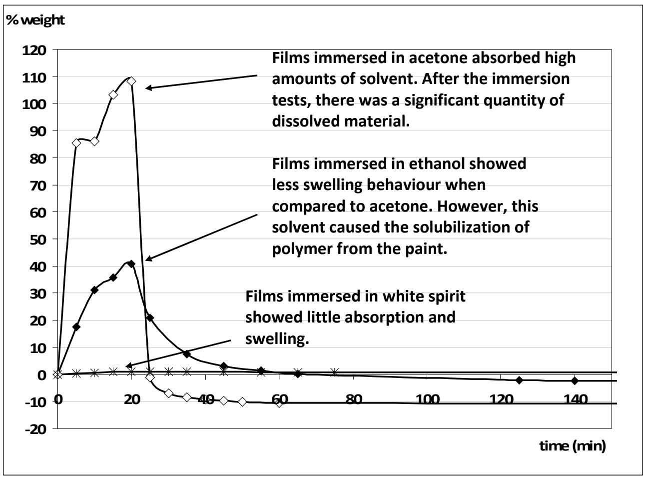
6.3.1.2- The effects of organic solvent immersions in acrylic paint films

Acrylic paint films comprising Liquitex® burnt umber, titanium white, naphthol red, phthalocyanine blue and Talens® raw sienna were immersed in ligroin (Fd= 97) and white spirit (Fd= 90). These are higly non-polar solvents with Fd values situated in the non solubility range of acrylics. Immersions in ethanol and acetone are also included for comparison purposes since they solubilize the binding medium from the films.

The absorption, retention, drying and leaching of acrylic films will be adressed by examining experimental absorption and drying profiles. To obtain this data, the samples are immersed in the corresponding solvent and weighted periodically during the length of the immersion test. The rate and amount of solvent absorbed reflects the affinity to the solvent and swelling behaviour. The weight of the sample is also measured after the immersion test is stopped, allowing to obtain information about the retention of each solvent in the film. After drying, if the sample accuses weight loss, this is related to the leaching of material from the film.

Figure 6.3.2-6.3.3 shows the absorption-drying profiles and weight loss of Liquitex® burnt umber immersed for 20 minutes in white spirit, acetone and ethanol. Acetone is fastly absorbed into the acrylic film in the first 5 minutes of the test and the samples accuse an increase in weight of about 110% after 20 minutes of immersion. After the immersion, there is a considerable weight loss attributed to the solubilization of polymeric material. It is worth mentioning that the integrity of the acrylic films was maintained because there was no mechanical action during the immersion tests. A swabbing test with acetone disrupts the films. The samples immersed in ethanol showed less swelling and leaching in comparison to the acetone. Interestingly, the material solubilized by this solvent comprised not only polymer chains, but also an octylphenol poly(ethoxylate) type surfactant.

The films immersed in non polar solvents behaved differently. During immersion, white spirit (ligroin presented similar results) was barely absorbed by the specimens accusing little increase in weight and swelling. It is interesting to underline that white spirit was retained in the films up to almost two months. Ligroin, on the other hand, was retained for approximately one month.



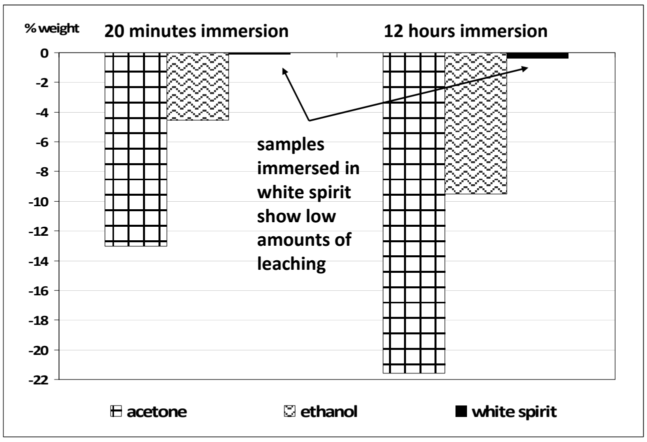


Figure 6.3.2-6.3.3: (Top) Absorption-drying profiles of Liquitex® burnt umber films immersed in organic solvents including acetone, ethanol and white spirit. (Bottom) Amount of material extracted from the paint samples after the immersions.

6.3.1.3- The effects of water immersions in the leaching of acrylic paint films

The effects of water on an acrylic paint sample are readilly visible during an immersion test. The film absorbs large amounts of water, which causes a significant swelling. In most cases, the weight of the absorpted water is greater than the films' initial weight. Since acrylic polymers are not water soluble, the sensitivity of these products to water is associated to the presence of additives, such as surfactants or thickeners, as well as small defects in the polymer latex (i.e. pores) that contribute to the water uptake by capillarity [6,17,41-45].

Figure 6.3.4 shows the water absorption of a series of Liquitex® test specimens during 20 minutes immersion tests. Each colour absorbs differently depending on the type of pigment used in the paint. In general, the colours formulated with inorganic pigments absorb less water when compared to organic synthetic pigments. This trend has been observed for all acrylic brands and is attributed to the different amounts of water-soluble additives, such as surfactants, wetting agents and thickeners, used to stabilize the dispersion[32]. The weight loss (leaching) registered after the films are fully dryed is shown in Figure 6.3.4. The films that leach more additives correspond directly to those that swell the most, this is in good agreement with results discussed priorly [1,15,16,27,28,40]. In the case of Liquitex®, the water sensitivity can be related to the amount of an octylphenol poly(ethoxylate) type surfactant, also characterized by other authors [27-35][33].

This is consistent with the results obtained by Ploeger et al in a study devoted to the characterization of surface tension, conductivity and swelling of acrylics during water immersions [17]. In this study, it is stated that the most important swelling of the acrylic paint films tested occurred in the first 5-10 minutes, which was accompanied with surface leaching of additives (surfactants and ionic salts). This effect continued, at a slower rate, in the following minutes, with extraction of materials from the bulk of the film. On the other hand, non pigmented films (less additives necessary to stabilise the pigment) showed less swelling. A similar behaviour was observed with the Liquitex® medium shown in Figure 6.3.4.

In order to simulate repeated cleaning treatments over time, another set of Liquitex® samples were immersed in water for 12 hours and their weight was periodically measured. The results obtained for phthalocyanine blue and burnt umber are shown in Figure 6.3.4, along with the results obtained for the 20 minutes immersions. The majority of water absorption occurs in the first 20 to 30 minutes and the weight stabilizes during the first hour of immersion. The leaching of additives registered after 20 minutes and 12 hours immersions are plotted in Figure 6.3.6. Some samples register up to 12 % weight in additives that are removable by water treatments.

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[32] Absorption-drying results obtained for other brands are shown in Appendix B.

[33] A more detailed characterization of the materials extracted with immersions tests is presented later in this chapter.

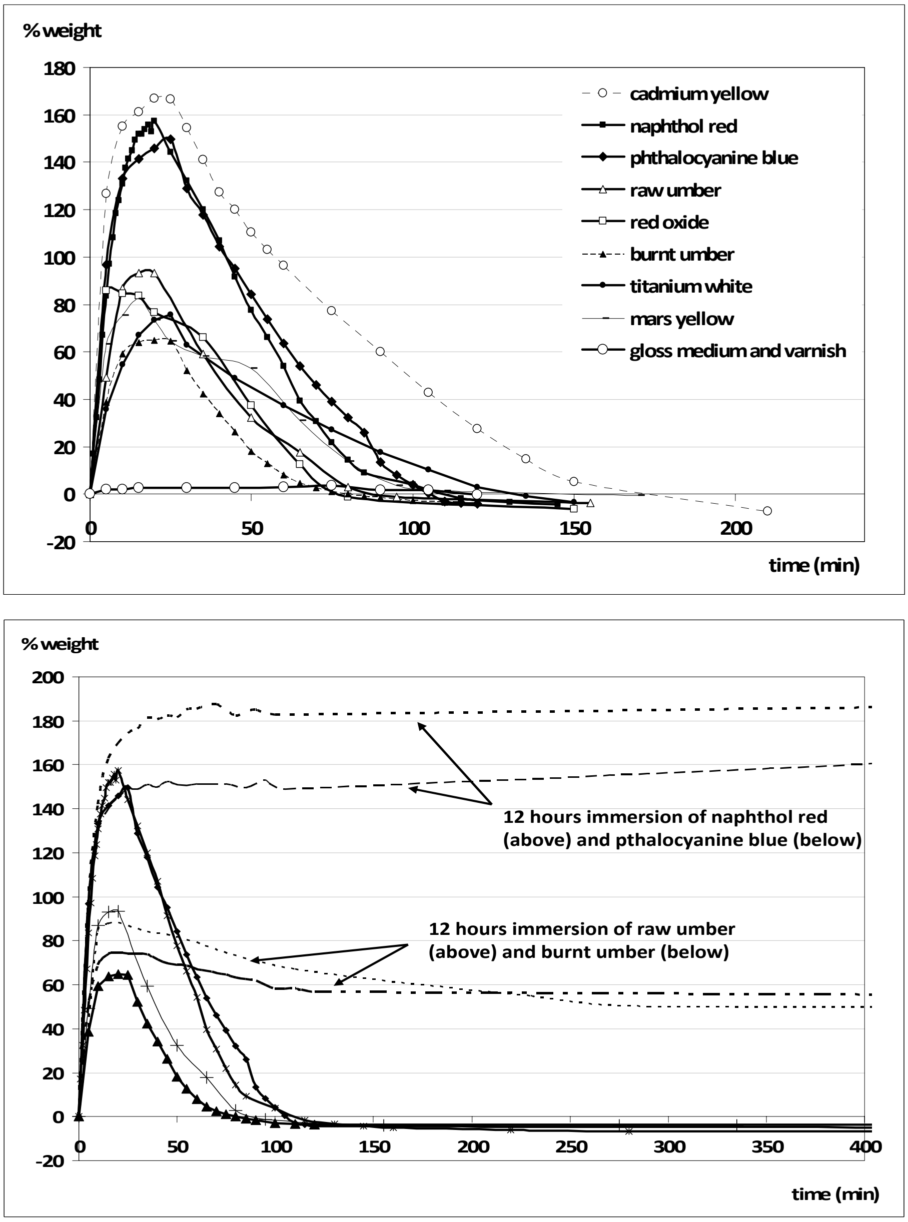

Figure 6.3.4-6.3.5: (Top) Experimental absorption and drying profiles obtained from immersions of Liquitex® paint films in water. It is evident that different colours from the same brand react differently in the presence of water. The general trend indicates that colours containing organic pigments are more water sensitive if they are compared to inorganic. (Bottom) the initial portion of the absorption profiles of Liquitex® where the immersion tests lasted 12 hours. 20 minutes absorptions have been introduced for comparison purposes.

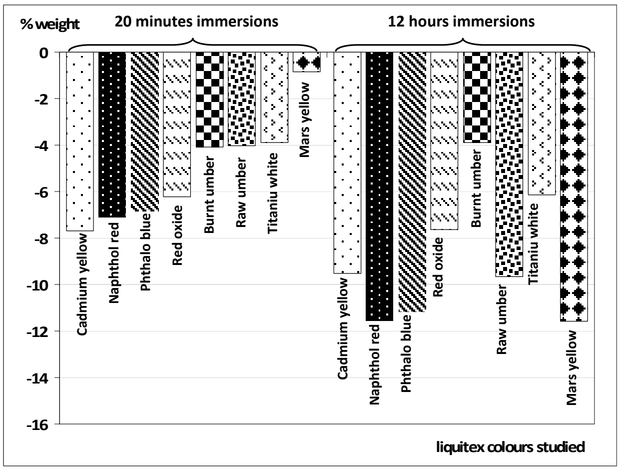

Figure 6.3.6: amounts of extracted material after 20 minutes and 12 hour immersion tests for several Liquitex® paint films. Weight loss during water immersions is related to the leaching of additives present in the dryed acrylic paint films.

The case of Pébéo® paint samples is rather interesting. During immersion, the samples present a moderate increase in weight and low additive loss, which should reflect some stability to water immersions, as depicted in Figure 6.3.7. However, after drying, these paints were significantly deformed, presented an evident change in colour and gloss and were brittle[34]. Evidently, not all sensitivity to water is related simply to water extractable additives present in the films. In fact, important changes in porosity and creation of defects in the latex have been observed by SEM after the immersion of these paint films in water. This will be discussed later in this chapter.

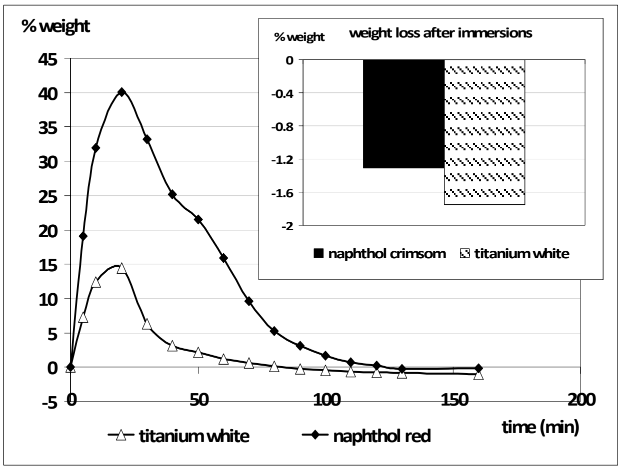

Figure 6.3.7: absorption and drying profiles of Pébeo® naphthol red and titanium white. The weight loss measured after immersion related to leaching of additives is presented in the upper right corner of the figure.

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[34] This will be discussed in the next section of this chapter devoted to the study of the effects of water immersions in the mechanical properties of acrylic paint films.

6.3.1.4- FTIR-ATR spectroscopic study of the materials extracted by water immersions of acrylic and PVAc films

The information presented in this section regards the analysis of the materials extracted from the paint films after water immersions. For this purpose, the aqueous phase of the immersion tests was dried in a laboratory oven at 40ºC until a solid residue was obtained. The material obtained resembled that of a white soft wax. IR aborption spectra were obtained in ATR mode directly on the extracts.

The solid extracts obtained from immersions in polar solvents consisted of mainly of polymer and, in some cases, organic pigments. These results are not discussed here, as they are out of the scope of this thesis. The immersion in non-polar solvents was less fruitful, since the amount of material extracted was very low, and FTIR-ATR spectra could not be obtained**.**

The IR-absorption spectra obtained for Liquitex® burnt sienna immersed in water for 5, 20 and 60 min are shown in Figure 6.3.8. They enable interesting information that is worth discussing. In general, all spectra resemble those of a poly(ethoxylate) type compounds, with characteristic absorptions at 1466, 1343, 1278, 1100, 1060, 958 and 864 cm^{-1}. Two sharp peaks at at 1610 and 1512 cm^{-1} indicate the presence of an octylphenol ethoxylate type surfactant, such as Triton X-405, as noted by other authors [1,27-35,46].

The carbonyl region shows a broad absorption that consists of a maximum peak at 1724 cm^{-1}, and include lower wavenumbers, which comprise the carbonyl absorption region of carboxylic acids (1725-1700 cm^{-1}) [47,48]. The presence of acid groups is confirmed by the broad band in the 2700-2500 cm^{-1} region, as well as a broadening of the peak at 930 cm^{-1} due to harmonic vibrations from combination and deformation vibrations of hydrogen bonds [48]. The detection of carboxylic acids is tentatively identified as a polyacrylic thickener/stabilizer.

There is a series of broad and overlapping absorptions present in the 1680-1500 cm^{-1} region. These are not separated enough to draw any conclusions. A broad weak absorption centered at 1650 cm^{-1} and broad absorption centered at 3600 cm^{-1} are attributed to water present in the extract due to the hygroscopic nature of these materials [47,48].

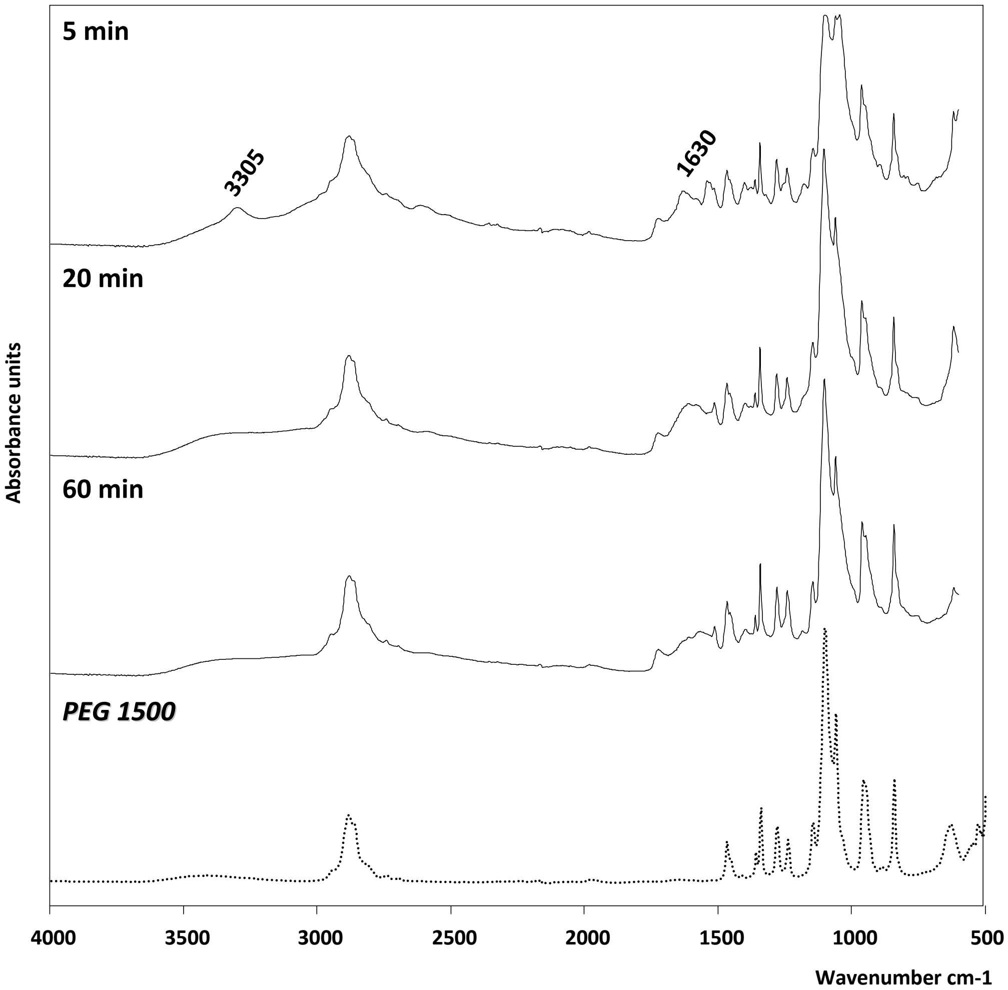

Figure 6.3.8: Liquitex® burnt umber solid extractions obtained from water immersions conducted at different immersion times comprising 5, 20 and 60 minutes. Below is included a FTIR-ATR spectrum obtained for a reference material poly(ethylene glycol) (PEO-1500).

The analysis of the solid extracts obtained from 5 minutes immersion provides some additional and interesting information. The magnification in the 1800-500 cm^{-1} region of the corresponding spectrum is shown in Figure 6.3.9.

A strong absorption at 3305 cm^{-1} together with an increase in 1630 cm^{-1} region indicates the presence of amide type compounds. The presence of these functional groups is characteristic of HEUR thickeners, as reported by Orgilés-Calpena *et al* and Zhumbuhl et al [2,49].

A considerable difference between the IR spectra from 5 minutes and 20-60 minutes immersions is the series of absorptions at 1060 cm^{-1} and 1046 cm^{-1} (with a shoulder at approximately 1000 cm^{-1}). Considering that these bands are in the general C-O absorption region of the spectra, they could be associated to the presence of PEO type compounds. However, none of the reference PEO-type compounds tested in this work present a C-O maximum absorption below 1100 cm^{-1}. These absorptions may be ascribed to other ether type functional groups, such as those present in cellulose ethers (often used as a protective colloids in the polymerization process), which presents a maximum absorption at 1050-1046 cm^{-1}. Phosphate-type additives also absorb in the 1050-990 cm^{-1} region and are used in pigment stabilization, especially inorganic pigments, such as burnt umber [1,28,44,50-52].

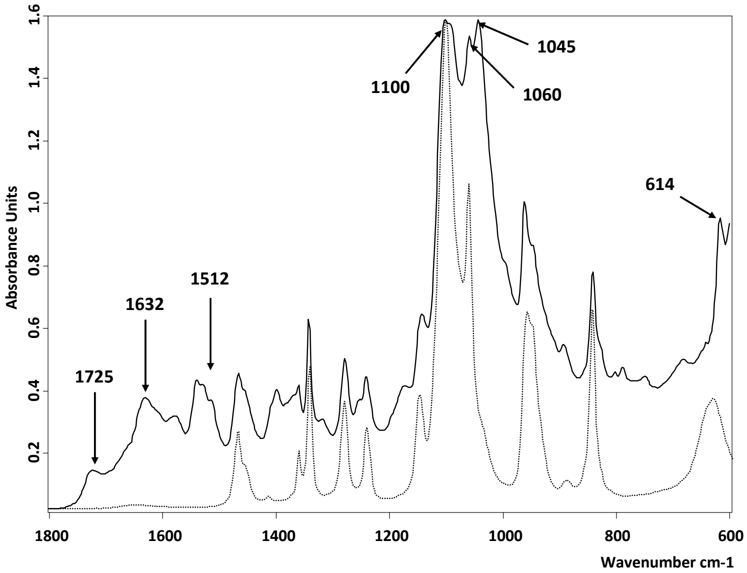

Figure 6.3.9: Detail of the IR absorption spectrum of the solid extract of Liquitex® burnt umber 5 minutes immersion (solid line) in the 1800-600 cm^{-1} region. The spectrum of PEG 1500 is also included in this figure (dotted line).

Another region of interest for the conservation scientist it that concerning the 1000-500 cm^{-1} region. According to several studies [44,50-52] this zone has been used for identifying specific surfactant types, since there are no main absorptions from the polymer. In Table 6.3.3 is a summary of the absorption bands that can be used for tracking specific compounds, according to the above mentioned references.

surfactants	**bands (cm^{-1})**	**assignement**
sodium dodecyl sulphate (SDS)	588, 634 (less intense)	S-O bending of sulfate group [44,50-52]
sodium dodecyl diphenyl ether disulphonate (SDED)	690	γ-vibration of –H of the monosubsituted aromatic ring [34]
sodium dioctyl sulfosuccinate (SDOSS)	581	SO_2 scissor mode [51]
sodium dodecyl benzene sulphonate (SDBS)	614	S-O bendind mode of SO_3 groups [51]
sodium sulphonate adduct of nonylphenol ethylene oxide (2units) (SNP2S)	947	C-O streching mode of ether (+ similar of S-O bending of sulfate group) [51]

Table 6.3.3: Main bands of analytical interest in the 1000-500 cm^{-1} region of the IR absorption spectrum that have been used to monitor the presence of some surfactants in acrylic latexes.

In the IR spectrum of the solid extract obtained from the 5 minutes immersion is a strong absorption peak at 618 cm^{-1}, this is tentatively ascribed to the presence of S-O bending modes from a sodium dodecyl benzene sulphonate (SDBS) type surfactant. Interestingly, this surfactant also shows a strong absorption in the 1046 cm^{-1} region.

Overall, in the analysis of the solid extracts of the Liquitex® paint samples, the characteristic absorption profile ascribed to octylphenol ethoxylate is predominant and impeeds the characterization of other minor compounds possibly present in the extract. It is worth commenting that the solid extracts of naphthol red exhibit strong, clear absorptions at 616 and 636 cm^{-1}, which are ascribed to the presence of two distinct sulphonate type compounds SDBS and SDS, respectively [50-52].

The analysis of Vallejo extracts showed similar absorption profiles to those of Liquitex® samples. A FTIR-ATR spectrum from a 12 hour water immersion of Vallejo® phthalocyanine blue is shown in Figure 6.3.10. The main absorptions indicate the presence of PEO-type compounds, and a sharp peak at 1512 cm^{-1} suggests the presence of an octylphenol type surfactant. In the carbonyl region, a maximum at 1720 cm^{-1} and the region comprising 1700-1500 cm^{-1} are ascribed to acid groups and amide type compounds. Due to the broad nature of the bands it is difficult to make clear assumptions about the exact type of compound responsible for these absorptions.

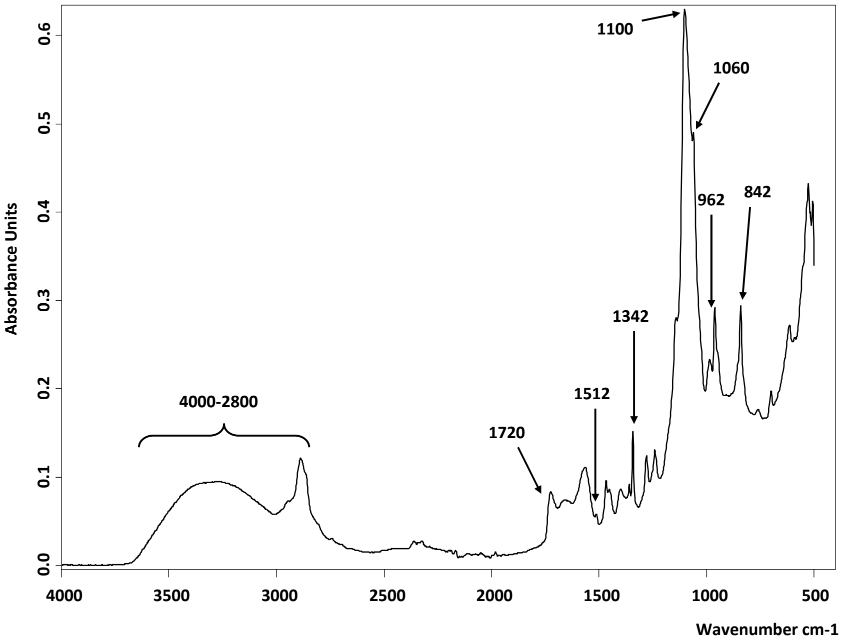

Figure 6.3.10: the FTIR-ATR spectra of the dryed leachate from a 12 hour immersion of Vallejo® phthalocyanine blue. The analysis show similar compounds to those found in Liquitex® extracts.

Figure 6.3.11 shows the FTIR-ATR spectrum of a solid extract obtained from a 12 hour immersion of a Talens® titanium white. The spectrum has been magnified in the 1800-500 cm^{-1} for clarity purposes. The IR absorption profile is different from that of Liquitex® or Vallejo® extractions. The most prominent peaks seen in this figure resemble those of a poly(ethoxylated) fatty alcohol type surfactant, such as Brij®30 [53], and a cellulose type thickener [2], such as Hydroxypropylcellulose. Both products have been included in the figure for comparison purposes.

In the carbonyl region, a broad absorption from 1740 to 1700 cm^{-1}, centered at 1720 cm^{-1}, indicates the presence of residual acrylic monomer and organic acids, possibly from a polyacrylic acid type additive.

The absorptions present in the 1700-1500 cm^{-1} region are very complex. These may comprise signals from different functional groups such as amides (1650-1600 cm^{-1}), amines (secondary amines 1650-1550 cm^{-1} (and 1190-1130 cm^{-1})) and carboxylic salts (1650-1550 cm^{-1} (and 1420-1300 cm^{-1})), absorbed water (broad band centered at 1650 cm^{-1}) and some contribution from aromatic rings detected at 1515-1480 cm^{-1} [48]. The resolution of this region is not sufficient to make further comments.

At lower wavenumbers a strong absorption at 617 cm^{-1} is tentatively ascribed to the presence of sulphonate groups from sodium dodecyl benzene sulphonate, among others.

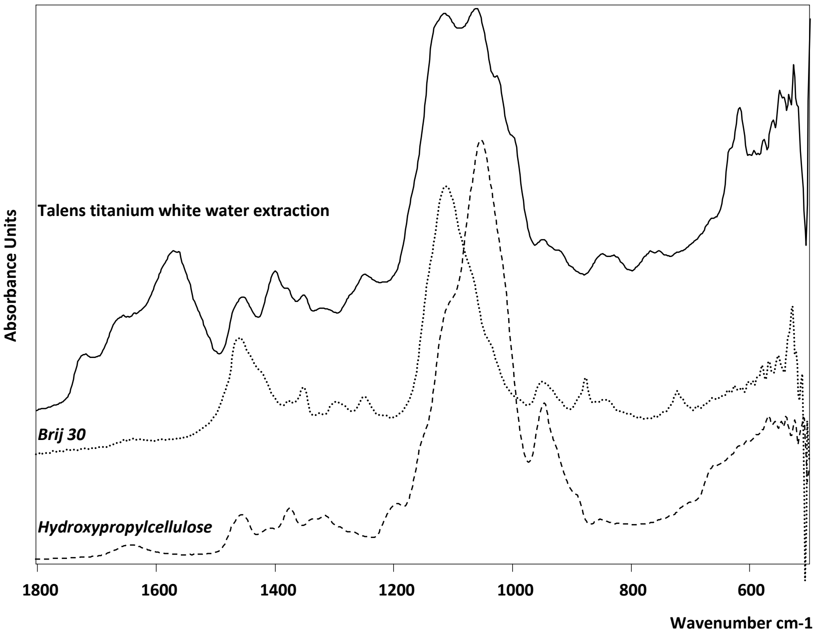

Figure 6.3.11: Detail of the 1800-500 cm^{-1} region of the FTIR-ATR spectrum of Talens® titanium white solid extract (solid line). The spectra of Brij® 30 (dotted line) and hydroxypropylcellulose (dashed line) have also been included for comparison purposes.

The spectra obtained for the Pébéo® solid extracts are complex, possibly due to the presence of many compounds. However, organic acid groups can be identified, which are ascribed to a Poly(acrylic) stabillizer or thickener. There is evidence of acrylic monomer in the carbonyl region (1728 cm^{-1}) and also, it is possible that PEO-type compounds are present as well as a cellulose type compound.

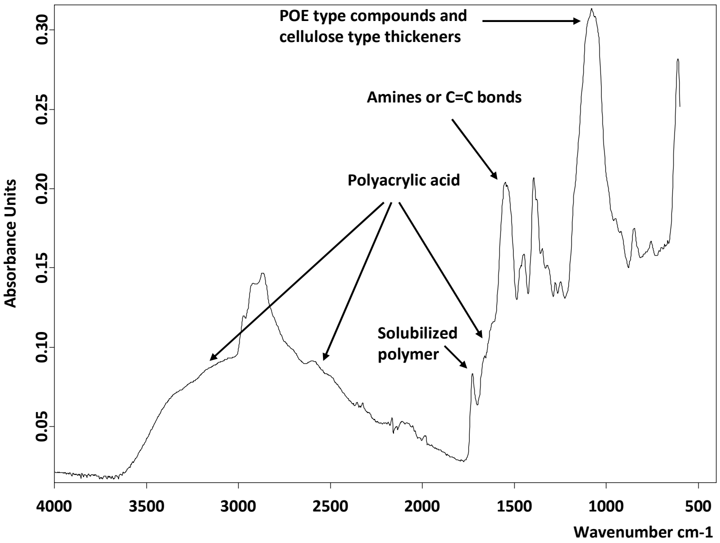

Figure 6.3.12: FTIR-ATR spectrum of Pébéo® naphthol crimson extraction in water.

6.3.1.5- Py-Silylation-GC-MS study of the materials extracted by water immersions of acrylic films

The use of HMDS as a derivatising reagent for Py-GC-MS analysis of acrylic and PVAc products has been proposed in this work for performing *in-situ* thermally assisted Py-silylation-GC-MS. This analyitical method enables the convertion of carboxylic and hydroxyl groups into a less polar TMS derivatives so that their signal in the pyrogram are enhanced. Side reactions and fronting peaks are thus reduced. In the following section of this chapter, *in-situ* thermally assisted Py-silylation-GC-MS is used for the characterization of solid extracts obtained from water immersions of acrylic films.

Liquitex® burnt umber, Vallejo® naphthol red and Talens® gloss medium were immersed for 12 hours in deionised water. After this, the films were removed from the immersion aqueous bath and then the aqueous phase was dried in a laboratory oven at 40ºC.

The analyses by means of *in-situ* thermally assisted Py-Silylation-GC-MS of a 5 minutes and 60 minutes Liquitex® burnt umber water extractions are shown in Figure 6.3.13.

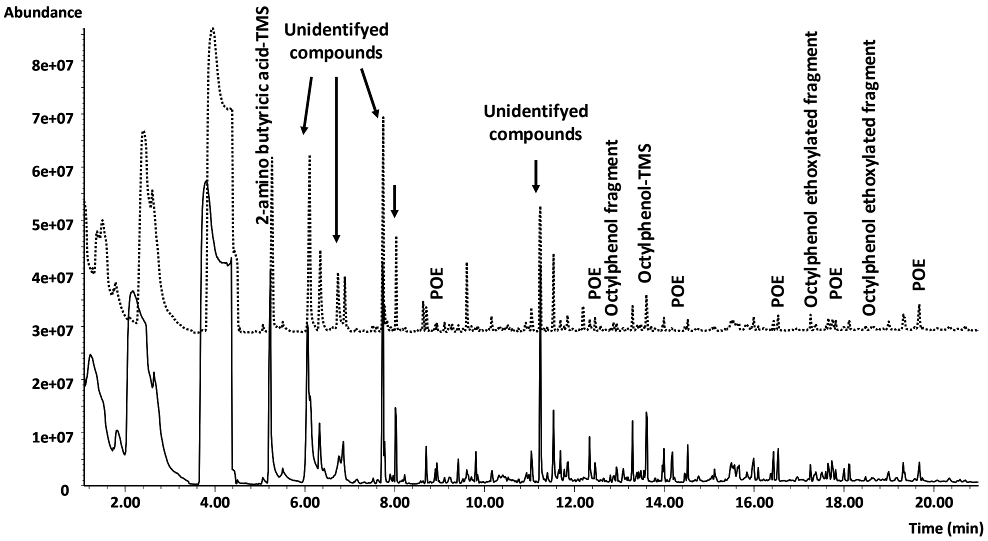

Figure 6.3.13: pyrograms corresponding to the analysis by means of Py-Silylation-GC-MS of a 5 minutes (below) and 60 minutes (above) water extractions from Liquitex® burnt umber paint samples.

Early in the pyrogram corresponding to the *in-situ* thermally assisted Py-Silylation analysis can be distinguished three compounds that appeared as fronting peaks in conventional pyrolysis. These peaks are ascribed to amino-based compounds, which is in good correlation with the results obtained from the FTIR-ATR spectra. These compounds have not been fully characterized to date.

PEO fragments in their derivatised form appear mostly at high retention times, which are ascribed to long chain polyethoxylate type additives. Interestingly, these peaks are not found in the direct Py pyrogram.

A strong and defined peak corresponding to the TMS derivative form of octylphenol dominates the mid section of the *in-situ* thermally assisted Py-Silylation pyrogram. Other peaks corresponding to the poly(ethoxylated) octylphenol fragments are also pointed out in the figure. A pyrogram corresponding to a poly(ethoxylated) octylphenol surfactant (Triton®X-100) can be found in Appendix A.

The pyrogram obtained from the solid extract of Vallejo® naphtol red is show in Figure 6.3.14. This is a good example of the interest of analysing solid extracts, and how the abundant pyrolysates from the acrylic polymer can hinder the detection of additives. There are important differences between the analysis of the paint sample and that of the solid extract. In fact, several additional peaks appear throughout the pyrogram that are attributed to PEO fragments in their derivatized form. An octylphenol type surfactant has also been detected, which is in good agreement with those previously obtained by means of FTIR-ATR spectroscopy.

The analyses of the Talens® gloss medium solid extract show two unidentified peaks in the pyrogram. The analysis of the fragmentation patterns suggests the presence of nitrogen in their structures but the identity of the compounds has not been determined to date. Ethylene glycol is also detected in its derivatised form and strong peaks ascribed to derivatised PEO fragments appear at different retention times. Interestingly, in the pyrogram is evident the presence of dodecanol and tetradecanol in their derivatised form, as well as fragments corresponding to dodecane, dodecene and tetradecene. Also pointed out in the figure are polyethoxylated ether fragments of dodecanol. These peaks are ascribed to a poly(ethoxylated) fatty alcohol type surfactant, which has not been detected by conventional pyrolysis. A description of a pyrogram corresponding to a poly(ethoxylated) fatty alcohol surfactant (Brij®30) has been included in Appendix C. Similar results have been obtained in the analysis of other Talens® products such as the gel medium and the pigmented samples.

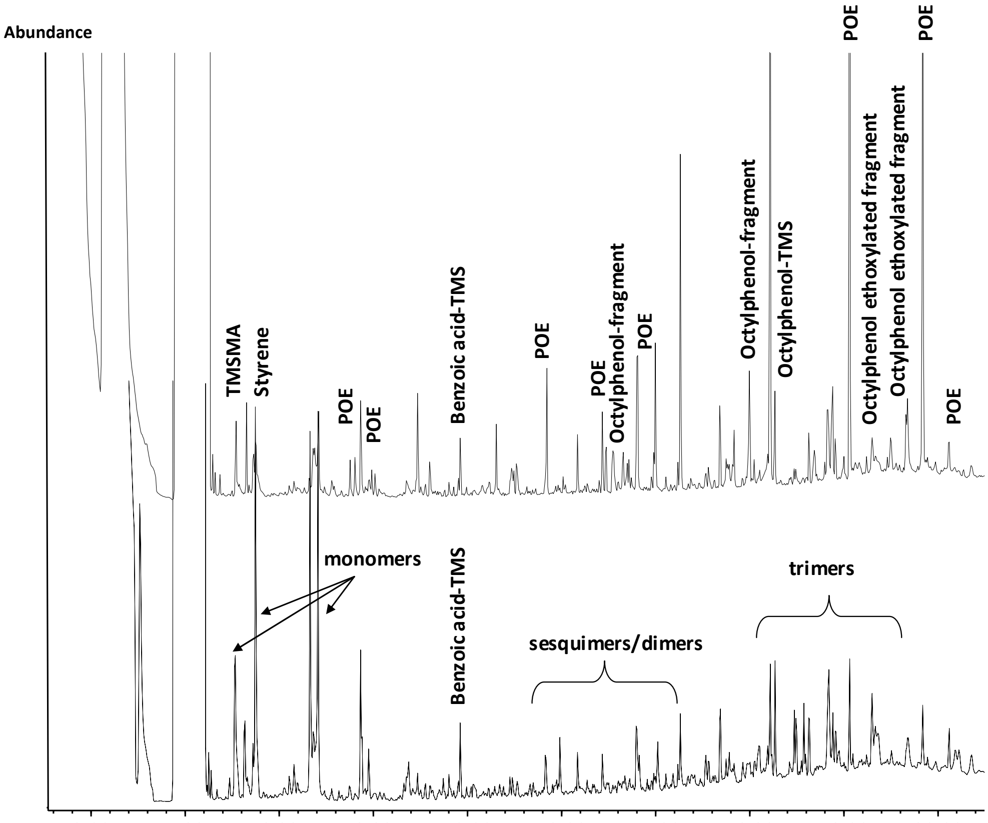

Figure 6.3.14: pyrograms corresponding to the analyses by means of Py-Silylation-GC-MS of a (above) water extractions from Vallejo® naphthol red and (below) paint film, included for comparison purposes. The presence of the main polymer pyrolysates clearly enhibits the detection of other minor compounds seen in the extraction. Among the products found are PEO-type compounds throughout the pyrogram as well as strong signals of an octylphenol ethoxylate type surfactant.

6.3.1.6- The effects of organic solvent immersions in the mechanical properties of acrylic paint films

The mechanical properties of Talens® raw sienna paint film specimens immersed for 30 minutes in ligroin and white spirit are shown in Figure 6.3.15. The paint film specimens immersed in the non-polar solvents exhibit similar mechanical behaviour to that of the control sample. This is in good correlation to the results obtained by other authors [1-5]. On the other hand, the film immersed in white spirit presents higher flexibility when compared to the control specimen. This solvent was retained in the bulk film for more than 2 months exherting the plasticizing effect seen in Figure 6.3.15. The results shown in the figure correspond to a paint film that was tested 2 months after the immersion and, nevertheless, the effects of the solvent are still evident. The test specimens immersed in ligroin exhibited less solvent retention in the bulk film, and similar mechanical propertiesto the control.

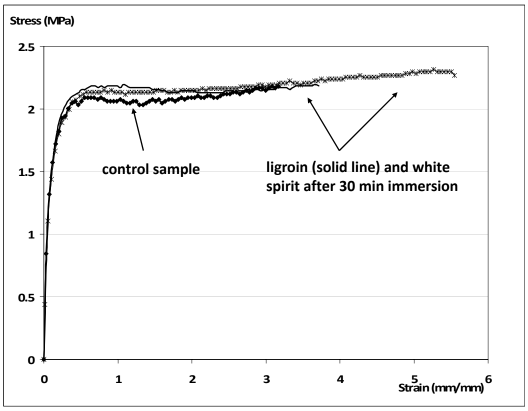

Figure 6.3.15: The mechanical properties of Talens® raw sienna after 30 minutes immersion tests in the non-polar solvents white spirits and ligroin illustrated by the stress-strain curve..

The immersions of Liquitex® burnt umber in ethanol and acetone on the mechanical properties of are shown in Figure 6.3.16. The films evidence brittleness due to the solubilization of polymeric material. The films maintained a minimum cohesionand stress-strain tests could be performed because no mechanical action was applied during the immersion treatment.

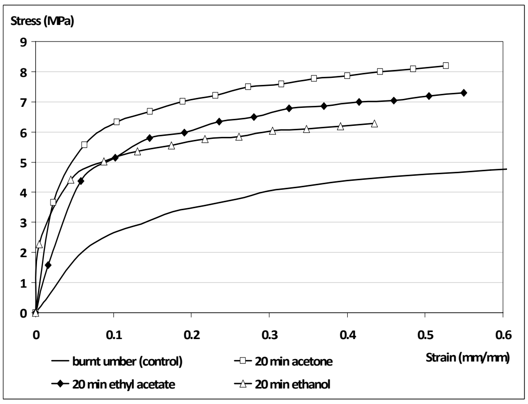

Figure 6.3.16: The mechanical properties of Liquitex® burnt umber after 20 minutes immersion tests in the ethanol and acetone illustrated by the stress-strain curve. (magnification of the initial part of the stress-strain curve).

6.3.1.7- The effects of water immersions in the mechanical properties of acrylic paint films

A set of Liquitex® paint film specimens immersed in water for 20 minutes and 12 hours were tested for recognizing changes in their mechanical properties. Long immersion tests represent cleaning treatments where water is in contact with the surface enough time to cause swelling and leaching of additives[35]. In Figure 6.3.17-18 are shown the results obtained for Liquitex® naphthol red, burnt umber, phthalocyanine blue and red oxide test specimens.

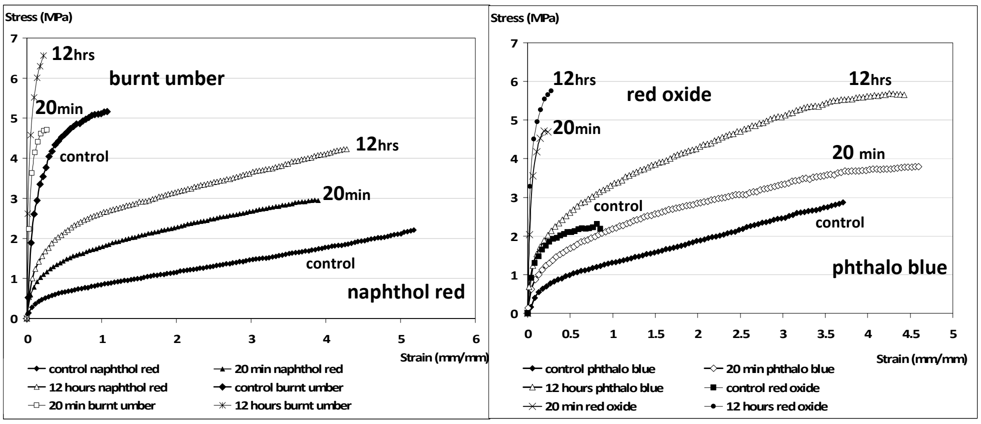

Figure 6.3.17-6.3.18: The effects of 20 minutes and 12 hours immersion tests in the mechanical properties of Liquitex® burnt umber and naphthol red (left) and red oxide and phthalocyanine blue (right).

All colours exhibit an increase in Young's Modulus after the 20 minutes immersion, and this effect is more evident after the 12 hours immersions. Two other trends in the mechanical properties can be pointed out. Naphthol red and phthalocyanine blue became stronger (higher modulus without loosing flexibility), which has been observed by Hagan in previous studies [22-25]. Nevertheless, other colours such as red oxide and, especially, burnt umber, lost a significant amount of flexibility after the immersion tests. This was also registered for mars yellow, cadmium yellow and raw umber, not shown here. The trend seen here indicates that the colours formulated with organic synthetic pigments were soft enough to deform back into a cohese film when redimensioning during drying. On the contrary, paint film specimens with inorganic pigments were not able to do so. This may be due to the higher PVC present in the inorganic colours, defects in the homogeneity of the film, and also due to particle type and size. In the case of earth colours, the expansion of the clay minerals during the immersion tests and the high water retention of these during drying impeeds the polymer particles to re-arrange around the pigment [20]. This creates a more fragile structure, which

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[35] In Appendix C are described a series of tests consisting of the effects of short immersions and swabbing tests in the mechanical properties and leaching of acrylic paint samples that help understanding why long immersion tests as representative of extreme or repeated cleaning treatments.

is reflected in the significant loss of mechanical properties. This is in good agreement with the information obtained by SEM, in which a network of defects and pores is created during the immersion tests in the surface (and bulk) of the specimens and this affects the mechanical properties of the films. This will be discussed later in this chapter.

The Pébéo® paint films presented more pronounced water sensitivity during the immersion tests when compared to the previous acrylic brands. The immersion tests resulted in a permanent deformation and severe embrittlement of the specimens. In Figure 6.3.19 are shown the stress-strain curves obtained for 25 minutes and 12 hours immersion of napthol crimsom, as well as 12 hours immersion of titanium white. The data reveals an important increase in stiffness and loss in flexibility with increasing time of immersion. After 12 hours immersion the films exhibited the mechanical behaviour of a brittle material. The justification for this trend in the mechanical behaviour can not be fully attributed to the additive leaching since weight loss was fairly lower than those registed for other paint brands. The evident damage may be related to the impossibility to re-form a cohese latex structure during drying, especially due to the permanent deformation that occurred during the expansion of the paint film on swelling and leaching of additives [20]. This has been observed by SEM imaging of the surface of these films.

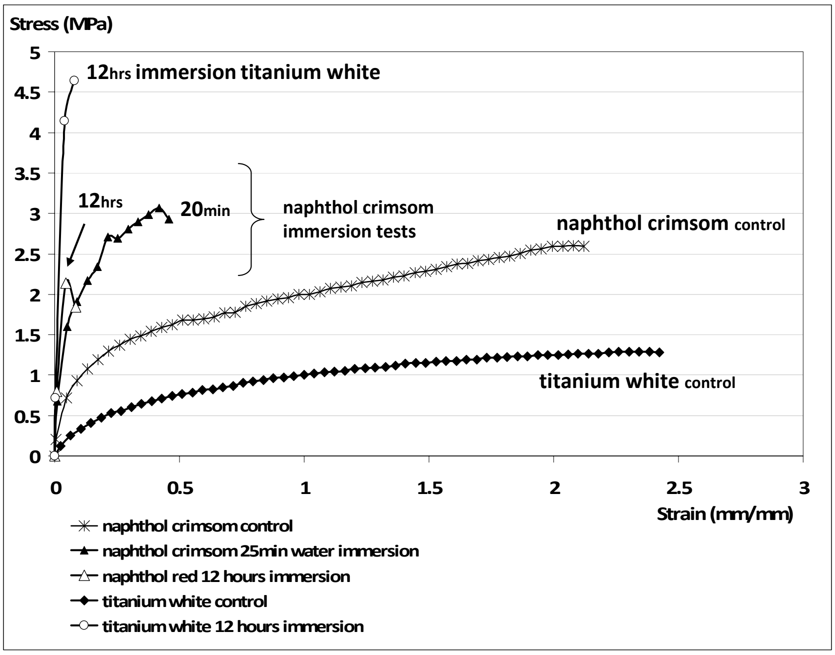

Figure 6.3.19: the effects of water immersion tests in Pébéo® naphthol crimsom and titanium white. Immersion tests concerned 20 minutes and 12 hours. The changes in the mechanical properties of these specimens are noticeable.

6.3.1.8- Morphological study of acrylic paint films subjected to water immersions by Scanning Electron Microscopy (SEM)

The effects of water based cleaning treatments in the surface of acrylic paint films were studied by SEM. In Figure 6.3.20 are shown the surfaces of Liquitex® burnt umber: control sample, 20 minutes and 12 hours immersions in water.

The control sample (top left image) shows a continuous polymeric surface with some poorly bound pigment particles and dust accumulation. At this magnification there are no evident defects such as pinholes, cracks or fissures. After the 20 minutes water immersion test (top right image) the surface shows less amount of unbound pigment and adhered particles. Interestingly, a network of small pinholes and defects were created throughout the surface of the polymeric matrix.

In the image corresponding to the 12 hours immersion (bottom) these defects are much more pronounced and extended, presenting heterogeneous size and shapes, and the majority of poorly bound particles at the surface have been eliminated [14,38]. The alterations observed by SEM are in good agreement with the changes in the mechanical properties after immersion in water: increase in stiffness and decrease in the strain to brake. The increase in stiffness has been generally attributed to the loss of additives that act as plasticizers in the bulk film [1,2,6,14,18-25,28,38,40,43]. But it is evident that the creation of a network of defects is an important effect that may contribute positively to the early failure observed in the stress-strain curves [19,20]

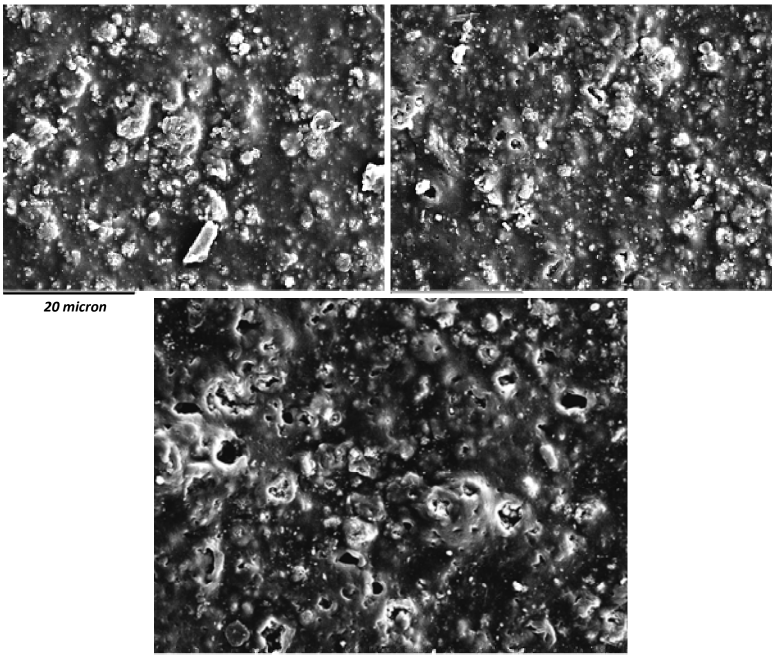

Figure 6.3.20: Secundary electron images of Liquitex® burnt umber (x2000 magnification): control sample (top left image), sample from a paint film subjected to 20 minutes water immersion (top right corner) and 12 hours water immersion (bottom). Water promotes the creation of several defects in the polymers latex that can be correlated with early the failure observed in the mechanical properties of the films.

The Pébéo® paint films are severely affected by water immersions. It is visible in Figure 6.3.21 that water is not only causing leaching but also also affecting physically the latex structure forming a network of pores and cracks. Also evident in the figure, and especially for phthalocyanine blue (image below in the figure), that after drying the polymer is not fully able to reaccomodate around the pigment particles. The resulting film is not cohese, since the particles are not well bound, and this explains their brittle behaviour, described previously.

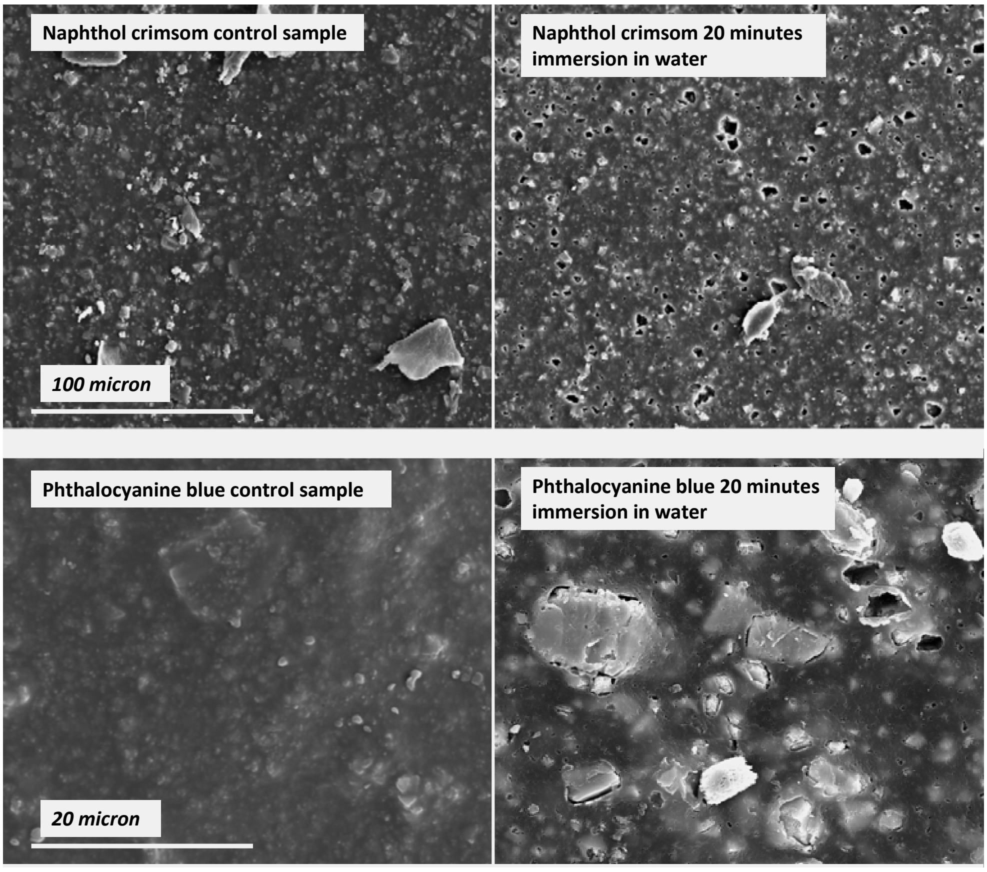

Figure 6.3.21: Secundary electron images of Pébéo® paint film specimens after water immersions: (above) naphthol red at x500 magnification and phthalocyanine blue at 2000x magnification. Water promotes the creation of a network of pores that can be correlated with early the failure observed in the mechanical properties of the films. It interesting to notice that the the polymeric matrix is partially dissolved after immersion and, as consequence, polymer can hardly reaccomodate around the pigment particles.

6.3.2.1- The solubility range of PVAc films in the TEAs chart

The solubility of PVAc paint films was determined by a similar procedure to that of acrylics. The LA-LE-EA tests revealed that PVAc products are very sensitive to organic solvents, similarly to acrylics. This is especially true for Flashe® paint films, in which solvents, such as white spirit (Fd=90), affect the surface of the paint film specimens. The only free solvent that caused no apparent change in the surface of the films were iso-octane (Fd=100) and ligroin (Fd=97), which is situated in the most non-polar extreme of the TEAS chart. Figure 6.3.22 shows the solubility of Mowilith® DMC2, which is similar to that of acrylics. The effects of immersions tests of PVAc paint samples in organic solvents will not be discussed in this work, as they present similar results to those observed for the acrylics.

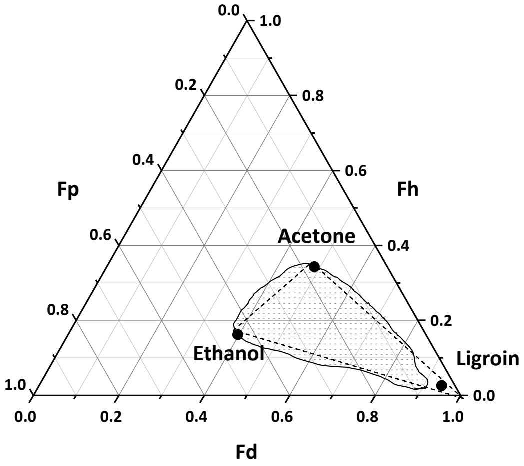

Figure 6.3.22: experimental solubility region of Mowilith DMC2® medium obtained with a standard LA, LE and AE solubility test (the polarites of the mixtures are delimited by the triangle composed of dashed lines). The PVAc medium is soluble solubility most mixtures of the solubility test.

6.3.2.2- The effects of water immersions in the leaching of additives of PVAc products

Water immersions of Flashe® films caused similar effects to those seen for acrylics. An example of this is shown in Figure 6.3.23, for a series of 20 minutes immersions of Flashe® paint specimens. During the immersion, the samples absorb water, swell, and lose weight after drying that corresponds to additive leaching. After the 12 hour immersion tests, the earth colours from Flashe® suffered the damage visible in Figure 6.3.24, not observed for the other colours tested. This is attributed to the expansion of the clay minerals from the pigments that cause internal stresses superior to the cohesion forces of the film.

The analysis of the extractions of these films revealed the presence of PEO type compounds as well as cellulose type thickeners. Other compounds have been found and will be discussed in detail in the next section of this work.

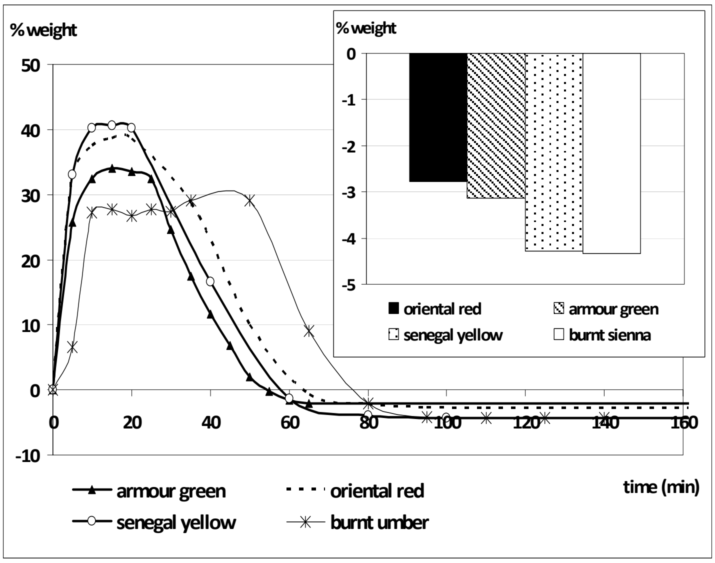

Figure 6.3.23: absorption-drying profiles of paint films from Flashe®, including armour green, oriental red, senegal yellow and burnt umber. The resulting weight loss measured after the immersions is shown in the right of the figure.

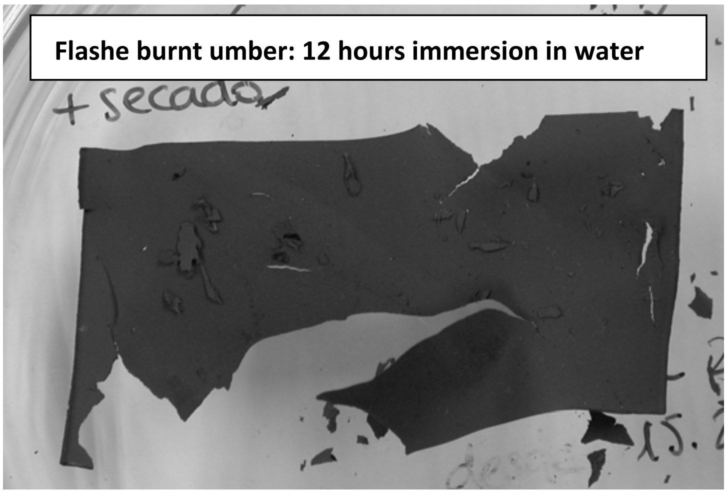

Figure 6.3.24: damage caused by a 12 hour immersion test on a Flashe® burnt sienna film.

Conrayt®, Vinavil® 59 and Mowilith® DMC2 were immersed in water for 20 minutes and 12 hours. The weight losses registered after these trials are shown in Figure 6.3.25.

The Conrayt® and Vinavil® 59 products experienced an important water absorption and swelling effect as well as additive leaching. This is related to the swelling and extraction of a poly(vinylalcohol) (PVOH) protective colloid/thickener present in the dryied film. In the case of Conrayt®, the leaching of this additive was slower than for Vinavil® 59, but both products showed similar weight loss after the 12 hours immersion tests.

In contrast, Mowilith® DMC2 showed fairly less water absorption and leaching when compared to the other PVAc media, the analysis of the extraction revealed the presence of a cellulose type thickener. A more detailed characterization of the leachates is described in the following section of this chapter.

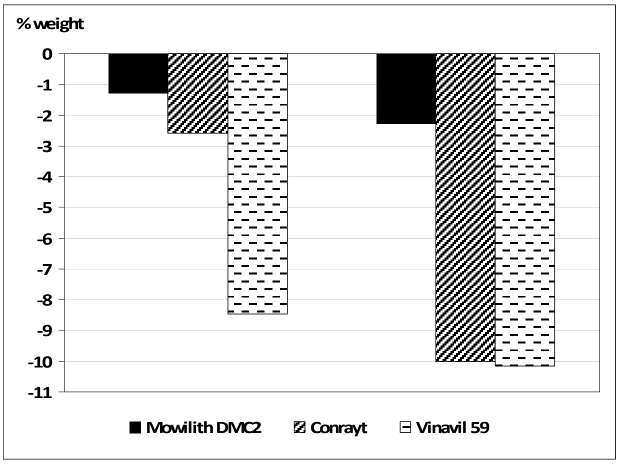

Figure 6.3.25: the leaching of additives from PVAc based products, measured after 20 minutes and 12 hours water immersion tests.

6.3.2.3- FTIR-ATR study of the materials extracted by water immersions of PVAc films

The water extractions obtained from 12 hours immersions of Flashe® armour green, oriental red, titanium white, burnt umber and raw umber have been studied by FTIR-ATR spectroscopy. The results can be divided into two groups, according to the spectral similarity. One group comprises the organic synthetic pigments armour green and oriental red, and the second the inorganic pigments titanium white, burnt umber and raw umber.

The FTIR-ATR spectrum of oriental red water solid extracts is presented in Figure 6.3.26. The major absorption profiles are coincident with PEO type of compounds (1466, 1343, 1278, 1100, 1060, 958, 864 cm^{-1}), as well as a cellulose ether type (major absorptions in the –OH region and ether broad absorption centered at 1070 cm^{-1}). This region, as well as the carbonyl absorption at 1730 cm^{-1} seem to indicate the presence of residual monomer from the original PVAc polymer. The broadening of the carbonyl region up to 1715 cm^{-1} indicates also the presence of carboxylic acids, which correlates with an increase in the –OH region as well as 2700-2500 cm^{-1}.

The most significant difference between the spectra from this group of extractions regarding the second group is the presence of two strong peaks at 760-700 cm^{-1}, which are ascribed to aromatic rings, confirmed by the absorptions in the 3130-3070 cm^{-1} region. The presence of aromatic compounds is associated to the extractions of paints with synthetic organic pigments in their composition. This suggests that such additives come from the pigment mill, rather than from the binding medium. The results obtained from Py-GC-MS reveal the presence of styrene and methacrylic acid in these extracts [36], which will be discussed later in this chapter.

Finally, the window comprising the range 1700-1500 cm^{-1} presents several strong absorptions that are tentatively ascribed to amide type compounds (also double bonds). Nevetheless, there is no other evidence of peaks that can be associated with this and draw further conclusions.

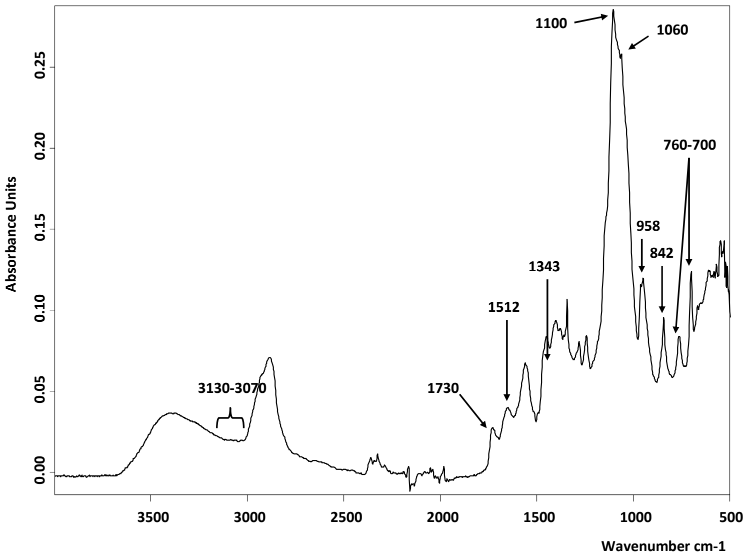

Figure 6.3.26: FTIR-ATR spectra of flashe® oriental red extraction after 12 hours water immersion. Refer to text for comments on the assigned peaks.

The FTIR-ATR spectra of the solid extract of Vinavil® 59 and Conrayt® are shown in Figure 6.3.27 and are contrasted to a poly(vinylalcohol) (PVOH) reference (Mowiol®).The general absorption profiles match the reference sample, identifying the extraction product. The characteristic absorptions of PVAOH are 3321 (broad band), 1736, 1427, 1376, 1244 and 1092 cm^{-1} with a less intense, but characteristic, broad absorption centered at 846 cm^{-1}. PVOH has been used as a protective colloid or thickener in many PVAc formulations, as described in the introduction of this work.

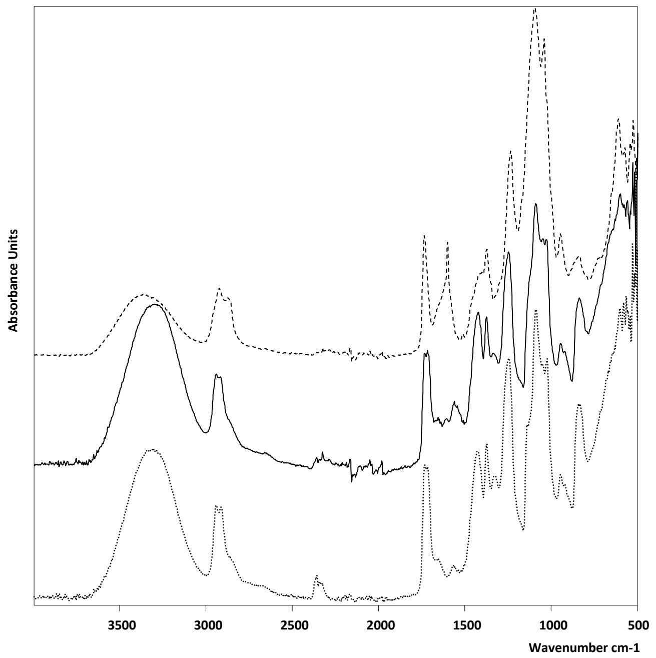

Figure 6.3.27: the FTIR-ATR spectra of solid extracts after 12 hours immersions of: Conrayt® (dashed line), Vinavil® 59 (solid line) and a spectrum of a reference poly(vinyl alcohol), Mowiol® (dotted line).

The analysis of the 12 hours extraction of Mowilith® DMC2 revealed the presence of a cellulose type thickener. A comparison between the extraction and a reference Hydroxypropyl cellulose is shown in Figure 6.3.28. It reveals very similar patterns, with diagnostic peaks at 1046 cm^{-1} and in the –OH region. It is also important to mention that there is a strong absorption in the carbonyl region at 1733 cm^{-1} which is related to the presence of residual monomer, confirmed by the presence of peaks a 1117 and 1028 cm^{-1} from PVAc absorptions. At 614 cm^{-1} there is a sharp peak that is tentatively ascribed to the presence of sulphonate groups, related in the literature to the presence of dodecylbenzene sulphonate [50-52].

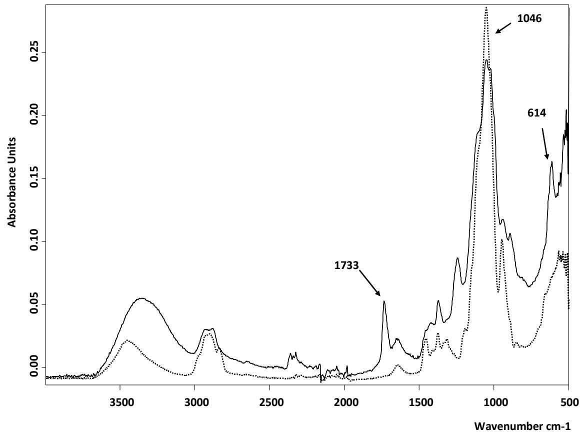

Figure 6.3.28: analysis by FTIR-ATR spectra of the solid extract of Mowilith® DMC2 after 12 hour immersion (solid line). A reference spectrum of hydroxypropylcellulose is included for comparison purposes (dotted line).

6.3.2.4- Py-Silylation-GC-MS study of the materials extracted by water immersions of PVAc films

A series of 12 hour water extractions from Flashe® oriental red, armour green, raw umber, burnt umber and white films were studied by *in-situ* thermally assisted Py-Silylation-GC-MS. The analysis of the extractions allowed to separate some water soluble additives present in minor quantity that are hindered in the general pyrograms of the pant samples due to the presence of polymer pyrolisates. In Table 6.3.4 are summarized the main compounds identified with this method, and the pyrogram obtained for armour green solid extract is presented in Figure 6.3.29.

Early in the pyrogram is a well-defined peak corresponding to ethanoic acid in its derivatised form characteristic of PVAc resins. Benzene is not seen due to the presence of HMDS. However, methyl-naphthalene is identified later in the pyrogram which confirms the presence of residual monomer or polymer chains solubilized during the immersion. A series of peaks corresponding to o-xylene, styrene, α-methylstyrene and methyl-naphthalene are ascribed to recombination reactions. These were not detected in the pyrogram corresponding to the paint sample. Two intense peaks are found in the pyrogram that correspond to butanedioic acid and pentanedioic acid, both in their silylated form.

The signal of PEO-type additives are pointed out in the figure. Mostly all PEO-type products appear in their derivatised form, which proves the efficiency of HMDS in the derivatisation of –OH functional end groups. It is interesting to notice that, in the case of the analysis of the extract from white paint sample, it has been possible to detect the presence of PEO-type products with C=C double bond and C–C bond end groups. This is an indicator of different cleavage pathways that occur during the pyrolytic process, in good agreement with previous studies [40].

Finally, a peak corresponding to methenamine is also indentified and can be ascribed to a preservative added to the paint formulation.

Characterizing as much as possible the compounds from a micro-sample is not only of analytical interest, but also to the conservator. By detecting additives such as PEO type compounds, carboxylic acids and thickener fragments such as PVOH or from cellulose ethers, can be of paramount interest for planning conservation treatments such as cleaning, or predict aging characteristics.

Figure 6.3.29 summarizes the main peaks identified in the pyrogram corresponding to the Py-Silylation-GC-MS analysis of the extraction of Conrayt®. The main peaks are ascribed to the presence of PEO-type compounds possibly from surfactants or stabilizers (anti freeze-thaw agents). The presence of acetic acid can be attributed to both residual monomer and to the pyrolitic degradation of PVOH. The presence of PVOH is confirmed by its main by-products such as hexanedial, benzaldehyde and acetaldehyde and is in good agreement with the FTIR-ATR spectrum of this extract [54]. Other compounds of interest identified in this extract are nonanol and decanol in their derivatised forms. These are tentatively ascribed to the presence of surfactants with a fatty acid chain, possibly with an ethoxylated chain. There are no further peaks in the pyrograms that can clarify the origin of these compounds.

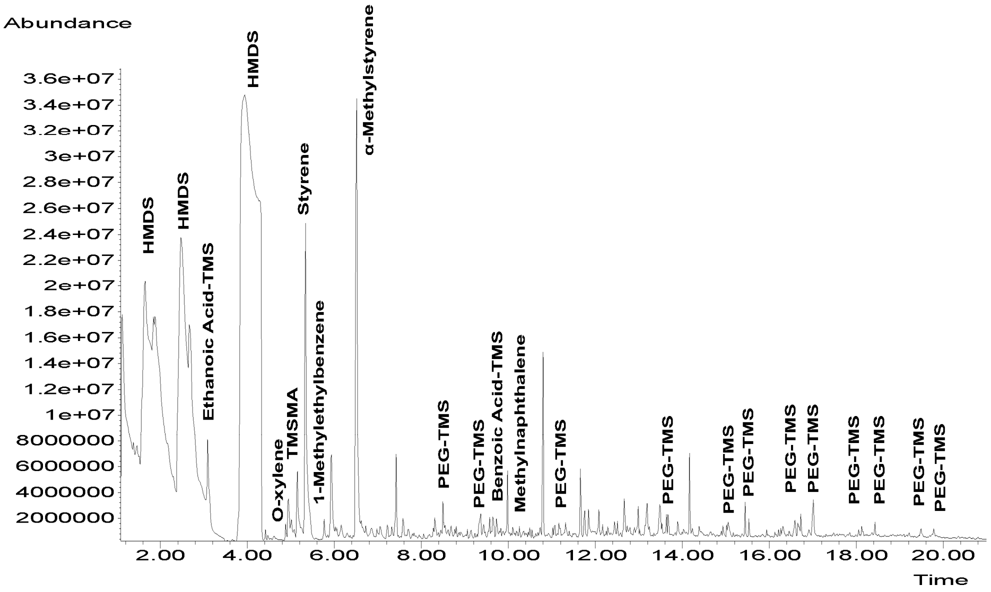

Figure 6.3.29: pyrogram obtained for Flashe® armour green solid extract. Peaks assigned correspond to ethanoic acid-TMS, o-xylene, styrene, 1-methylethylbenzene, α-methylstyrene and methylnaphthalene. PEO-type compounds were also identified as well as methenamine.

Extractions		Flashe® Oriental Red	Flashe® Armour Green	Flashe® Raw Umber	Flashe® Burnt Umber	Flashe® White
Supplier		**Lefranc & Bourgeois**				
Declared composition by supplier		**PVAc paints**				
Compounds Identified	*m/z* ion fragments					
ethanoic acid, TMS ester	117, 75, 59, 45	V	V	V	V	V
propanoic acid, 2-methyl-TMS ester	160, 145, 75,73, 58, 45	V	V	V	V	V
ethanol, 2-[(TMS)-oxy]-TMS ester	119, 103, 85, 58, 43	-	-	-	-	V
o-xylene	106, 91, 77, 65, 51, 39	-	V	-	V	V
methacrylic acid-TMS ester	158, 143, 73, 69, 41	V	V	V	V	V
styrene	104, 78, 63, 51, 39, 27	V	V	-	V	V
vinylcarbitolether	160, 87, 72, 59, 45	-	-	-	-	V
α-methylstyrene	118, 103, 91, 78, 51, 39	V	V	-	V	V
phenoxy-TMS	166, 151, 77, 43	-	-	-	-	V
propanoic acid-2-methyl-TMS ester	145, 117, 75, 73, 58, 45	V	V	V	V	V
ethanoic acid 2-oxy-TMS ester	220 205, 147, 73	V	V	V	V	V
vinyl ethyl carbitol	160, 85, 72, 59, 45, 31, 29	-	-	-	-	V
divinylcarbitol	158, 117, 73, 71, 57, 45, 27	-	-	-	-	V
2-pyrrolidinone, 1-ethenyl	111, 82, 68, 56, 41, 28	-	-	-	-	V
methenamine	140, 112, 96, 85, 69, 53, 42	-	V	-	-	V
benzoic acid-TMS ester	194, 179, 135, 105, 77, 51	-	V	V	V	V
pentanedioic acid-TMS ester	276, 261, 158, 147, 73, 55	-	V	-	V	-
butanedioic acid-TMS ester	247, 218, 172, 147, 129, 73, 55, 45	-	V	-	-	V
Hexanedioic acid-TMS ester	(290), 275, 147, 11, 83, 73, 55, 45	-	V	-	V	-
PEG-TMS	45, 73, 101-103, 116-117, 145, 161 (…)	V	V	V	V	V
Phosphate-TMS	314, 299, 73, 45	-	-	-	V	-

Table 6.3.4: main compounds detected by means of Py-Silylation-GC-MS in the Flashe® extractions.

Extraction Conrayt®	
Compounds identified	***m/z* ion fragments**
ethanoic acid, TMS ester	117, 75, 59, 45
ethanol, 2-[(TMS)-oxy]-TMS	119, 103, 85, 58, 43
2,4-hexadienal	96, 81, 53
unidentified compound	75, 73, 70
benzaldehyde	106, 105, 77, 51
propanoic acid-2-methyl-TMS	145, 117, 75, 73, 58, 45
2-methyl-4-pentenoic acid-TMS	186, 171, 73, 41
1-ethenyl-2-pyrrolidone	111, 83, 69, 56, 41, 28
2-hexenoic acid-TMS	186, 171, 143, 129, 99, 75, 55, 45
benzoic acid-TMS	194, 179, 135, 105, 77, 51
nonanoic acid-TMS	229, 215, 145, 117, 75, 73, 55, 43, 28
decyloxy-TMS	230, 229, 215, 75
1-naphthalene carboxaldehyde	339, 156, 101, 75, 43, 28
dibutylphthalate	278, 223, 149, 57
PEO-TMS	(...)161, 145, 116-117, 101-103, 73, 45

Table 6.3.5: main compounds detected by means of Py-Silylation-GC-MS in Conrayt® 12 hours water extraction.

The analysis of Vinavil® 59 extractions revealed similar results, which is in good agreement with FTIR-ATR data. The main compounds identified are summarized in Table 6.3.6, where the results by both conventional Py-GC-MS are contrasted to those of Py-Silylation-GC-MS, since the presence of HMDS eclipsed some of the peaks of interest. The analysis confirm the presence of PVOH characterized by FTIR-ATR, as well as several peaks acribed to the presence of PEO-type compounds. The presence of residual monomers are also evident in the extracts.

Extraction Vinavil® 59 with Py-Silylation-GC-MS		**Extraction Vinavil® 59 with conventional PY-GC-MS**	
compounds identified	*m/z* ion fragments	compounds identified	*m/z* ion fragments
acetaldehyde	44, 28	acetaldehyde	44, 28
-	-	acetone	58, 43
Acetic acid-TMS	132, 117, 75	Acetic acid	60, 45, 43, 29
-	-	2-butenal	70, 41
-	-	benzene	78
-	-	3-pentene-2-one	84, 69, 41
methyl benzene	91	methyl benzene	91
styrene	104, 78, 51	styrene	104, 78, 51
2, 4-Hexadienal	96, 81, 67, 53	2, 4-Hexadienal	96, 81, 67, 53
benzaldehyde	106, 77, 51	benzaldehyde	106, 77, 51
2-hexenoic acid-TMS	186, 157, 143,127, 97, 75, 73, 55, 45, 27	D-limonene	136, 121, 107, 93, 79, 68, 53, 39, 27
Benzoic acid-TMS	194, 179, 135, 105, 77, 51	1,2,3-trimethyl benzene	94, 66, 39
Ethanol, 2-(2-butoxyethoxy)-, acetate	204, 101, 87, 57, 43	ethanol, 2-(2-butoxyetoxy) (Dowanol DB)	100, 87, 75, 57, 45, 29
PEO-TMS	(...)161, 145, 116-117, 101-103, 73, 45	-	-

Table 6.3.6: summary of the main compounds detected by means of Py-Silylation-GC-MS for a Vinavil® 59 12 hours water extraction.

6.3.2.5- The effects of water immersions in the mechanical properties of PVAc products

The effects of water immersions in the mechanical properties of PVAc based products revealed similar trends comparing to acrylics. Figure 6.3.30 illustrates this for a Flashe® oriental red paint sample. During the water immersion additives such as PEO type compounds, cellulose thickeners and residual monomers were leached, causing a stiffening effect, which is clearly observed in the increase in the Young's Modulus. It is fair to say that all Flashe® specimens showed this behaviour after the immersion tests. The films also lost a significant amount of flexibility and tended to a brittle behaviour. In the case of oriental red, the strain to brake of the samples decreases from 18% to 6% after immersion. After the 12 hours immersion tests, the Flashe® colours tested presented similar mechanical properties. However, the earth colours tended to loose integrity, as mentioned priorly. The susceptibility of the earth colours is likely to be related to the expansion of the clay minerals present in these pigments. The migration of earth pigments to the surface with water immersions has been detected by SEM in Talens® raw sienna paint samples, which are described later in this chapter.

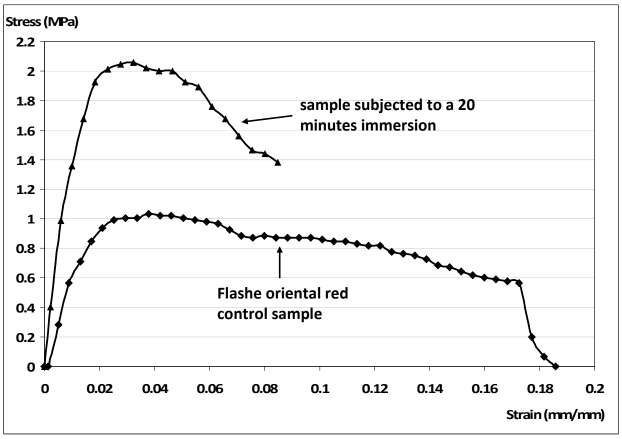

Figure 6.3.30: The mechanical properties of Flashe® oriental red after 20 minutes immersion in water. All Flashe® colours presented a similar behaviour: increase in stiffness and lost in flexibility.

Conrayt® medium experienced measurable changes in the mechanical properties (increase in stiffness) only after the 12 hours immersion test, in which the PVOH thickener was fully extracted. Vinavil® 59 samples showed similar changes in the mechanical properties to those observed for Conrayt®, which may be explained by the similarity of the compounds found in the extractions.

Mowilith® DMC2, on the other hand, showed little alterations after both immersion tests revealing good stability to water based treatments.

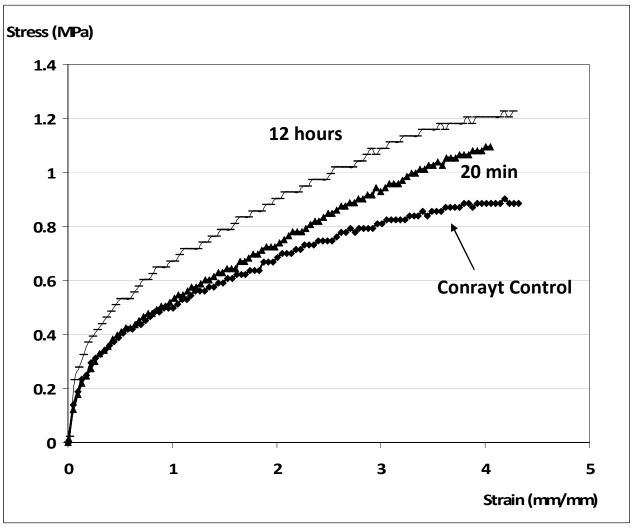

Figure 6.3.31: The mechanical properties of Conrayt® oriental red after 20 minutes and 12 hours immersion in water.

6.3.2.6- Morphological study of PVAc paint films subjected to water and solvent cleaning treatments by Scanning Electron Microscopy (SEM)

The changes in the morphology of Flashe® Senegal yellow paint films after 20 minutes immersions in water, ligroin and acetone are shown in Figure 6.3.32. Both ligroin and water immersions solubilized material from the paint films, which can be detected by the rougher aspect of the surface, and the sharper shape of the pigments particles. This effect is much more pronounced in the water immersion, which is expected [2].

An immersion test in acetone was included to illustrate the effects of a polar solvent in these films. Clearly, the paint structure is fully destroyed and large amounts of binding medium migrate to the surface, covering completely the pigment particles. With mechanical action, such as swab rolling, the paint film is readily disrupted [3].

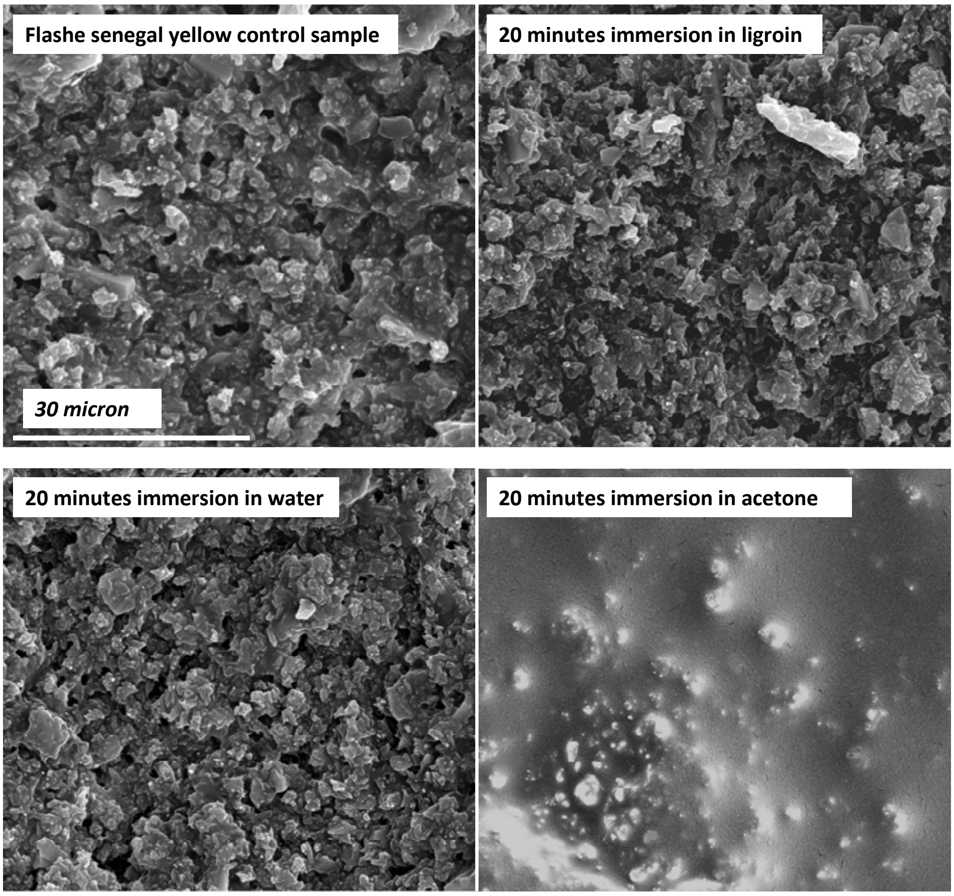

Figure 6.3.32: Secondary electron image (magnification of x2000) of Flashe® Senegal yellow paint samples immersed in water, ligroin and in acetone.

6.3.3- The use of alternative methods for the surface cleaning of acrylic paintings

6.3.3- The use of alternative methods for the surface cleaning of acrylic paintings

The use of water (or solvents) gelled systems is considered, at the present day, as an *alternative approach* to the cleaning of paintings, even though their introduction in the conservation field dates back to the 1980's, by Richard Wolbers work. From then to the present, there has been an increasing number of studies on these systems that reflect interest in some of the advantages both to the paintings as well as the conservator [9-13,19,55].

Generally, a water-based gel system is a formulation thickened with a high molecular weight material that can include other ingredients such buffers, sequestring agents or surfactants. In this way, these systems can be designed for a specific action during the cleaning treatment.

A gel system is useful to maintain the solvent or mixture of ingredients in contact with the surface for a long time, since the thickening agent slows down the evaporation of the solvent. Furthermore, the gel also limits the penetration and diffusion of the liquid into the paint layers, which can avoid unnecessary leaching from the bulk of the paint as it could occur with the free solvent.

In the next section of this work, the advantages of using water-based gel systems in the cleaning of acrylic surfaces are discussed. The gels tested included Klucel® G (hydroxypropylcellulose), Vanzan® NF-C (xantan gum), Carbopol® ultrez 21 (polyacrylic acid) and agar-agar® (agarose)[36].

A Water-in-Oil (W/O) emulsion system has also been tested. These systems combine the action of solvents with opposite polarities emulsifyed by a surfactant. The W/O emulsion system chosen for testing comprises a non-polar solvent as the main solvent (ligroin) and a small amount of water emulsifyed by means of a surfactant (Brij® 30) [37].

A similar methodology to that of water immersions has been adopted. This comprised measuring the water absorption and drying of the acrylic paint samples when exposed to the water based gels[38]. This allows assessing the swelling effect and leaching of additives from the surface of the paint film. The resulting paint films were tested for mechanical properties, and the morphological changes characterized by SEM imaging.

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[36] The reader is referred to the experimental section of this work for details on the formulation of the water based gels.

[37] The reader is referred to the experimental section of this work for more details of the W/O formulation.

[38] Exposure to the gel means that a thick layer (excess) of gel is applied with a brush on the surface of the acrylic sample and a silicone coated Mylar® sheet is put on top to avoid water evaporation. The gel is then removed by dry swabbing and, when necessary, limited water swabbing was performerd for elimination of gel residues when needed. This represents a standard gel application in surface cleaning of paintings.

6.3.3.1- The effects of water based gels in the water absorption and leaching of additives of acrylic products

The test specimens subjected to cleaning with gel systems were raw sienna, zinc white, phthalocyanine blue, naphthol red and black oxide from Talens®, and titanium white and naphthol red from Pébéo®. The water based gel systems have been mentioned previously and include Klucel® G (hydroxypropylcellulose), Vanzan® NF-C (xantan gum), Carbopol® ultrez 21 (polyacrylic acid) and agar-agar® (agarose). It has been chosen to separate the results into the type of gel tested and, similarly to water immersions, into results obtained from weight measurements and stress-strain tests. Due to the amount of information gathered with these tests, only some representative results are described.

6.3.3.1.1- Vanzan® NF-C

Similar Talens® raw sienna samples have been exposed to a Vanzan® gel for intervals of 5, 10, 20 and 30 minutes. The absorption[39] and drying profiles are shown in Figure 6.3.33. The use of water gellyfied with Vanzan® limits water absorption into the acrylic films considerably when compared to a standard immersion or swabbing test. This is true even for long exposure times such as 30 minutes. The amount of material extracted from the samples after the gel is removed is also present in Figure 6.3.33 The reduction of leaching indicates that the the gel system is acting mainly on the surface. This has been observed for all Talens® samples tested.

The Pébéo® commercial brand paint samples also showed a decrease in the general water absorption and additive leaching when the gel was applied on the surface and compared to water immersions. This is of particular interest for this brand since the mechanical properties were strongly affected by water immersions. The absorption and drying profiles of Pébéo naphthol crimsom subjected to a 20 minute water immersion and Vanzan® gel are presented in Figure 6.3.33.

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[39] It is important to mention that the initial part of the absorption are represented as a straight line, since the weight measurements were not obtained periodically during contact with the gel but only at the moment the gel was removed from the surface of the acrylic samples. In any case this initial part of the curve is included only to better understand the trend of the data. The weight loss during drying was measured periodically as in immersion tests.

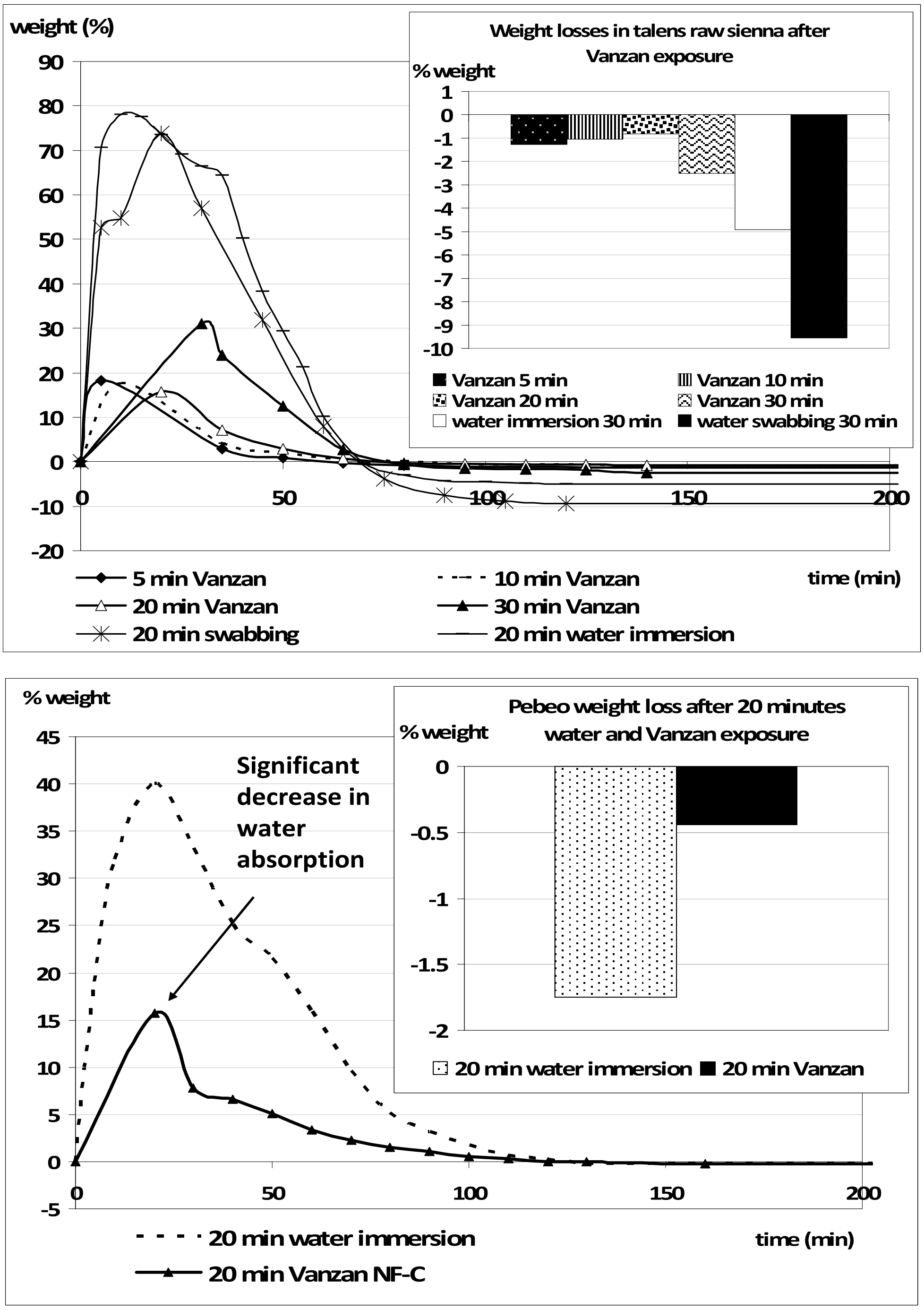

Figure 6.3.33-6.3.34: The absorption and drying curves tests obtained after immersion tests in water and exposure to Vanzan® NF-C water based gels and respective leaching of: (Top) Talens® raw sienna; (Bottom) Pébéo® naphthol red.

6.3.3.1.2- Klucel® G

The Talens® raw sienna samples exposed to a Klucel® G gel for 5, 10 and 20 minutes showed a similar trend in the asborption and drying profile trend as well as leaching of additives, which are shown in Figure 6.3.35 (left). When exposed to Klucel® G, the effects of water are concentrated on surface and, thus, less absorption into the bulk film and less additive leaching is registered.

6.3.3.1.3- Carbopol® Ultrez 21

A dense carbopol® gel has been tested in Talens® raw sienna and Pébéo® naphthol crimsom test specimens. In general, these gels proved to be a very effective form for retaining water, and can be easily applied in the surface of the films. The Figure 6.3.35 (right), shows the leaching effects of water gelled with Carbopol® in comparison to water. Similarly to the other gelled systems there is less leaching.

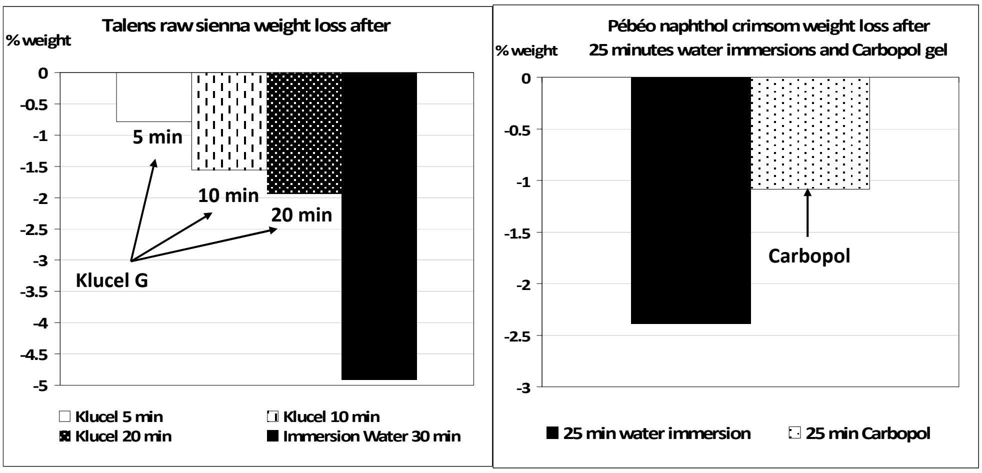

Figure 6.3.35-6.3.36: (Left) Talens® raw sienna additive leaching measured after exposures to Klucel® G water based gel. (Right) Pébéo® additive leaching after the exposure to the carbopol® ultrez 21 gel. These are both compared to the leaching after the water immersion. The use of gellyfied systems appear to be useful in reducing additive leaching from acrylic dispersion paints.

6.3.3.1.4- Agar-agar® rigid gels

Agarose is used for preparing rigid gels known for being good water supportants for surface cleaning of water sensitive materials [45,46]. In this study, two rigid gel formulations were tested. One comprised a *less* rigid gel (prepared by 1g agar-agar®/100ml water) and a second *more* rigid gel that retained more water (prepared by 2g agar-agar®/100ml water).

The results obtained for Talens® phthalocyanine blue exposed to agarose gels for 30 minutes are shown in Figure 6.3.37, an immersion test is also included. The data shows that increasing the concentration of the gel significantly reduces the amount of water absorbed into the film and consequent leaching, especially if compared to immersions. Also, the more rigid agar-agar® gel gave improved results when compared to the previous discussed aqueous gels Klucel® G and Vanzan® NF-C. The study of the mechanical properties is in good agreement with this.

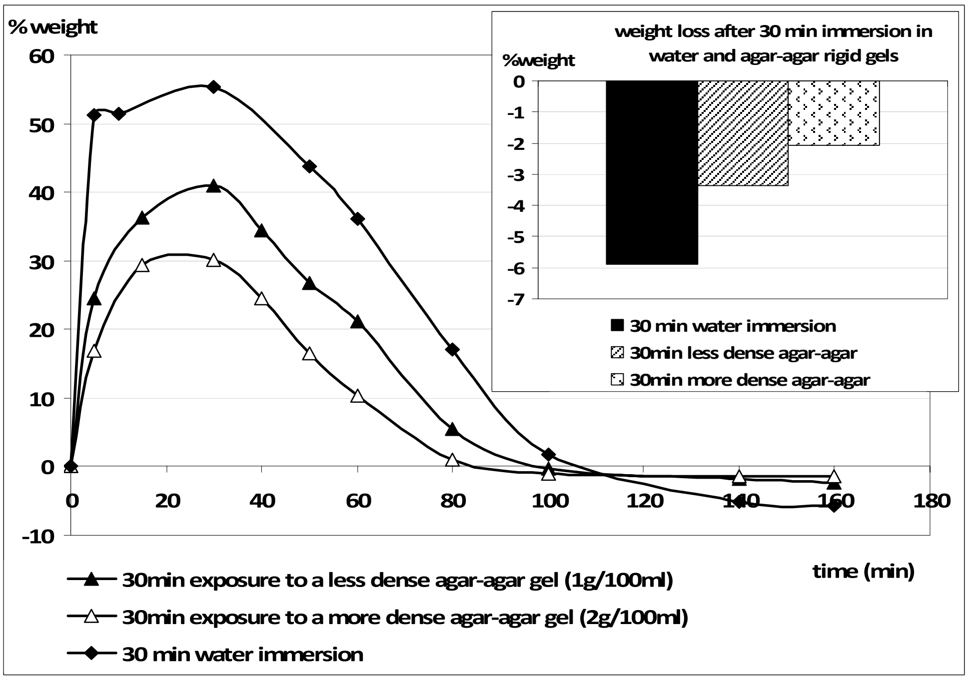

Figure 6.3.37: water absorption and drying of a Talens® phthalocyanine blue sample from an immersion test and exposure to agar-agar® gels of different characteristics (density of the gel is translated in more rigidity). The use of different gels can be tailored to reduce the swelling and leaching effect in the paint films.

6.3.3.2- The effects of water based gels in the mechanical properties of acrylic products

6.3.3.2.1- Vanzan® NF-C

The mechanical properties of Talens® raw sienna tests specimens are shown in Figure 6.3.38. The results indicate that the exposures to the gels from 5 minutes until 20 minutes do not induce significant changes in the mechanical properties of the specimens. Only after 30 minutes of contact with the gel there were suficient changes in the paint film to be measured with the stress-strain tests. This data correlates precisely with that of the absorption, drying and leaching of additives. It is worth underlining that the changes in the mechanical properties that occur in the paint films subjected to these gels is fairly lower when compared to the 20 minutes immersion test.

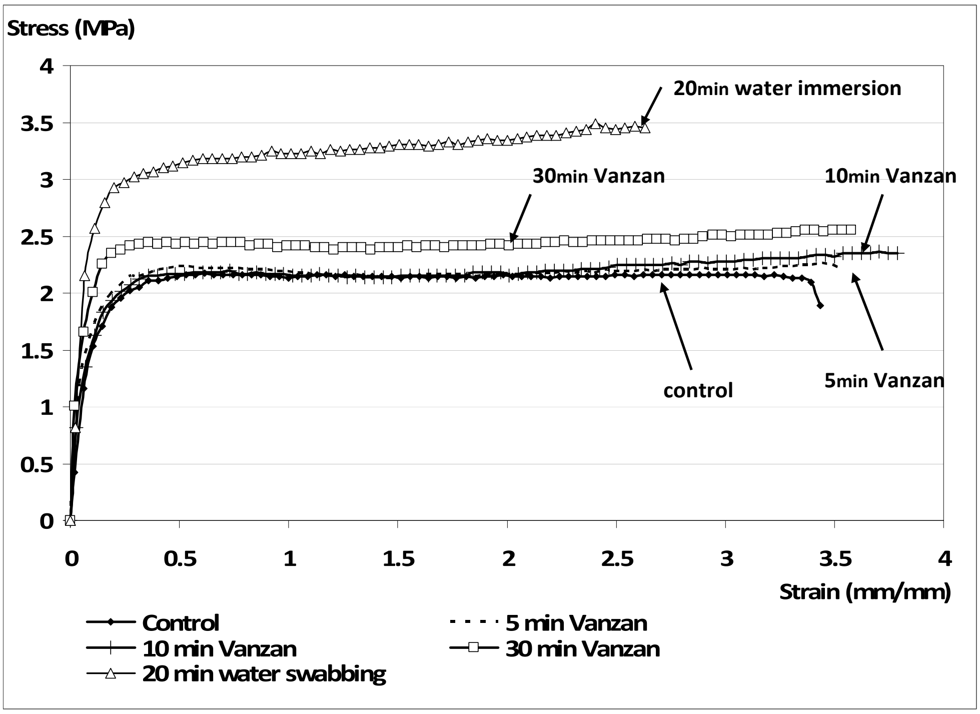

Figure 6.3.38: the effects of the exposure of Talens® raw sienna to a Vanzan® NF-C water based gel. The paint film specimens were tested for 5, 10, 20 (not shown here) and 30 minutes of exposure. A specimen immersed for 20 minutes was also included for comparidson purposes.

6.3.3.2.2- Klucel® G

A similar trend to that observed previously for Vanzan® gels has also been observed for the case of Klucel®. In Figure 6.3.39 are the effects of 20 minutes water immersions and Klucel® on Talens® raw sienna. A third stress-strain curve concerning the application Klucel® in surface as a consolidant has been included for comparison puroposes[40]. When compared to the immersion tests, the sample exposed to the Klucel® gel exhibited less increase in stiffness, which correlates with the moderate additive leaching discussed before in this chapter. The impregnation of the surface, on the other hand appears to have no measurable effects in the mechanical properties of the film, despite the generous amount of material applied.

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[40] In this case the Klucel® G gel was applied in the surface with an easel and was left to fully dry. The mechanical properties were then measured with the film impregnated with Klucel® G. This can as well simulate the effect of a significant amount of residue in the mechanical properties of this film.

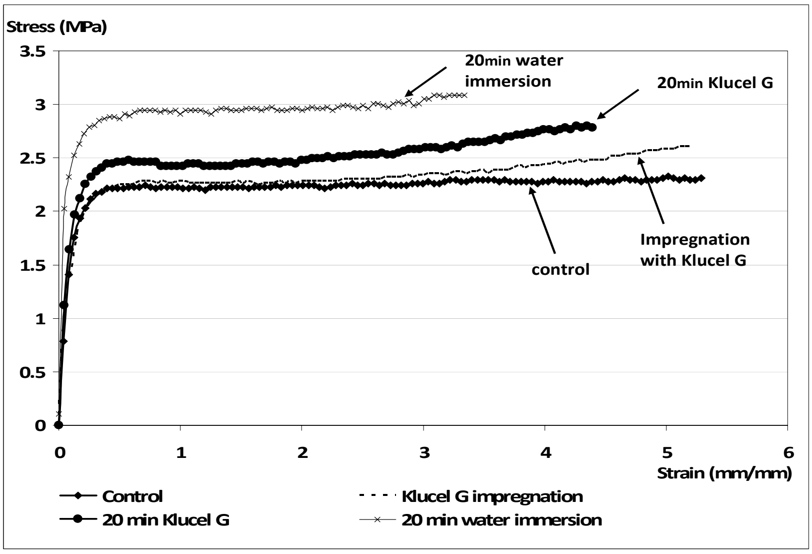

Figure 6.3.39: the effects of the exposure of Talens® raw sienna to Klucel® G water based gel. The specimens presented here were tested for 20 minutes of exposure to both gel and immersion in water. A Similar trend to that observed for Vanzan® gels is seen. An additional sample was impregnated with the gel in order to verify the effects of a large amount of residue in the overall mechanical properties of the resulting films (about 2% weight increase was measured in the test samples).

6.3.3.2.3- Carbopol® Ultrez 21

A Talens®raw sienna and Pébéo® naphthol crimsom were tested for 25 minutes exposures to a Carbopol® gel. The results obtained from these trials were fairly promising, since the gel seems to be a good water supportant and interact moderately with the acrylic surface. This was especially true in the case of Talens® raw sienna, as shown in Figure 6.3.40. For the case of Pébéo® specimens, which are very water sensitive, the use of such gel allowed to reduce dramatically the general embrittlement caused by water. Nevertheless, a considerable stiffening effect is detected in these paint films, even though samples maintained flexibility, in contrast to those immersed in water.

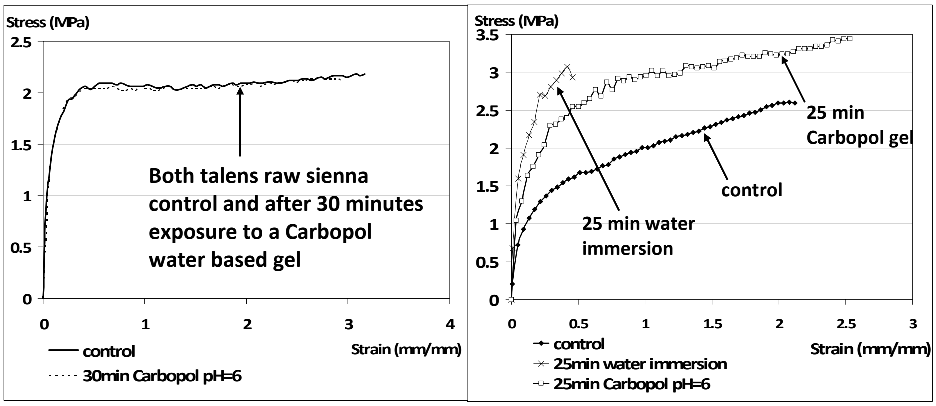

Figure 6.3.40: the effects of 30 minutes exposure of Talens® raw sienna (left) and Pébéo® napthol crimsom (right) to a Carbopol gel.

6.3.3.2.4- Agar-agar® rigid gels

Pébéo® naphthol crimsom specimens were tested for 25 minutes exposure to both formulation of agar-agar® rigid gels. The stress-strain data shown in Figure 6.3.41 is in full agreement with the results obtained from the absorption-drying profiles and leaching described previously. The use of a rigid gel, especially the highly concentrated agarose gel, allows bringing water in contact with the surface of the acrylic samples for long a time, showing considerably less changes in the mechanical properties when compared to free water.

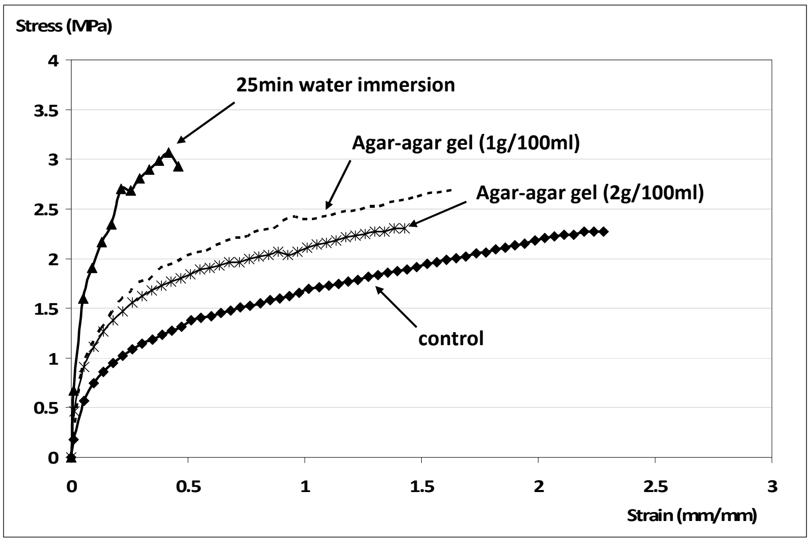

Figure 6.3.41: the effects of 25 minutes exposure to two agar-agar® gels on a Pébéo® naphthol crimsom paint sample. The results show that the gel that retains more water (2g/100ml) is causing less changes in the mechanical properties of the films.

6.3.3.3- Water-in-oil emulsion systems (W/O)

A similar approach used for the study of the effects of gels in the swelling, leaching and mechanical properties has been adopted to study the viability of using W/O emulsion systems in the surface cleaning of acrylic paints. The emulsion was applied in excess to the surface of the test specimen and cleared first with a dry swab and, finally, with 10 seconds swabbing with ligroin. Some PVAc products were included such as Flashe®, Conrayt®, Mowilith® DMC2 and Vinavil® 59.

6.3.3.3.1- The effects of Water-in-oil emulsion systems (W/O) in the leaching of additives of acrylic products

The W/O emulsion tested was composed of ligroin (Oil) and a small amount of water (Water) emulsified with Brij®30. In order to better understand the results obtained from the absorption and drying curves, both solvents (i.e. ligroin and water) were tested separately and confronted with those from the emulsion. The results obtained for Talens® raw sienna are illustrated in Figure 6.3.42. The 30 minutes immersion in ligroin shows that the solvent is barely absorbed into the test film specimen. Water, on the other hand, was fastly absorbed into the film. The used of the W/O emulsion reduced significantly the general absorption of solvents, to about half of that supplied by a Vanzan® or Klucel® gel for the same amount of time (30 minutes). Furthermore, there is a significant decrease in additive leaching as reflected by the low weight loss plotted in Figure 6.3.41. This correlates perfectly with the results obtained with stress-strain tests, presented in the following section.

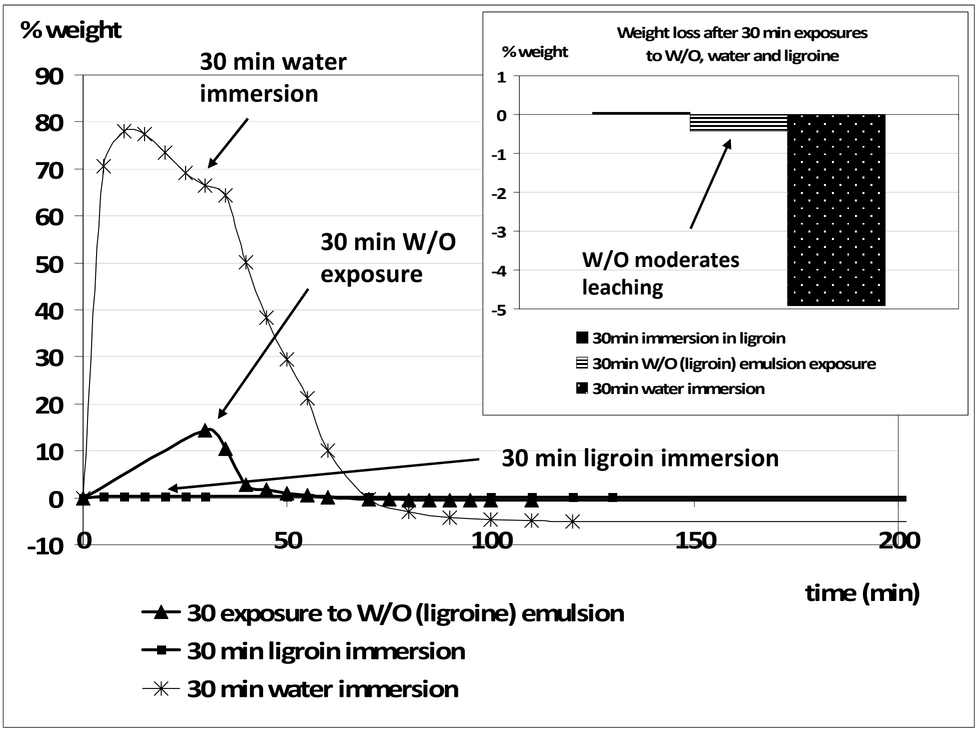

Figure 6.3.42: absorption and drying profiles of Talens® raw sienna subjected to 30 minutes water immersions, ligroin immersions and a W/O (ligroin) emulsion system. The leaching effects obtained from these tests are presented in the upper right corner.

Despite the promising results obtained for these Talens® raw sienna samples, it is also very important to mention that different brands exhibited a variable behaviour when in contact with these cleaning system. Often, within the same brand the results varied also according to pigment, which could go from compatibility to destruction of the film. Overall, this appeared to be related to the type of pigment and PVC. Films with inorganic pigments were less sensitive to treatments with W/O emulsions.

It is important to highlight that the high sensitivity to W/O emulsions was due to the presence of the surfactant in the emulsion (a poly(ethoxylated) fatty alcohol, Brij® 30). A solubility test showed that ligroin with a surfactant was able to dissolve the paint film, and that these two components gave the solvent the power observed with the W/O emulsion system. Testing the different components of an emulsion separately is an important point to bear in mind while performing preliminary solubility tests before the cleaning treatment itself. W/O cleaning methods have, clearly, to be further tested in order to be able to predict this behaviour. A summary of observations obtained for other test specimens are presented in Table 6.3.7.

		properties measured			
brand tested	**colour**	**length variation (ΔL)** [41]	**weight loss**	**retention of solvents**	**observations**
Talens®	raw sienna	15%	0.4%	that of water	sample did not show any particular changes
	zinc white	15%	-	that of water and ligroin	sample tacky
	black oxide	12%	-	that of water and ligroin	sample tacky
	phthalocyanine blue	15%	-	that of water and ligroin	sample very tacky and difficult to handle
	naphthol red	14%	-	that of water and ligroin	sample very tacky and difficult to handle
	medium	5%	-	that of water and ligroin	sample very tacky and difficult to handle
Liquitex®	naphthol red	24.6%	-	that of water and ligroin	sample very tacky and difficult to handle
	medium	15.8%	-	that of water and ligroin	sample very tacky and difficult to handle
Pébéo®	naphthol crimsom	film destroyed	film destroyed	film destroyed	film destroyed
	titanium white	film destroyed	film destroyed	film destroyed	film destroyed
Conrayt®	*medium*	4.4%	-	that of water and ligroin	sample did not show any particular changes
Mowilith® DMC2	*medium*	3.4%	-	that of water and ligroin	film showed mild tackyness
Vinavil® 59	*medium*	2.7%	-	that of water and ligroin	sample did not show any particular changes

Table 6.3.7: general summary of the results obtained from the exposures of several acrylic and PVAc products to a W/O (ligroin) emulsion. It is important to notice that these cleaning systems may present good results with some brands, or specific colours within a brand or, on the contrary. they can severely affect other films.

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[41] A simple approach to the swelling of the paint films was obtained by measuring the free length variation of the paint film after the exposure to the treatments: ΔL= (Lf-Lo/ Lo)*100. Lf =final length; Lo=initial length; ΔL= variation of length due to sweling.

6.3.3.3.2- The effects of Water-in-Oil emulsion systems (W/O) in the mechanical properties of acrylic products

After the exposure to the W/O system, the Talens® raw sienna paint film did not show in any significant change in its mechanical properties. Nevertheless, there was a considerable increase in elongation and a small decrease in stiffness that is attributed to the presence of ligroin in the the paint films as well as possible further coalescence, as observed in previous cases when acrylic samples are in contact with water for short periods of time.

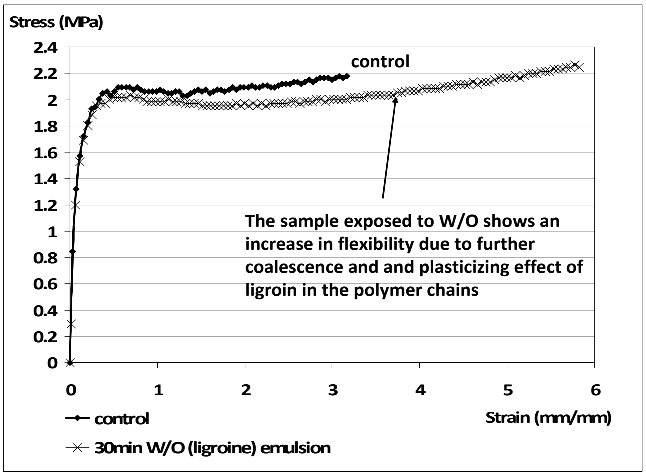

Figure 6.3.43: stress-strain data obtained for Talens® raw sienna exposed for 30 minutes to a W/O (ligroin) emulsion system.

6.3.4- Morphological study of acrylic paint films subjected to water based cleaning treatments by Scanning Electron Microscopy (SEM)

The effects of water based cleaning treatments in the surface of acrylic samples were studied by SEM. The results shown here are asummary of the large matrix of results obtained for many acrylic samples. The results discussed here are considered representative for all samples tested.

In Figure 6.3.44 are shown SEM images (500 magnifications) obtained for Talens® raw sienna subjected to different water based cleaning treatments for 20 minutes. The figure includes water immersion, Klucel® G and Vanzan® NF-C water based gels.

The images show that the degradation caused by water during the immersion tests is similar to that seen for the gel systems, such as the increase of porosity and leaching of additives. In the image concerning the water immersion, it is also visible the swelling and migration to the surface of the clay mineral present in the earth pigments. This effect has not been detected in the samples treated with the gels, since their effect is limited to the surface.

These images suggest that using water in the gellyfied form is a clear advantage for the painting conservator, if a water-based cleaning treatment is required.

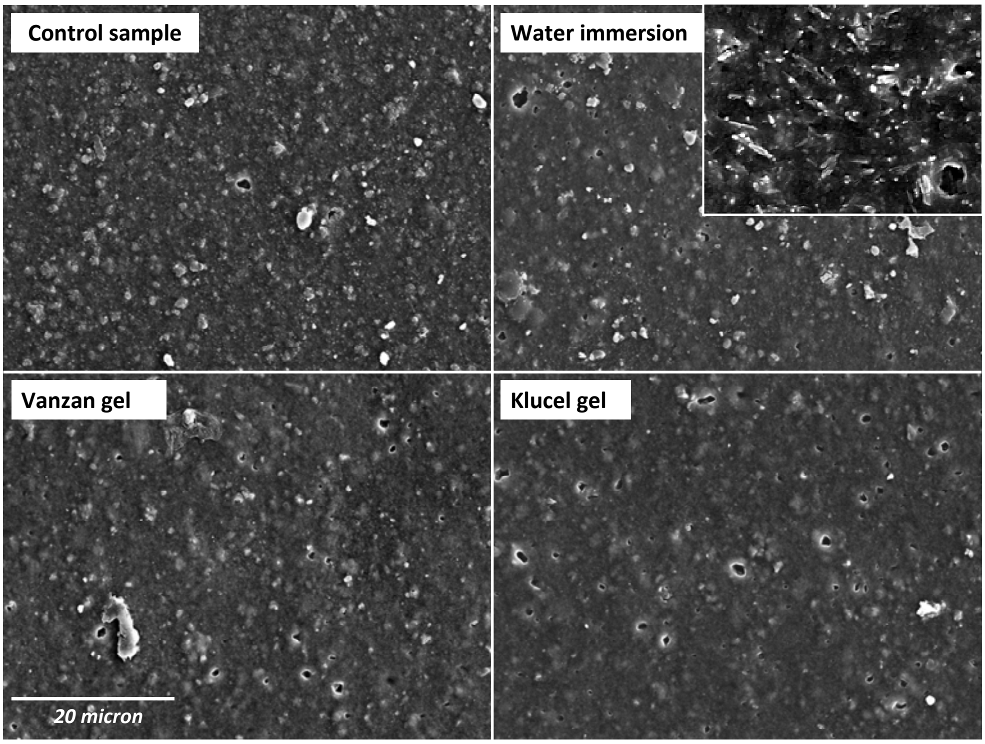

Figure 6.3.44: Secundary electron images of Talens raw sienna surface with different water based cleaning treatments. The images were obtained at 500 magnification. In the up right corner is a detail of the sample immersed in water surface at a magnification of 10000. The immersion promotes the migration of clay minerals to the surface. This has not been observed with the water based gels, which act mainly on the surface rather in the bulk film.

A set of SEM images obtained for Pébéo® naphthol crimson are shown in Figure 6.3.45 and show consistent results to those discussed previously. The images include the samples immersed for 20 minutes, and exposured to 20 minutes of Carbopol®, Vanzan® NF-C and Agar-Agar® water based gels.

The image corresponding to the water immersion reveals a profusion of micropores of variable dimensions spread throughout the surface. These defects are responsible for the early failure of these films when tested for mechanical properties. The exposure to water-based gels also originates defects in the paint surfaces. However, these were significantly less pronounced when compared to the water immersion. These observations by SEM are in fairly good agreement with the absorption-drying curves, as well as mechanical properties of the films.

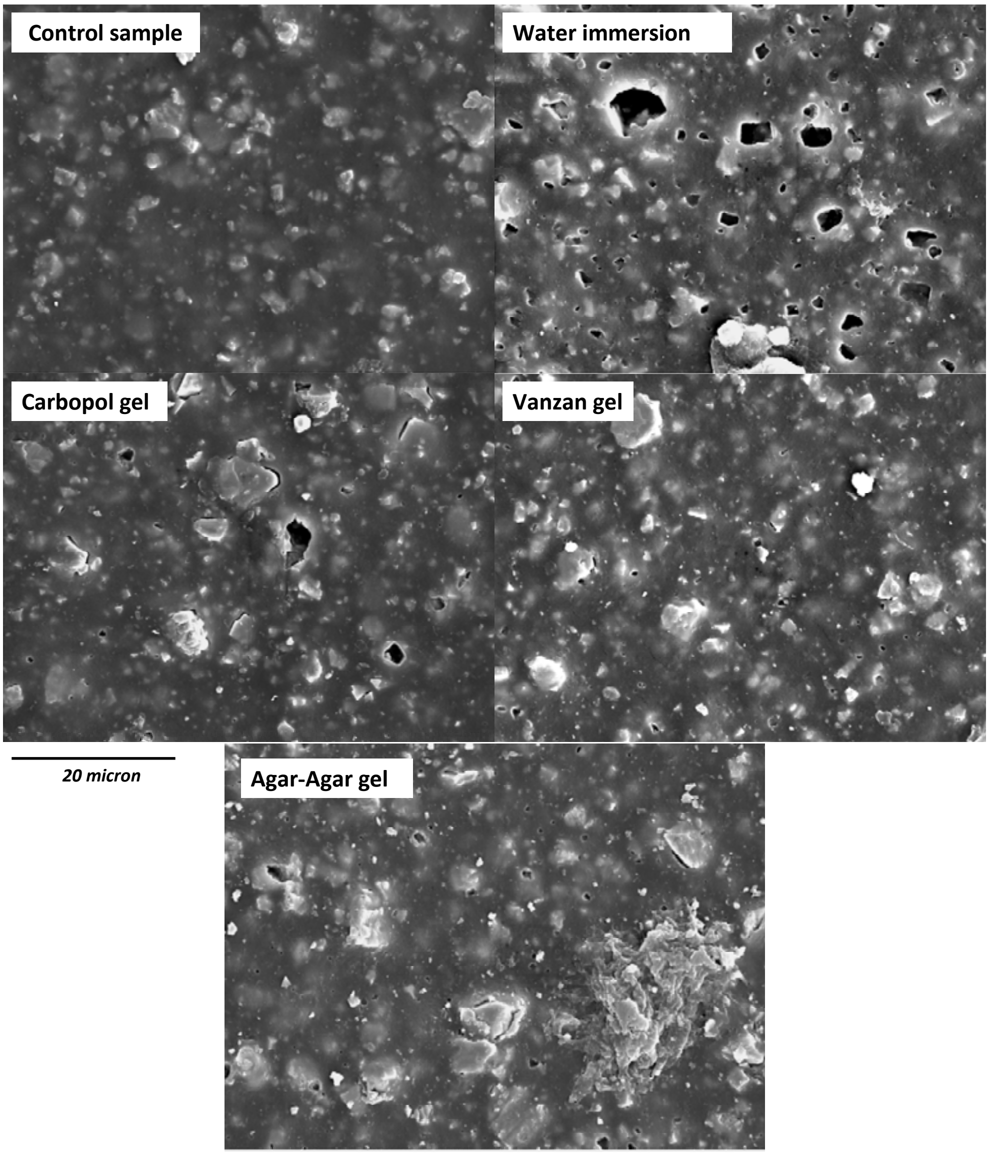

Figure 6.3.45: Secundary electron images of Pébéo® naphthol crimsom water based cleaning trials (2000x magnification). The samples shown were tested for 20 minutes of: water immersion, Carbopol® Ultrez 21, Vanzan® NF-C, and Agar-Agar® water based gels. The defects caused by free water in the immersion tests are reduced by the gels.

Figure 6.3.46 is shown a Talens® raw sienna film exposed to a ligroin W/O emulsion system for 20 minutes. An immersion in ligroin is included in the figure, since it is the main solvent present in the emulsion system (90 parts ligroin/10 parts water). Consequently, it is generally expected that W/O systems behave mostly as non-polar cleaning systems. However, the SEM images suggest that the immersion in ligroin does not promote visible damage in the surface of the sample, whereas the emulsion system causes alteration similar to that observed in water treatments (see figure 6.3.47). This suggests that water affects the most the surface of the sample, even though it is present in minor amounts.

In Figure 6.3.47 is shown a Pébéo® naphtol crimsom sample after a 20 minute cleaning treatment with a W/O (ligroin) emulsion system. Pébéo® films were extensively affected by the emulsion, becoming very rubbery, fragile and impossible to manipulate. In the figure it is visible that the polymer chains were dissolved and this caused the loss of cohesion observed macroscopically.

To test the solubility of these films in the different ingredients of the W/O formulation, a solubility test using ligroin, ligroin+surfactant, water, water+surfactant and the W/O emulsion (ligroin+water+surfactant) was applied by swab-rolling the acrytlic surface for30 seconds. The results are shown in Figure 6.3.48 and illustrate that adding a surfactant to the solvent that affects the most the acrylic paint film (in this case ligroin), enhances considerably its solubility power. In fact, the effects of ligroin and surfactant are very similar to those of W/O emulsion itself.

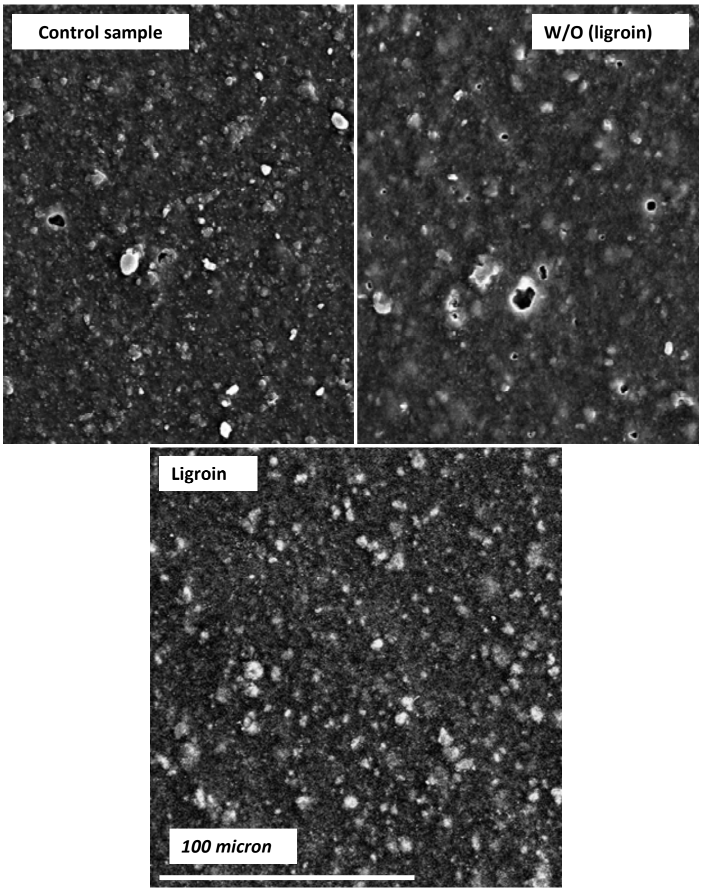

Figure 6.3.46: Secundary electron images of Talens® raw sienna: control sample (above left image), sample exposed to a W/O (ligroin) emulsion for 30 minutes (above right), and a 30 minutes immersion in ligroin (below). The exposure to athe emulsion caused alterations at the surface comparable to water based treatments whereas the immersion in ligroine caused no visible changes in the surface of the test specimen.

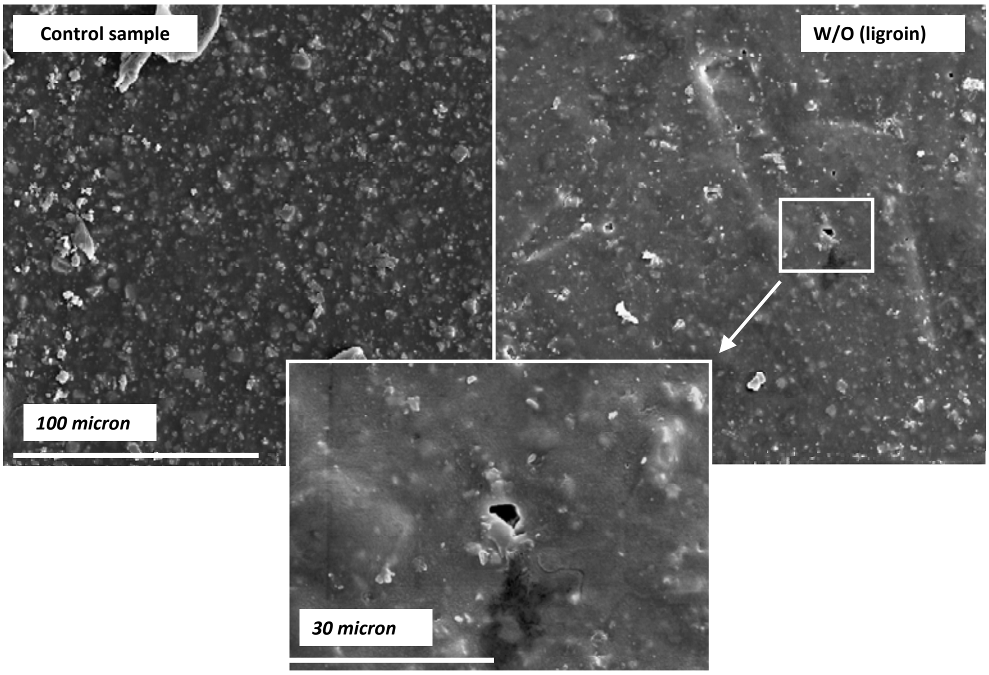

Figure 6.3.47: Secundary electron images of Pébéo® naphthol crimson (magnification of 500): control sample (left) and sample exposed to ligroin W/O system for 20 minutes. Below is shown a detail of the surface morphology of the cleaned sample at magnification of 2000. The images show that the latex is affected by the emulsion. Deformation and dissolution/destruction of the polymeric matrix is clearly visible.

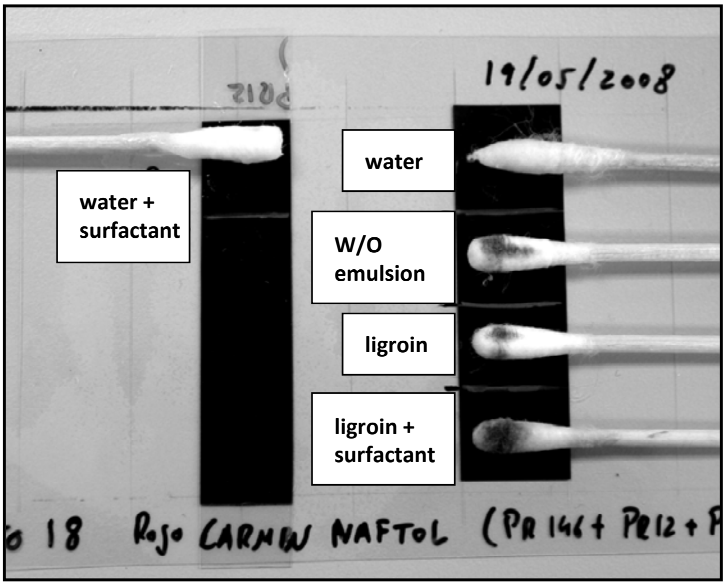

Figure 6.3.48: solubility tests of Pébéo® naphthol crimson comprising water, water+surfactant (Brij®30), ligroin, ligroin+surfactant(Brij®30) and a W/O(water in ligroin) emulsion system. The images show that ligroin+surfactant and the W/O emulsion both dissolve the paint film. Ligroin by itself also affected the paint films, which is generally not expected for acrylics, as discussed in this chapter.

6.5- Immersions, swabs and gels. Putting it into a practical context

The cleaning trials performed in this study were based on immersion tests and long exposures to gel cleaning treatments. Even though this a repeatable way to characterize the effects of solvents and water in a paint film, it may appear be too agressive as a cleaning treatment for an acrylic or PVAc paint surface. In this way, it may be considered as a non representative strategy for studying the effects of solvents in these materials. However, this subject is open to discussion. It is important to take into account that, when a wet cleaning method is required, it is normally because the acrylic/PVAc surface presents strongly bonded matter, such as heavy soiling, fingerprints or surfactant stains [1-6]. If the cleaning treatment concerns the elimination of non bonded soiling it is probably more adequate to consider other less invasive cleaning methods, such as dry/mechanical methods. In the case of removing surfactant stains, it has been proved that with time that the cleaned surfaces tend to be easily cleaned with cotton swabs with water, but the surfactants tend to migrate back at the surface [1]. In order to fully eliminate surfactant migration this treatment may have to be repeated many times with time, until surfactant is fully eliminated.

In the case of removing matter that is strongly adhered to the surface, it is necessary to swell the surface to a point where the adhered matter can be removed. This is when our action may affect more our materials. According to Whitmore et al [21], the penetration of water into a thick film, such as the samples studied in this work (0.2 mm), can be around 5 minutes. On the other hand, Ploeger et al [17] state that the leaching of additives from the bulk film can start occuring around this time. Whitmore et al, nevertheless, predicts that water penetration into very thin films (more likely to be found in reality) can occur within much less than one minute. The trials carried out in this thesis considers these cases, when water is in contact with the surface enough time to cause swelling and leaching.

A very effective way of comparing the effects of cleaning with water via swab rolling and immersion treatments is to measure the mechanical properties of the resulting films after such treatments. In Figure 6.3.49 is shown a Talens® raw sienna paint sample swab rolled for 5 minutes (when leaching occurs from the bulk) and 20 minutes (a very extreme case). This is contrasted to the effects of 5 minute and 20 minute immersion tests. It is clear that, in the first 5 minutes of swab rolling there is less stiffening of the film when compared to the immersion. The changes in the film are, nevertheless, occuring. The immersion and swabbing of 20 minutes show similar changes in the mechanical properties. This is because leaching and stiffening can occur irrespectively of the way water is applied. It is a matter of how long or how many times the treatment is done, and how much matter is leached.

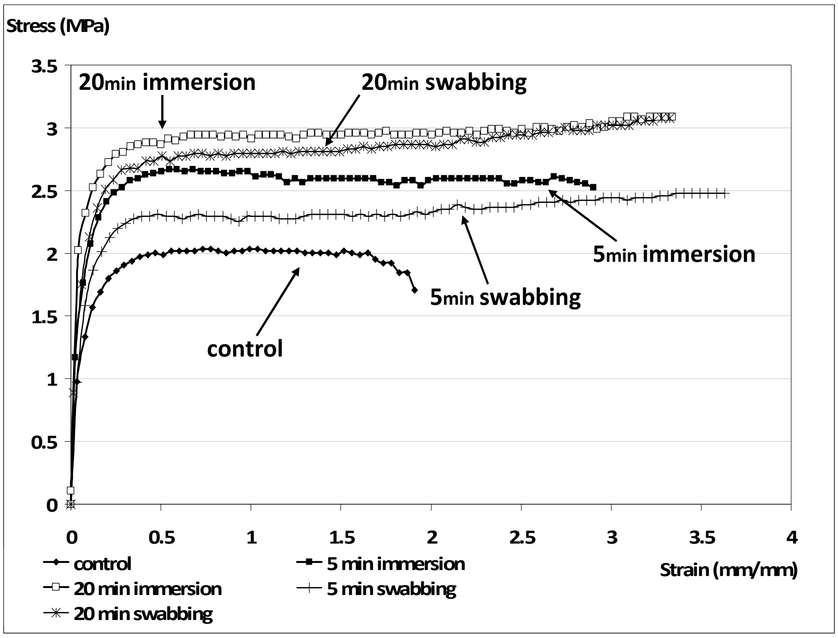

Figure 6.3.49: stress-strain curves obtained for Talens® raw sienna samples after 5 and 20 minutes immersion tests and 5 and 20 minutes swabbing tests. It is shown that the effects in the mechanical properties of both immersion and swabbing tests are comparable.

For the conservator context, it is interesting to find ways for minimizing the effects of our actions in painted surfaces. With this in view, the possibility of using alternative water based cleaning methods, such as gels, which retain water at the surface and allow working with a certain confidence seems of interest. In this work, long exposures to gels are compared to immersions for the same length of time. This was useful to prove a point that, at similar conditions, the leaching and stiffening effects can be somewhat minimized.

It is also of interest to compare gel applications to swabbing tests. In Figure 6.3.50 are shown the mechanical properties Talens® raw sienna swabbed for 2, 5 and 20 minutes. The samples exposed to the gels that had most leaching effects and induced more changes in the mechanical properties (Vanzan® NF-C and Klucel® G gels) are also included for comparison purposes. These were the least retentive gels of the gels tested and the ones that caused more leaching. Nevertheless, exposing the acrylic surface to these gels for 20 minutes was less damaging than when compared to the 5 minutes swabbing treatments. An additional stress-strain curve of a 2 minute swabbing test is also included in the figure and shows that the effects in the mechanical properties are few at such short exposure times. However, it is clear that the elimination of some additives from the film aids the film formation properties (promotes coalescence) which is visible from the high elongation values. This occurred in all the samples tested.

In summary, if a cleaning treatment requires swelling of an acrylic or PVAc surface, gels may come as a valid option to limit our action to the surface of our painting. Thus, causing less leaching and changes in the mechanical properties. If the gel used can retain water in very efficient way (such as the carbopol gel), then the changes in the materials can be almost negligeble for treatments that may require longer working times at the surface.

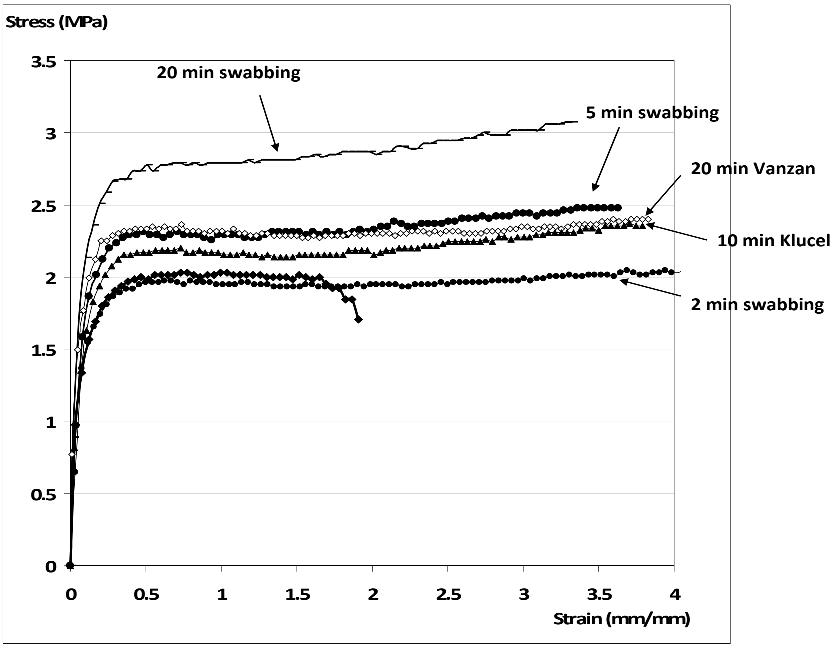

Figure 6.50: comparison of water based cleaning treatments. Swab tests and gel tests.

6.3.6- Conclusions

The effects of water-based cleaning treatments in acrylic and PVAc films have been simulated by immersion tests. These emulate cleaning treatments in which water is in contact with the surface for enough time to penetrate or swell the paint film and leach water soluble additives. The results obtained show the following trends, for both PVAc and acrylics:

- Water is readily absorbed during the immersion tests causing an important swelling effect. This happened in the first 20 minutes of the immersion for films with an average thickness of 0.2 mm.
- Once the immersion test is stopped water evaporates roughly within 2-4 hours, whereas some the residual water requires at least 1 to 2 days for complete evaporation

- The amount of water absorption of an acrylic film, hence its sensitivity to water, is dependent on the pigment/fillers and stabilization system (additive content) present in the dispersion. In general, colors containing synthetic organic pigments are more prone to water absorption and swelling than inorganic pigments. It has been observed that organic synthetic pigments also leach higher amounts of additives with immersions.
- All films tested for mechanical properties showed an increase in stiffness after water immersions. This is related to the leaching of additives that act as plasticizers in the bulk film.
- Interestingly, films that contained organic synthetic pigments became tougher (increased in stiffness without losing flexibility), whereas films containg inorganic pigments lost flexibility. Films from the Pébéo® brand showed a brittle behaviour with water immersions regardless of the pigment type.
- The morphological study of the paint surfaces after water immersions clearly show that water affects the films in two pathways: one by removing water soluble matter and loosely bound pigment; the second it creates a network of defects, such as pores, that were in full agreement with the changes measured in the mechanical properties of the films. Paint films containing earth or inorganic pigments seem to be more affected by water based treatments.

The analysis of the water extracts was performed by FTIR-ATR and Py-Silylation-GC-MS. Different additives have been indentified depending on the type of paint:

a) Acrylic products

- Liquitex® Heavy Body extracts contain an octylphenol poly(ethoxylate) type surfactant and possibly other PEO type compounds. There is a strong indication of the presence of an HEUR type thickener, as well as a polyacrylic type stabilizer. Sulphonate groups have also been found in the FTIR-ATR spectra and are tentatively ascribed to the presence of sodium dodecyl benzene sulphonate anionic surfactants.
- Vallejo® colours show an octylphenol poly(ethoxylate) type surfactant, and a cellulose ether thickener, detected in the FTIR-ATR spectrum.
- Talens® extracts show evidences of a poly(ethoxylated) fatty alcohol type surfactant, and also strong evidence of the presence of a cellulose type thickener. Evidence of sulphonate groups have been found in the FTIR-ATR spectra, these are ascribed to the presence of sodium dodecyl benzene sulphonate type surfactants.

b) PVAc products:

- Flashe® extracts reveal the presence of PEO type compounds and well as a cellulose type thickeners, methacrylic acid and PVAc residues. The water extractions performed for colours with organic synthetic pigments showed the presence of styrene. Phosphate-type compounds, glycol benzoates and methenamine have been detected by means of Py-Silylation-GC-MS analysis.
- Vinavil® 59 and Conrayt® extraction analysis revealed the presence of a PVOH type thickener/protective colloid, as well as VAc monomer.
- Mowilith® DMC2 extracts were composed of cellulose type thickeners, VAc monomers and also a sulphonate type compound, possibly, sodium dodecyl benzene sulphonate.

It is interesting to notice that the extractions obtained from the pigmented formulations, i.e. paints, contain extensive amount of surfactants whereas the unpigmented media contain essentially thickeners. This explains why paint films are more responsive to water in the first minutes of the immersion tests when compared to the pure mediums, as surfactants generally are show good affinity to water, whereas thickeners tend to be slower to hydrate and solubilize. However, for the conservator planning a cleaning treatment, it is very important to keep in mind that the thickener is, in fact, a gel and that the swelling of this compound with water may cause important stresses within the film, which is possibly what is observed in the Pébéo® samples.

Water-based gels and emulsion cleaning systems have been studied as alternative cleaning systems to water in the liquid form. The results obtained indicate the following trends:

- Water-based gels can be used for surface cleaning with an important reduction of the overall effects of water, such as absorption into the bulk film, leaching of additives, and increase in stiffness and decrease in flexibility. Generally, the most retentive gels (agar-agar® and Carbopol®Ultrez-21) affected less the paint surfaces, but general “recipes” are not defended in this work.
- W/O emulsion systems presented unpredictable results. For some paints films these systems showed optimum results in what swelling, leaching and changes in the mechanical properties concerns. However, for most of the paint films there was a variable sensitivity to the emulsion systems, and this appears to be related to the presence of the surfactant in the emulsion. Presently, new emulsion systems without surfactants are being tested and appear to be a fruitful field to explore in the cleaning of modern materials.

6.3.5- References

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7- Final Conclusions

7- Final conclusions

This thesis focused on the use of analytical techniques for the characterization of acrylic and PVAc materials before and after accelerated aging, as well as wet cleaning treatments. One of my efforts was to gather essential information published by other authors so that the conservator can find here a starting point to his, or her, own research. However, and ultimately, my hopes are that the experimental results obtained help understanding more about these materials than what was already written and serve as a starting point for further discussion.

The main conclusions obtained in this study will be divided in 1) characterization of acrylic and PVAc; 2) aging characteristics of these materials; 3) the effects of wet cleaning; 4) alternative methods for wet cleaning of acrylic and PVAc paints.

1) On the characterization of acrylic and PVAc

A combination of analytical techniques was applied in the physical and chemical characterization of a series of acrylics and PVAcs commercial products prepared as thin films over Mylar® sheets. My effort was to extract as much information possible on the organic fraction of these materials from analytical techniques such as FTIR-ATR and in situ thermally assisted Py-Silylation-GC-MS, which has been applied to identify minor polar compounds present in acrylic and PVAc paint samples, such as additives. Despite the interesting advances obtained with this method, I am confident that it is still possible to obtain more information by means of this technique. One area of interest is to increase the database of reference materials. This work is ongoing with promising results.

The characterization of the four acrylic paint brands revealed the following composition:

- Liquitex® and Vallejo® are BA-MMA type resins.
- Talens® media (gloss medium and gel medium) are EA-MMA-BA type polymers, whereas colours revealed two distinct compositions: EA-MMA or BA-MMA.
- Pébéo® paints contain Styrene-2EHA-MMA type resins.

The PVAc products were characterized as follows:

- Flashe® paint samples are PVA-VeoVa product.
- Conrayt® and Vinavil® 59 are PVAc resins.
- Mowilith® DMC2 is a VAc-dibutylmaleate resin.

The use of Py-Silylation-GC-MS in the analyses of these products allowed detecting minor compounds such as POE-type fragments in all materials and octylphenol type surfactants in the case of Liquitex® materials, with good resolution. This is an improvement comparing to the conventional analysis, in which these products where not identifies.

The characterization of the mechanical properties of acrylics and PVAc showed that these are highly flexible materials at room temperature, and I would not expected to see mechanical failure with appropriate manipulation. On the other hand, the softness of the films indicates that they are prone to dirt pick-up and embebment, which I witnessed in the films stored in our laboratory.

It was interesting to note that some acrylic and PVAc films were brittle, which contrasts to the general understanding of the mechanical properties of these materials. In this way, these films can be more prone to cracking during manipulation or transportation, especially at lower temperatures. This was the case of Flashe® and some Pébéo® paint films.

2) Aging characteristics of acrylics and PVAc

Acrylic and PVAc were subjected to two artificial aging programs: simulated daylight and UV light aging trials. These aging programs were selected because they were conducted close to ambient temperatures and relative humidity, simulating normal environmental conditions. Also, the light sources were specifically chosen to be representative of the light exposure conditions of indoor or museum illumination, as I wanted to avoid degradation reactions that may undergo under irradiation regimes that do not correspond to reality.

The acrylic samples considered for the aging programs consisted of Liquitex® (BA-MMA-(BMA)), Talens® (EA-MMA, BA-MMA or EA-MMA-BA), Vallejo® (BA-MMA) and Pébéo® (Styrene-2EHA-MMA). The samples were studied by FTIR-ATR and stress-strain tests for crossing information of chemical and mechanical data.

The results show that these materials are very resistant to both aging conditions. The degradation processes detected were related esentially to the photo-degradation of additives. This was observed in all brands. Few paint brands showed clear degradation that could be readily associated to the binding medium.

The following conclusions were extracted:

- Liquitex® gloss medium and varnish (a dispersion BA-MMA-(BMA) non pigmented medium) did not show measurable changes in the mechanical properties with both aging trials. However, the samples did show some yellowing under the daylight aging regime, and this indicates that chemical changes are occurring either on the binding medium or additives.

- The pigmented Liquitex® samples (also BA-MMA-(BMA) products) showed loss of strength and decrease in Young's Modulus after aging, which is a tipical consequence of chain-scission reactions. This technique was very sensitive to the degradation of additives, mainly surfactants, on the surface of the samples. Taking into account the resistance to wheathering of the unpigmented Liquitex® binding medium, it is proposed that the changes in the mechanical properties (loss of strength and decrease in Young's Modulus) are associated to a complex process that may involve the plasticizement of the film due to the formation of small degraded additive fragments in the film.

- The pigmented samples from Vallejo®, also a BA-MMA co-polymer, did not show evident changes in mechanical properties, indicating that they were resistant to the light aging regimes. Nevertheless, some samples showed changes in the IR absorption spectra that could not be correlated to the study of the mechanical properties. This suggests two possibilities: that the changes observed are occurring only in surface or with additives or that there are competing (at similar rate) cross-linking and chain-scission reactions, as suggested by FTIR-ATR spectroscopy.

- EA-MMA-BA unpigmented binding media from Talens® showed changes in the mechanical properties which were not accompanied by evidence of spectral changes by FTIR-ATR. The mechanical tests suggest that the main degradation pathways followed by these products are chain-scissions. The pigmented samples, on the contrary, were fairly more resistant to light degradation and few changes have been detected in this study. The trends in the data for the samples aged at these conditions also showed that chain-scissions may be the predominant aging steps, even though to a very limited extent.

- Styrene-acrylic polymers from Pébéo® showed evident degradation which is in good agreement with the theory, that suggest that lower stability is expected from styrene-acrylic co-polymers when compared to pure acrylics. The main degradation is associated to side group elimination or chain-scissions. Interestingly, the UV light aging regime evidenced higher degradation when compared to the daylight aging trial.

The PVAc tested in this work consisted of Flashe® paint samples (PVAc-VeoVa), Conrayt® (PVAc + DBP) and Mowilith® DMC2 (PVAc-Butylmaleate). The aging of these products showed the following trends:

- The degradation mechanisms of Flashe® paint films indicate that chain-scissions are the most predominant processes occuring under these aging conditions. They were possible to identify in both FTIR-ATR and stress-strain analyses.

- Conrayt® samples aged under the daylight regime were possible to test for mechanical properties only after the first 400 hours aging step. After 800 hours the films adhered to the Mylar® support and could not be tested. With the UV light aging program there were no such problems and all films were tested. The results obtained here showed evidences of predominant chain-scission processes under these aging regimes, consistent for both aging trials. FTIR-ATR analysis was also useful for the detection of DBP plasticizer elimination under the daylight aging conditions.

- The mechanical properties of Mowilith DMC2® were not possible to test after aging with the simulated daylight regime since the samples turned to a yellow product, adhered to the support. However, the samples aged under UV light were possible to test and showed that cross-linking reactions are possibly the most predominant aging features suffered by these films under these aging conditions.

I would like to emphasize that the combination of mechanical tests and FTIR-ATR analyses have shown new results and widened the knowledge on the aging of acrylic and PVAc based paints and media. The combination of these analytical methods has shed light on the most predominant degradation pathways of these materials. This study would benefit from further research on the specific chemical degradation pathways acrylic and PVAc suffer with aging, which was out of the scope of this thesis.

3) The effects of wet cleaning treatments on acrylic and PVAc

The effects of water-based cleaning treatments in acrylic and PVAc films were simulated by immersion tests, in which water penetrates and swells the paint films, causing leaching of water soluble additives. The results obtained show the following trends, for both PVAc and acrylics:

- Water is readily absorbed during the immersion tests causing an important swelling effect. This happened in the first 20 minutes of the immersion for films with an average thickness of 0.2 mm.

- Once the immersion test is stopped water evaporates roughly within 2-4 hours, whereas some the residual water requires at least 1 to 2 days for complete evaporation

- The amount of water absorption of an acrylic film, hence its sensitivity to water, is dependent on the pigment/fillers and stabilization system (additive content) present in the dispersion. In general, colours containing synthetic organic pigments are more prone to water absorption and swelling than inorganic pigments. It has been observed that organic synthetic pigments also leach higher amounts of additives with immersions.

- All films tested for mechanical properties showed an increase in stiffness after water immersions. This is related to the leaching of additives that act as plasticizers in the bulk film.

- Interestingly, films that contained organic synthetic pigments became tougher (increased in stiffness without loosing flexibility), whereas films containg inorganic pigments lost flexibility. Films from the Pébéo® brand showed a brittle behaviour with water immersions regardless of the pigment type.

- The morphological study of the paint surfaces after water immersions clearly show that water affects the films in two pathways: one by removing water soluble matter and loosely bound pigment; the second it creates a network of defects, such as pores, that were in full agreement with the changes measured in the mechanical properties of the films. Paint films containing earth or inorganic pigments seem to be more affected by water based treatments.

One of the endeavours of this works has been to extract as much information as possible on the additive content of materials. With this purpose, the additives extracted with the water immersions were studied by FTIR-ATR and Py-Silylation-GC-MS. The additives identified were different for each material:

a) acrylic products

- Liquitex® Heavy Body extracts contain an octylphenol poly(ethoxylate) type surfactant and possibly other POE type compounds. There is a strong indication of the presence of an HEUR type thickener, as well as a polyacrylic type stabilizer. Sulphonate groups have also been found in the FTIR-ATR spectra and are tentatively ascribed to the presence of sodium dodecyl benzene sulphonate anionic surfactants.

- Vallejo® colours show an octylphenol poly(ethoxylate) type surfactant, and a cellulose ether thickener, detected in the FTIR-ATR spectrum.

- Talens® extracts show evidences of a poly(ethoxylated) fatty alcohol type surfactant, and also stong evidence of the presence of a cellulose type thickener. Evidence of sulphonate groups have been found in the FTIR-ATR spectra, these are ascribed to the presence of sodium dodecyl benzene sulphonate type surfactants.

b) PVAc products:

- Flashe® extracts reveal the presence of POE type compounds as well as cellulose type thickeners, methacrylic acid and PVAc residues. The water extractions performed for colours with organic synthetic pigments showed the presence of styrene. Phosphate-type compounds, glycol benzoates and methenamine have been detected by means of Py-Silylation-GC-MS analysis.

- Vinavil® 59 and Conrayt® extraction analysis revealed the presence of a PVOH type thickener/protective colloid, as well as VAc monomer.

- Mowilith® DMC2 extracts were composed of cellulose type thickeners, VAc monomers and also a sulphonate type compound, possibly, sodium dodecyl benzene sulphonate.

An interesting remark is that the extractions obtained from the pigmented formulations contain considerable amounts of surfactants whereas the unpigmented media contain essentially thickeners. This explains why the paint films are generally more responsive to water when compared to the pure mediums. However, for the conservator planning a cleaning treatment, it is very important to keep in mind that the thickener is, in fact, a gel and that the swelling of this compound with water may cause important stresses within the film, which is possibly what is observed in the Pébéo® samples.

I was very interested in studying the possibility of using water-based gels and emulsion systems as alternatives to cleaning with water in the liquid form. The main results obtained for cleaning surfaces with Klucel® G, Vanzan® NF-C, and Carbopol® Ultrez 21 water based gels, as well as Ligroin in Water emulsion systems were the following:

- Water-based gels can be used for surface cleaning with an important reduction of the overall effects of water, such as absorption into the bulk film, leaching of additives, increase in stiffness and decrease in flexibility. Generally, the most retentive gels (agar-agar® and Carbopol®Ultrez-21) affected less the paint surfaces, but general “recipes” are not defended in this work.

- W/O emulsion systems presented unpredictable results. For some paint films, these systems showed optimum results in what swelling, leaching and changes in the mechanical properties concerns. However, for most of the paint films there was a variable sensitivity to the emulsion systems, and this appears to be related to the presence of the surfactant in the emulsion. Presently, new emulsion systems without surfactants are being tested and appear to be a fruitful field to explore in the cleaning of modern materials.

Some cleaning tests were performed in two case studies, which are described in Appendix F of this work. Even though these are preliminary short studies, the results indicate that the observations obtained from the test specimens are in correlation to those obtained *in situ*, in real painted surfaces. The study of the effects of wet cleaning is still on going.

PART V

Appendixes

APPENDIX A –Characterisation of test specimens

A.1 FTIR-ATR of acrylic test specimens

A.1.1- Liquitex Heavy Body

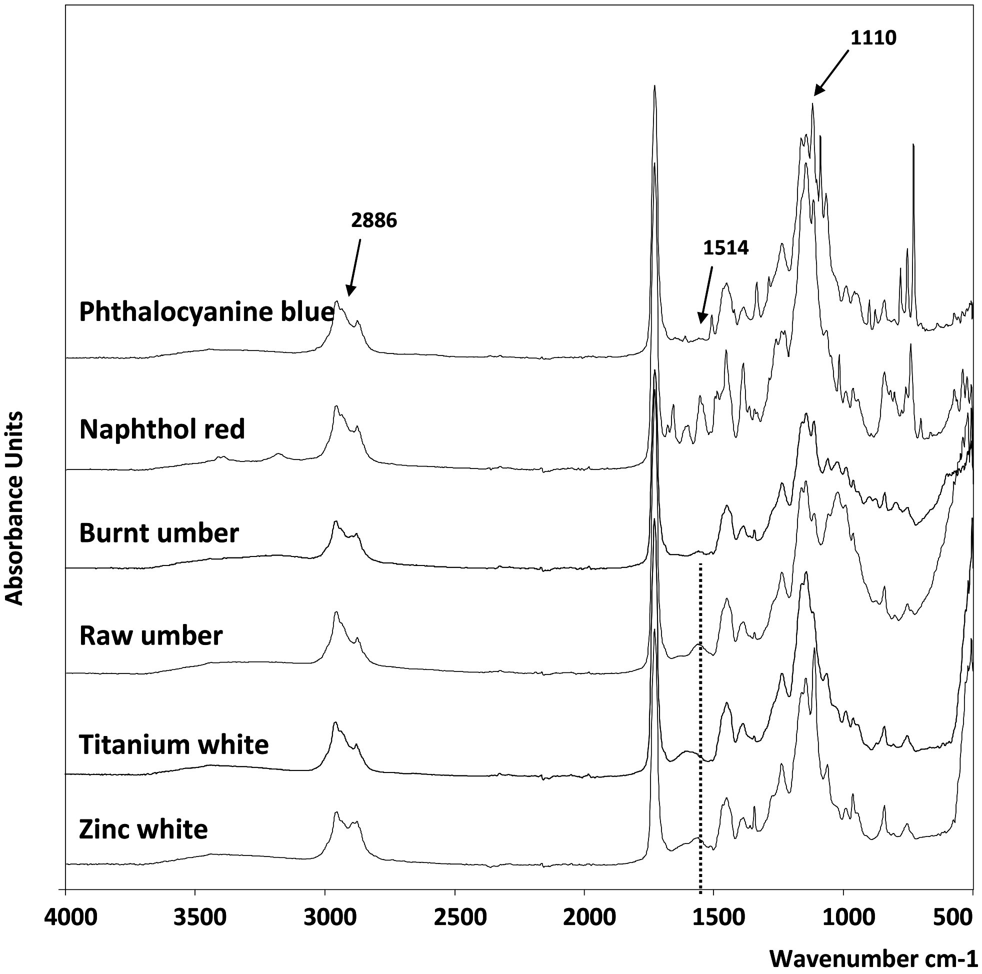

Figure A.1: FTIR-ATR spectra of other Liquitex® Heavy Body paint samples. The medium profiles are similar to those of BA-MMA. The PEO type additives are pointed out in the figure and can be identified in all paint samples. The dotted line shown in the spectra corresponds to the possible formation of metal complexes. These complexes were only identified in the inorganic pigments such as burnt umber, raw umber a zinc white.

A.1.2- Vallejo®, Royal Talens® and Pébéo

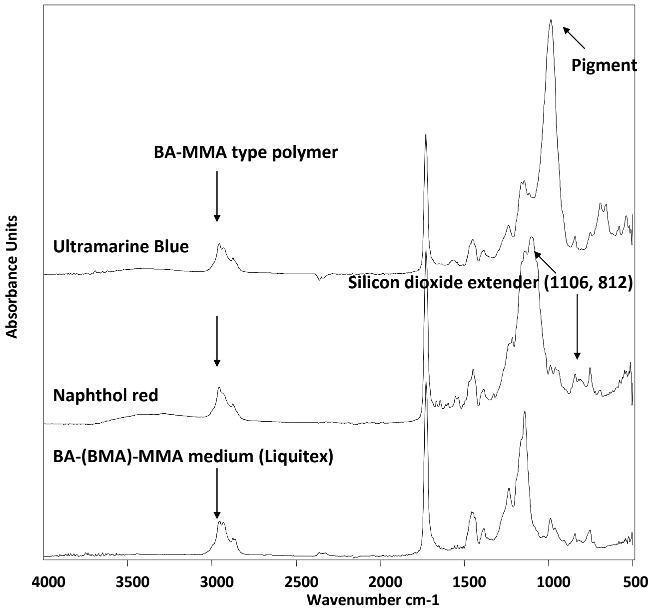

Figure A. 2: FTIR-ATR spectra of Vallejo® paint samples. A pure BA-MMA medium is included for comparison purposes.

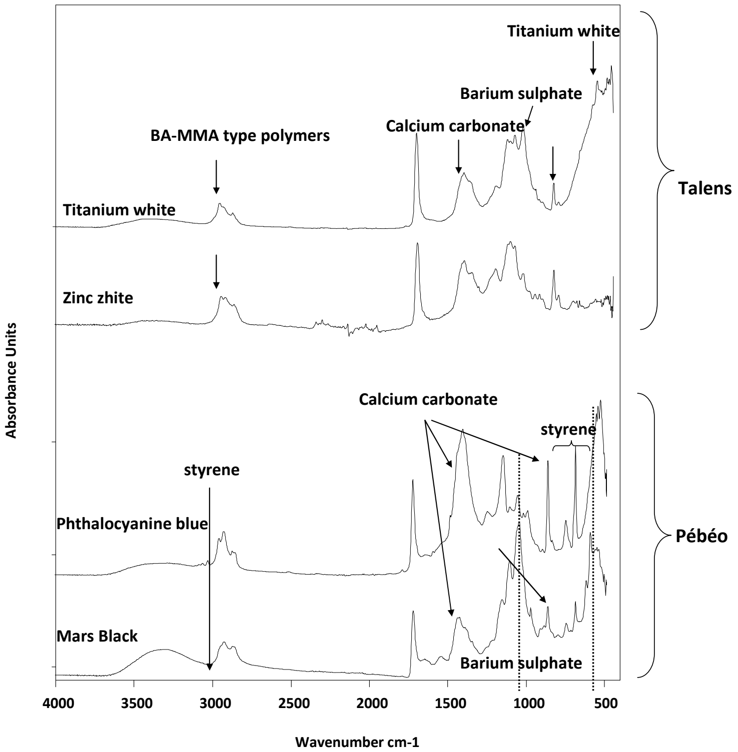

Figure A.3: FTIR-ATR spectra of Talens® and Pébéo® paint samples.

A.2 FTIR-ATR of PVAc specimens: other Flashe® colours

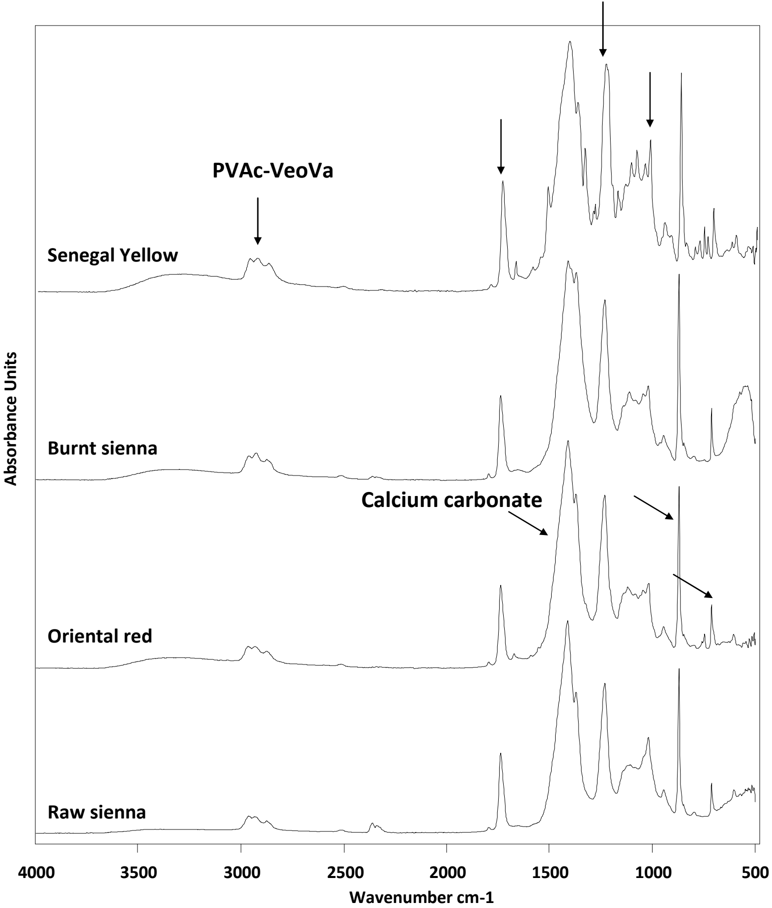

Figure A. 4: FTIR-ATR Flashe® of films specimens. The analysis detects clearly calcium carbonate as the extender. In burnt and raw sienna are visible bands corresponding to iron pigments. Senegal Yellow shows a more complex spectrum from PY 74 (1676, 1597, 1557, 1522, 1340, 1181, 1025, 806, 783, 760, 742 cm^{-1} [42]. Oriental red, a PR112, does not show charateristic bands of the pigment.

A.2- Py-Silylation-GC-MS spectra of reference compounds

The analyses by Py-GS-MS or Py-Silylation-GC-MS of poly(ethoxylated) type surfactants resulted in the separation of the ethoxylated chain from the hydrocarbon moiety. In the case of the analysis with HMDS derivatising reagent, the resulting alcohol fragment is detected in its TMS ester form. This has been observed for both Triton® X-100 and Brij® 30. The pyrograms are shown below.

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A.2.1. Pyrogram of the analysis of an poly(ethoxylated) octylphenol: Triton® X-100

The main peaks present in the pyrogram of Triton® X-100 are related to the formation of an octylphenol fragment (*m/z=206*) and its corresponding fragmentation with marker ion *m/z=135.* Another strong peak with ions *m/z= 161* (also 232) has also been found in the pyrogram and is of analytical interest. Ions *m/z= 161* and *m/z= 135* may be used together for a quick identification of a Triton X type surfactant, since they are produced irrespectively of the polyethoxylated chain length. A proposed pathway for the formation of these fragments is shown in Figure A.2. At higher retention time, several peaks are ascribed to ethoxylated fragments of octylphenol. The full identification of this product is not likely by this technique due to the fragmentation of the POE chain during pyrolysis.

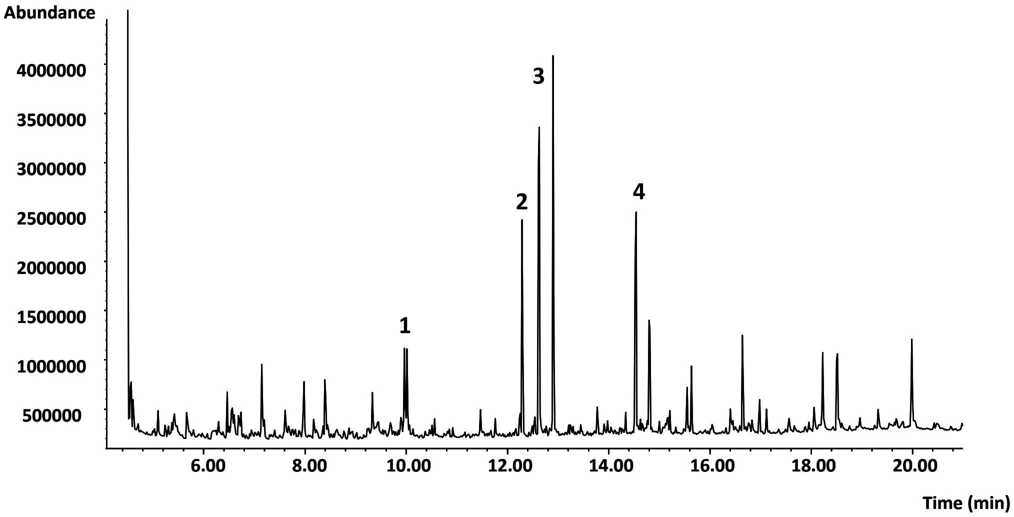
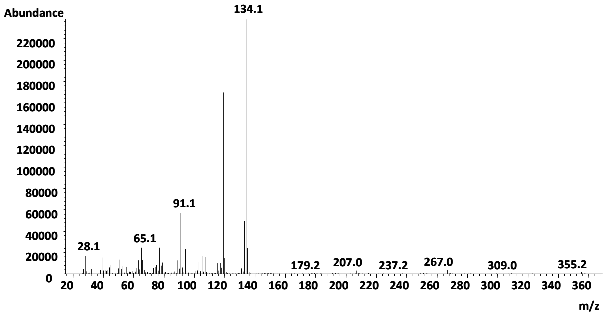
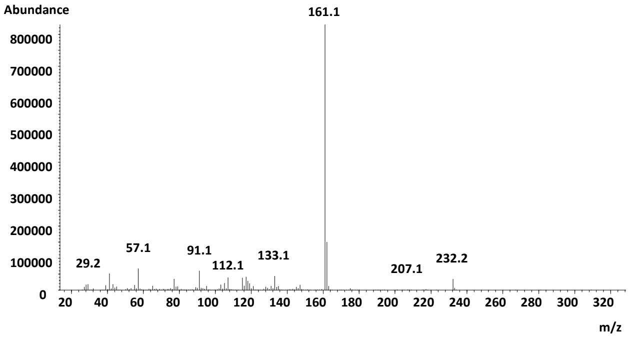


Figure A. 5: Pyrogram of Triton® X-100 obtained by Py-silylation. The mass spectra of the peaks signed are shown below.

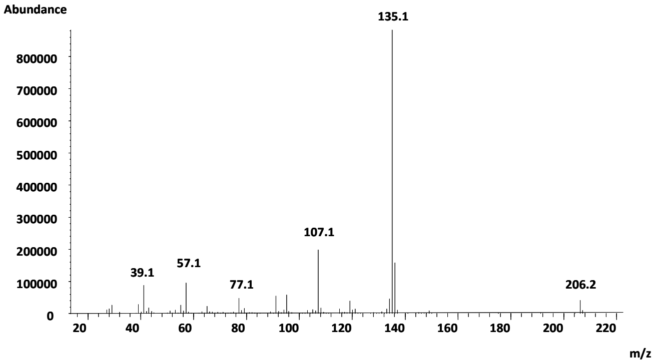
1. Iso-Propylphenol



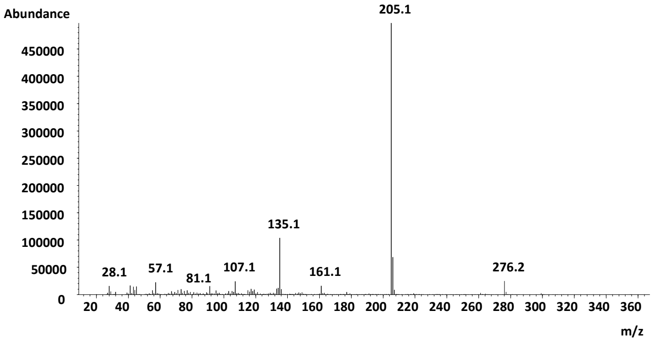
2. Octylphenol fragment



3. Octylphenol



4. Octylphenol-TMS derivative



The mass spectra fragmentation pathways of the most intense peaks found in the Triton® X-100 pyrogram are proposed in Figure A. 5.

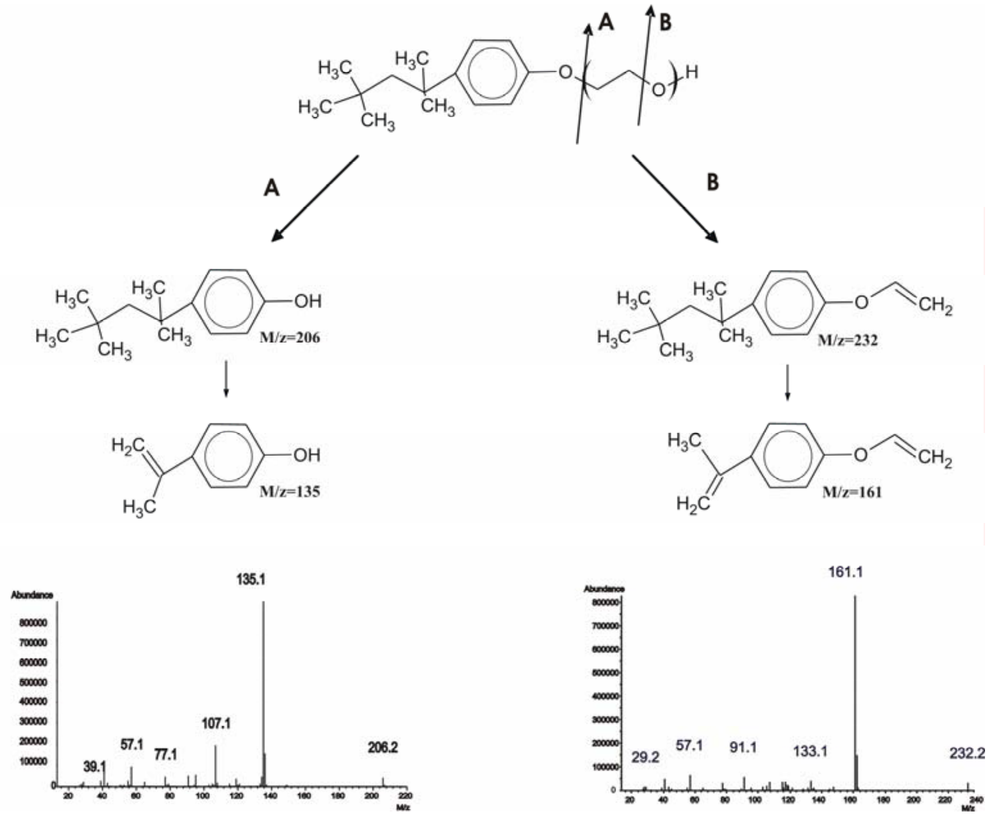


Figure A. 6: fragmentation pathways proposed for the fragmentation of Triton® X 100 during pyrolysis.

A.2.2. Pyrogram of the analysis of Brij® 30: a fatty alcohol ethoxylate

The pyrograms of Brij® 30 obtained by conventional pyrolysis and pyrolysis with HMDS gave, in both cases, a group of fragments corresponding to the surfactant aliphatic chain. These include dodecene and dodecanol, as well as tetradecene and tetradecanol, which are pointed out in the pyrograms. This reveals that these products contain different alifatic chains in their composition.

The analysis of Brij® 30 with HMDS is shown in Figure A. 7. There are strong peaks attributed to the partial derivatisation of the alifatic alcohol chains, i.e. dodecanol and tetradecanol, as well as polyethoxylated fragments, and polyethoxylated fragments in their derivatised form (some peaks fragments were not derivatised). The peaks corresponding to POE fragments could only be detected by means of Py-Silylation: These appear in their derivatised form. It is relevant to notice that the derivatised pyrolysates trendly are the most intense peaks found in the analysis of Brij® 30. Interestingly, no peak corresponding to the full molecule has been detected, which is due to fragmentation of the surfactant during pyrolysis. This implies that the full identification of this product is not likely by this technique.

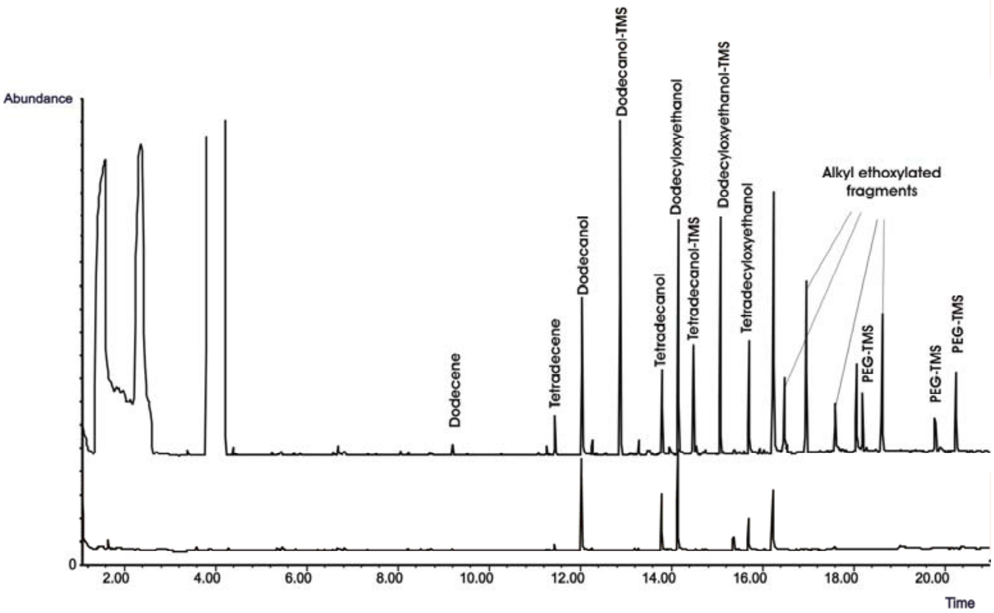
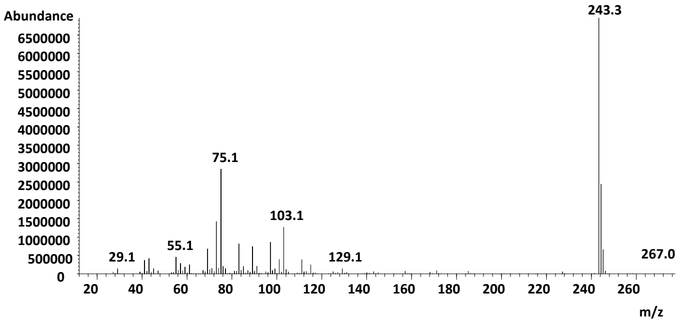
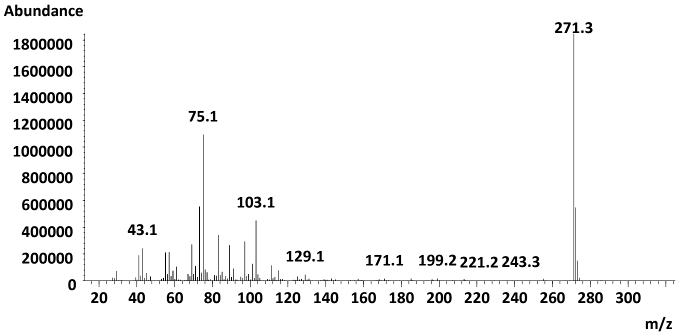


Figure A. 7: Pyrogram of Brij® 30 obtained by Py-silylation (Top), and by conventional pyrolysis (bottom). The mass spectra of the peaks signed are shown below.

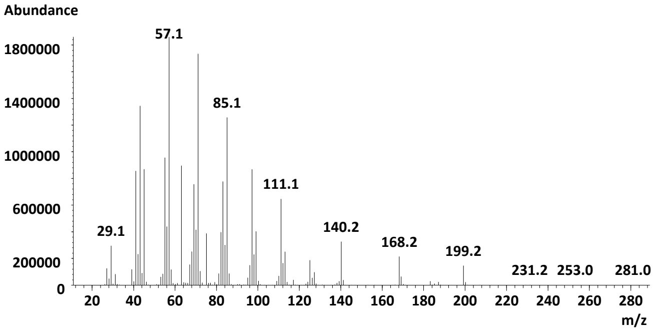
Dodecanol-TMS derivative



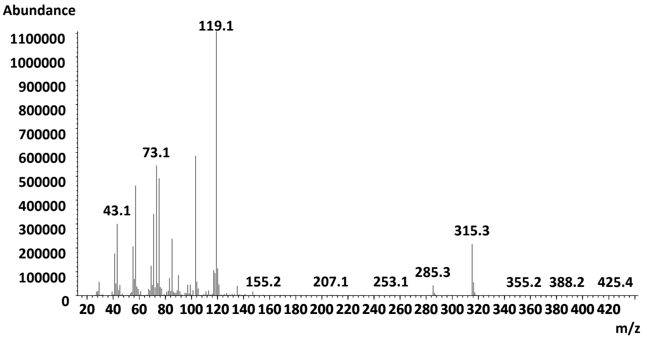
Tetradecanol-TMS derivative



Dodecyloxy-2 ethanol



Dodecyloxy-2 ethanol – TMS derivative



APPENDIX B – Other results of interest obtained from the aging trials not shown in the text

B.1- FTIR-ATR aging study of acrylic test specimens

B.1.1- Liquitex® Heavy Body paint samples subjected to both aging trials

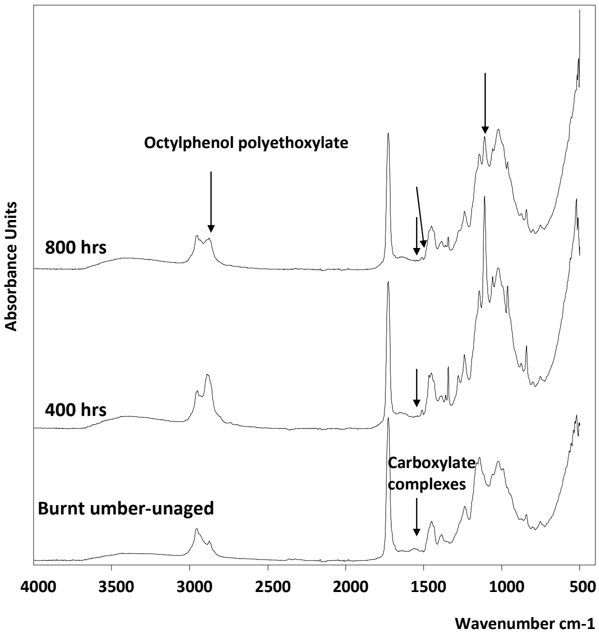


Figure B. 1: FTIR-ATR spectra of Liquitex® burnt umber subjected to the daylight aging trials. Samples were aged for 400 and 800 hours.

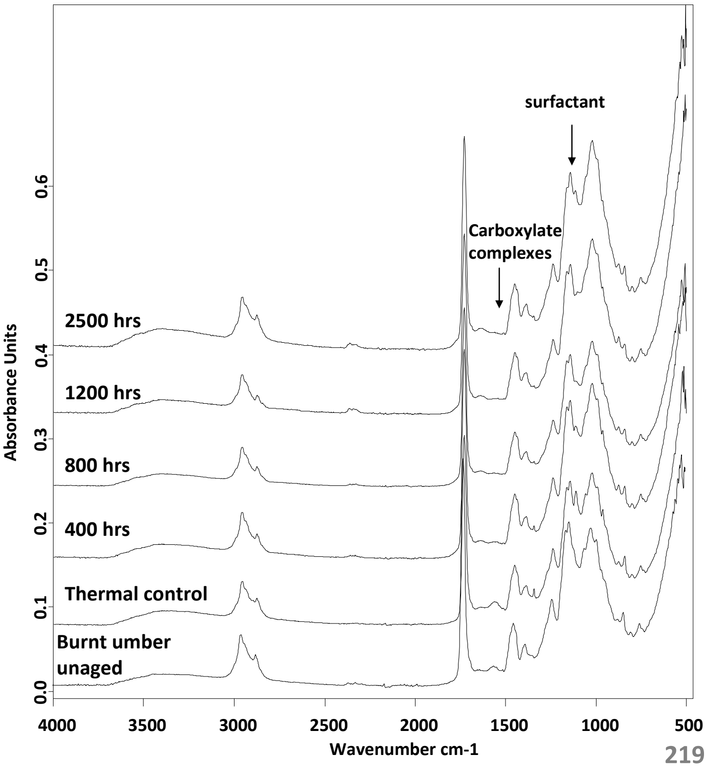


Figure B. 2: FTIR-ATR spectra of Liquitex® burnt umber subjected to the UV light aging trials. Samples were aged for 400, 800, 1200 and 2500 hours. Also included is the thermal control sample. The results are in good agreement with the previous aging trial.

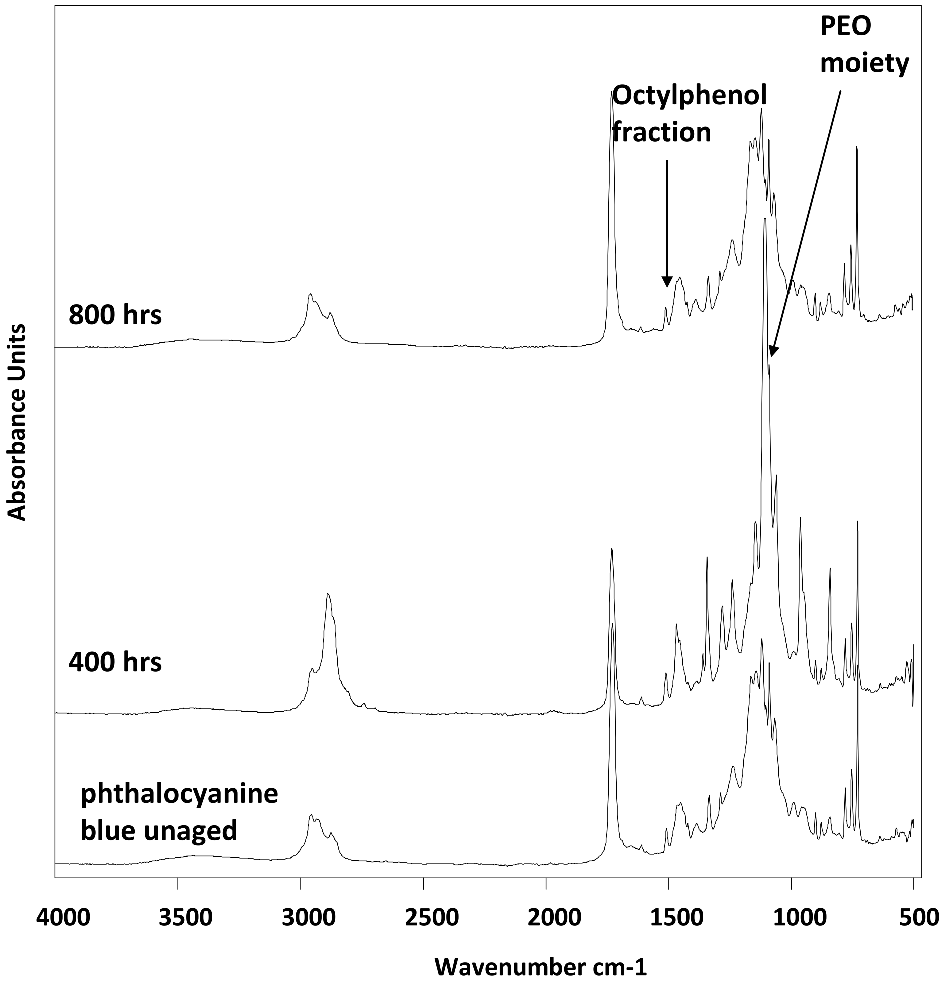


Figure B. 3: FTIR-ATR spectra of Liquitex® phthalocyanine blue subjected to the daylight aging trials. Samples were aged for 400 and 800 hours. In the spectra is visible the considerable amount of exudation of surfactant to the surface at 400 hours aging (graphic is compressed in order to be seen). With aging, the absorptions corresponding to the PEO fraction disappear, whereas the non-polar fraction is still visible. This suggests that the degradation of surfactant is mainly occuring in the polar chain. This is in good agreement with the mechanical tests that show a plasticising effect with aging, possibly due to these fractions of surfactant in the film that may act as plasticisers.

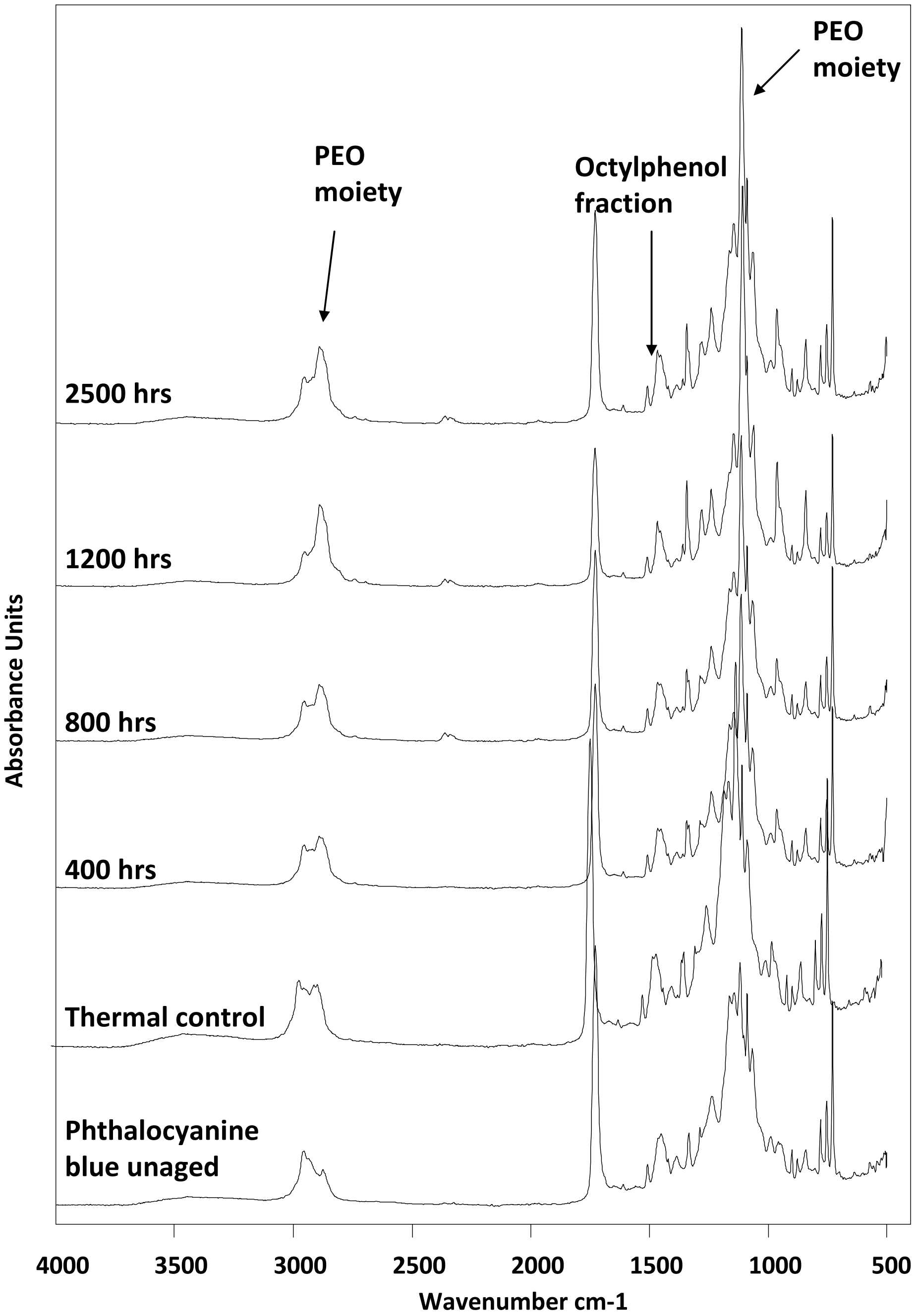


Figure B. 4: FTIR-ATR spectra of Liquitex® phthalocyanine blue subjected to the UV light aging trials. Samples were aged for 400, 800, 1200 and 2500 hours. Also included is the thermal control sample. The results are in good agreement with the previous aging trial. The exudation of surfactant is clear and increases up to 1200 hours aging. At 2500 hours aging the samples exhibit a decrease in surfactant signal. These films present high amounts of surfactants, as described in the study of the water extractions.

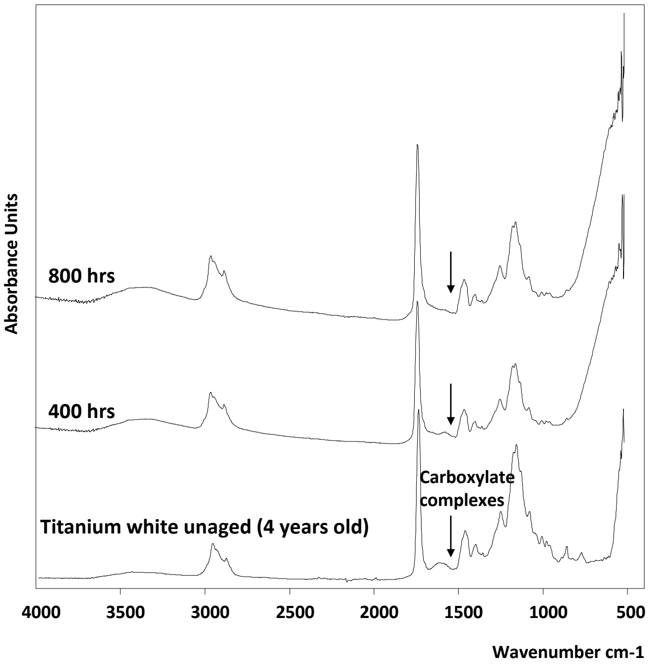
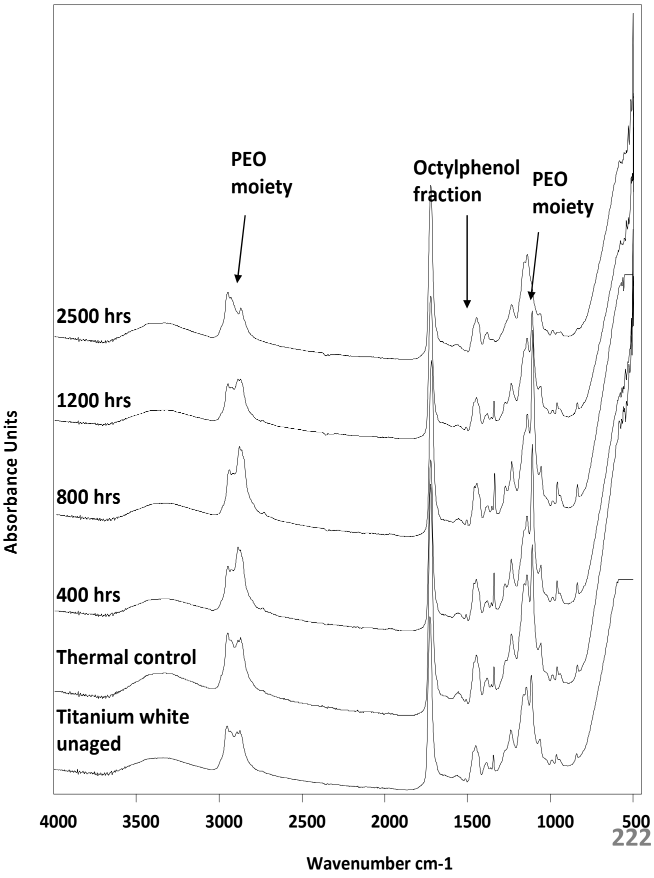


Figure B. 5: FTIR-ATR spectra of Liquitex® Titanium white subjected to the daylight aging trials. Samples were aged for 400 and 800 hours. The results show similar trends on aging when compared to the previous samples.

Figure B. 6: FTIR-ATR spectra of Liquitex® Titanium white subjected to the UV light aging trials. Samples were aged for 400, 800, 1200 and 2500 hours. Also included is the thermal control sample. The results are in good agreement with the previous aging trial. There is a strong evidence of exudation of surfactant to the surface, when compared to the previous Figure. The signal of this compound at the surface of the sample increases up to 800 hours aging. At 2500 hours aging the samples exhibit a decrease in surfactant signal.



B.1.2- Vallejo® paint samples subjected to both aging trials

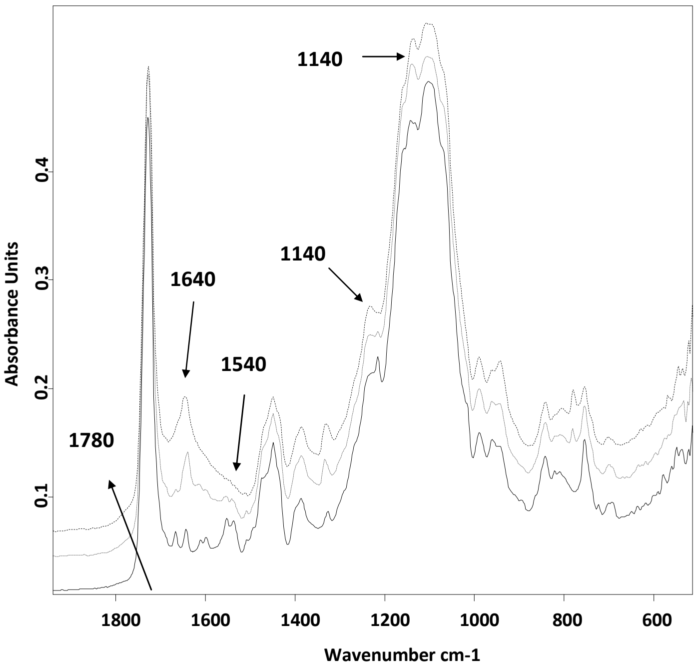


Figure B. 7: FTIR-ATR spectra of Vallejo® naphthol red subjected to the daylight aging trials. Samples were aged for 400 and 800 hours. The results show the same aging trends on aging with the UV light aging program (this has been described in the main text).

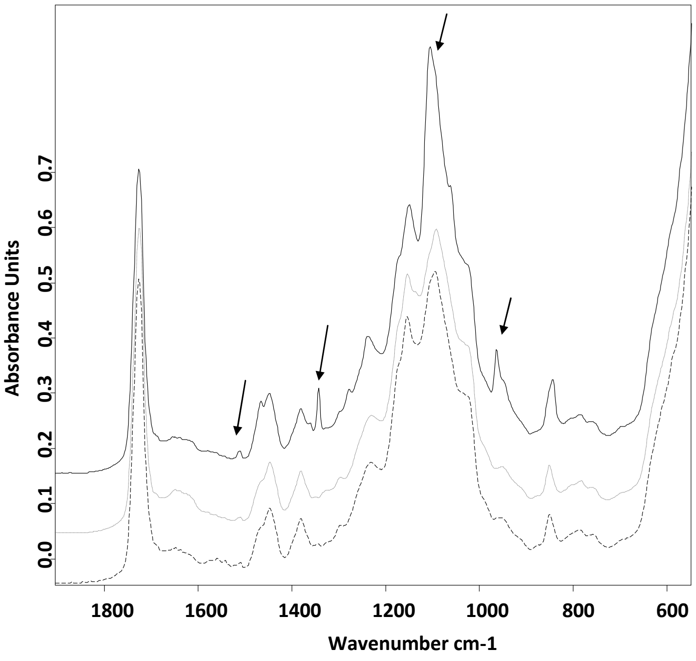


Figure B. 8: FTIR-ATR spectra of Vallejo® Iron Oxide red: (top-solid line) unaged; (middle dotted line) 800 hours aged with daylight aging; (bottom dashed line) 1200 hours aged with UV light. Results show degradation of surfactant, while polymer absorptions are unaffected with aging.

B.1.3- Talens® paint samples subjected to both aging trials

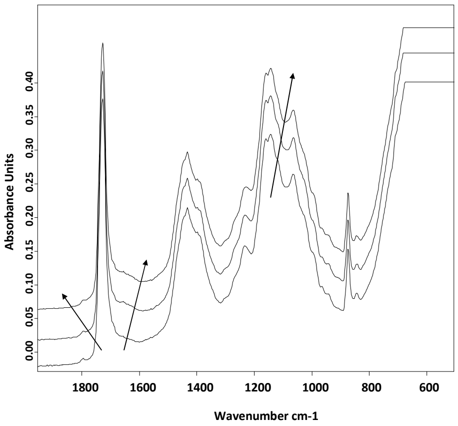


Figure B. 9: FTIR-ATR spectra of Talens® Titanium white subjected to the daylight aging trials. Samples were aged for 400 and 800 hours (bottom to top). There is no degradation detectable in these samples, which is good correlation to the stability of the mechanical properties of the paint films. The arrows indicate the typical regions in the FTIR spectrum where degradation of polymer can be studied. Similar results were seen with the UV light aging trials.

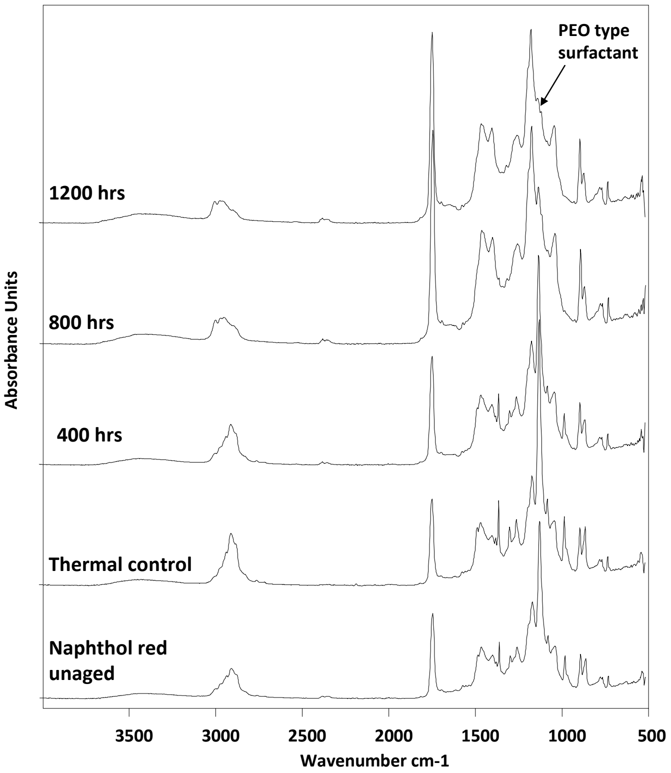


Figure B. 10: FTIR-ATR spectra of Talens® Naphthol red subjected to the UV light aging trials. Samples were aged for 400, 800 and 1200 hours. The results are in full agreement to those presented in section 6.2.2.1 of the thesis.

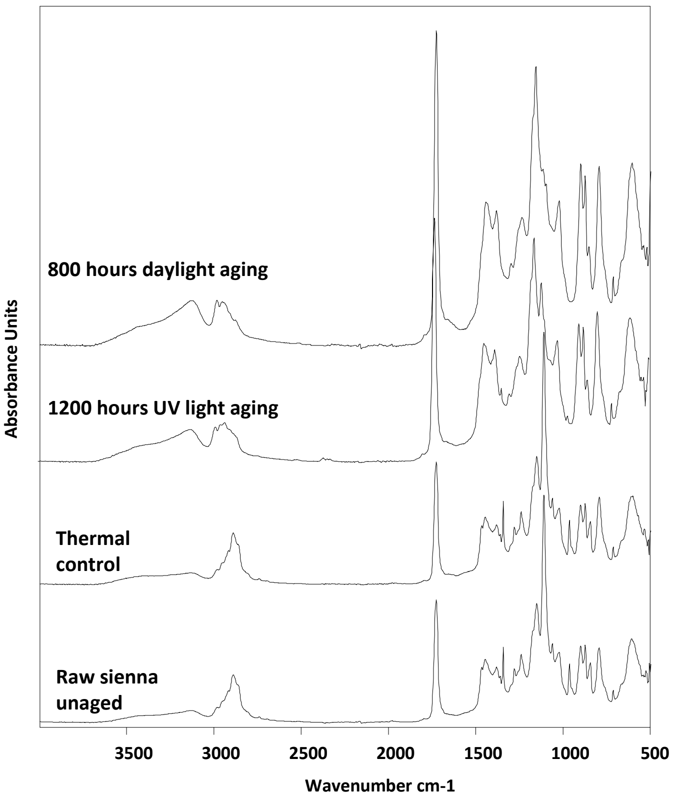


Figure B. 11: FTIR-ATR spectra of Talens® raw sienna aged by both aging trials. The results repeat the same aging patterns as seen for the other paint samples, where degradation of the surfactant is dominating process at the surface.

B.1.4- Pébéo® paint samples subjected to both aging trials

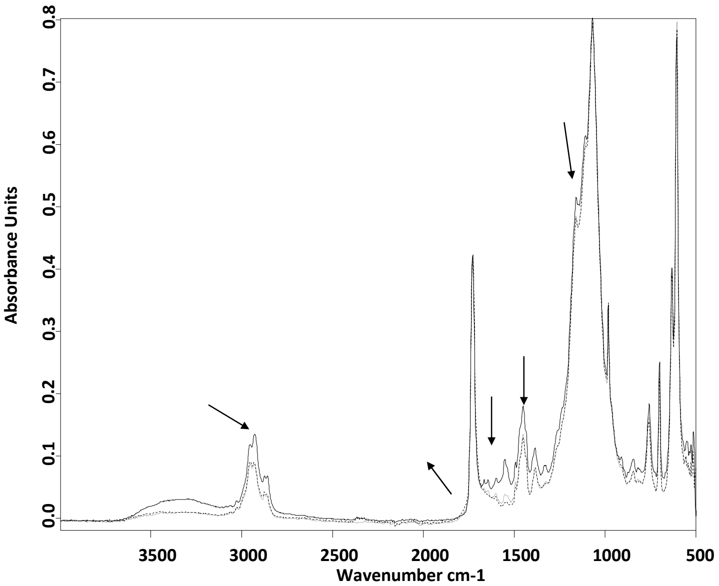


Figure B. 12: FTIR-ATR of Pébéo naphthol crimson subjected to daylight aging trials: solid line control sample; dotted line 400hours and dashed line 800 hours. The aging trends are identical to those previously described in the main text for red oxide.

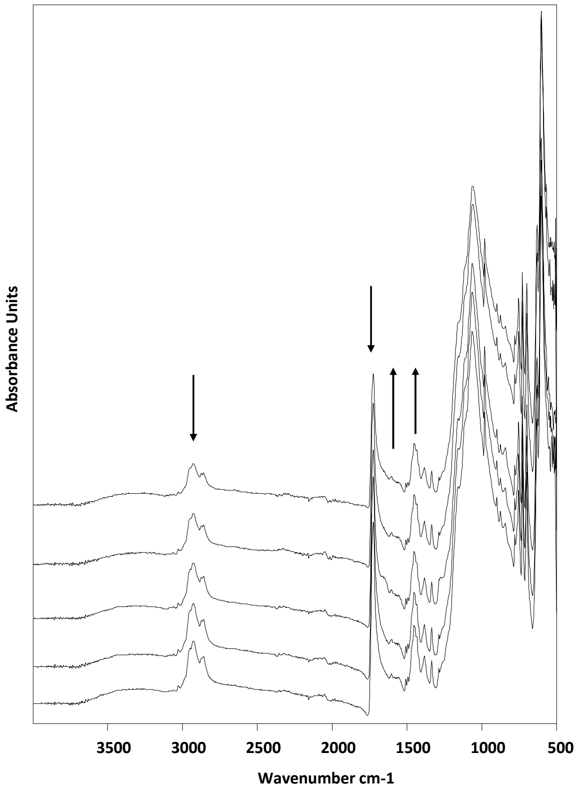


Figure B. 13: : FTIR-ATR of the Pébéo phthalocyanine blue sample subjected to UV-light aging. Aged samples are (from bottom to top) control sample, thermal control sample, 400 hours, 800 hours and 1200 hours. The arrows indicate the degradation of the main polymer bands. This aging trend is identical to those previously described in the main text for naphthol red aged with the same protocol.

B.2- Study of the mechanical properties of acrylic test specimens subjected to both aging trials

B.2.1- Liquitex® Heavy Body paint samples subjected to both aging trials

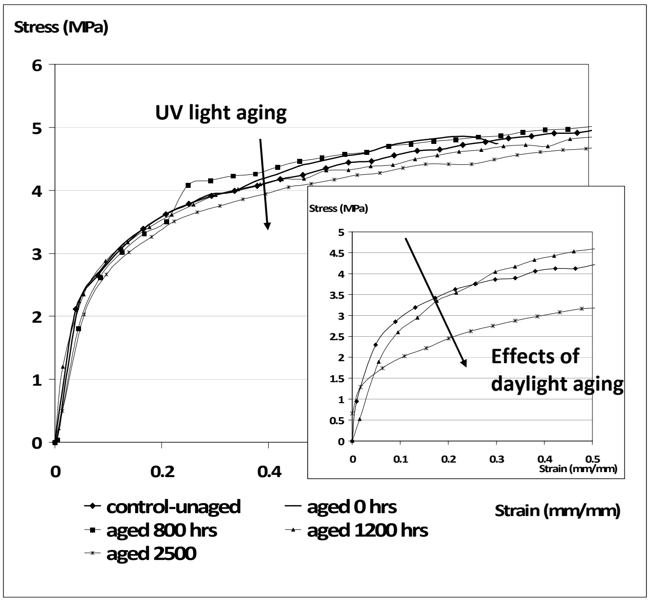


Figure B. 14: mechanical properties of Liquitex® burnt umber with both aging trials. The samples aged by UV light maintained similar mechanical properties whereas with daylight there was an increase in flexibility.

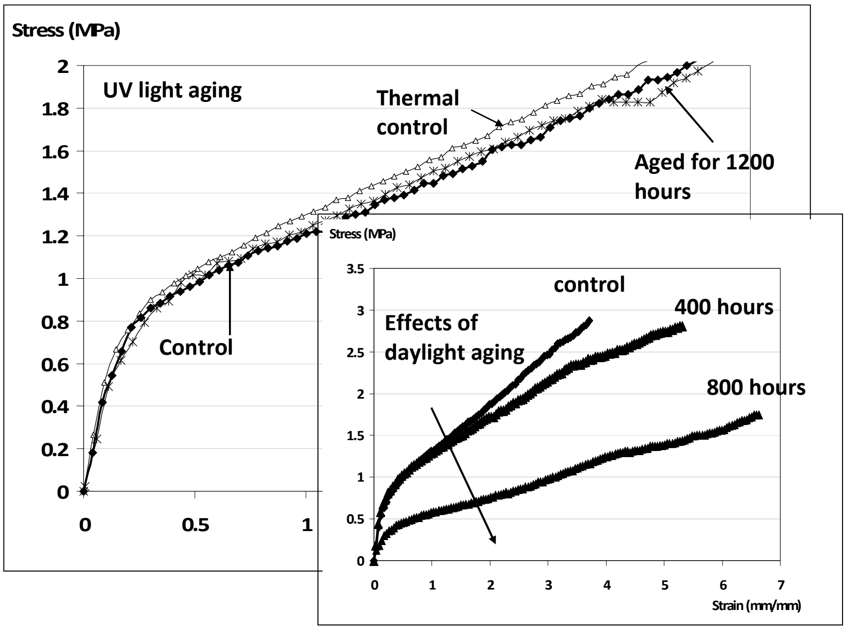


Figure B. 15: mechanical properties of Liquitex® phthalocyanine blue with both aging trials. The samples aged by UV light maintained similar mechanical properties whereas with daylight there was an increase in flexibility, similarly to the previous samples.

B.2.2- Talens® paint samples subjected to both aging trials

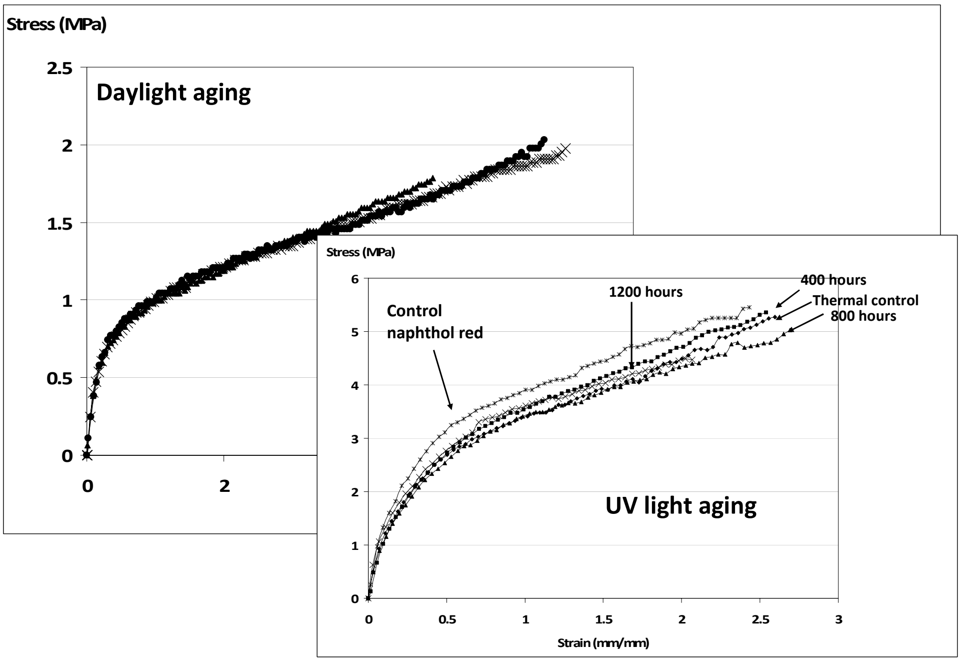


Figure B. 16: mechanical properties of Talens® naphthol red with both aging trials. The samples aged by the Daylight aging trial maintained similar mechanical properties whereas with UV-light there was an increase in flexibility. These results indicate similar trends to the unpigmented medium.

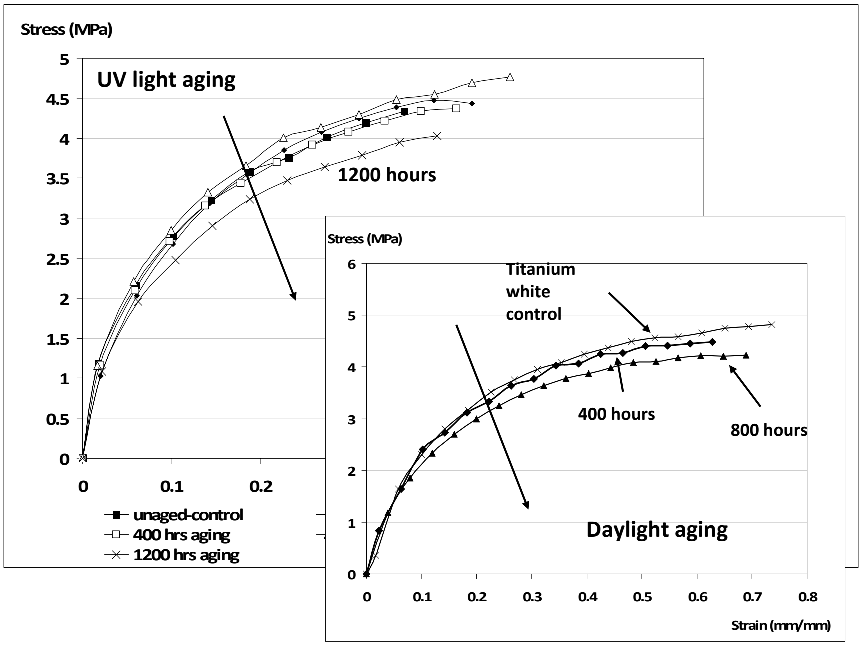


Figure B. 17: mechanical properties of Talens® Titanium white with both aging trials. The samples aged by both aging trials show similar trends to those described previously.

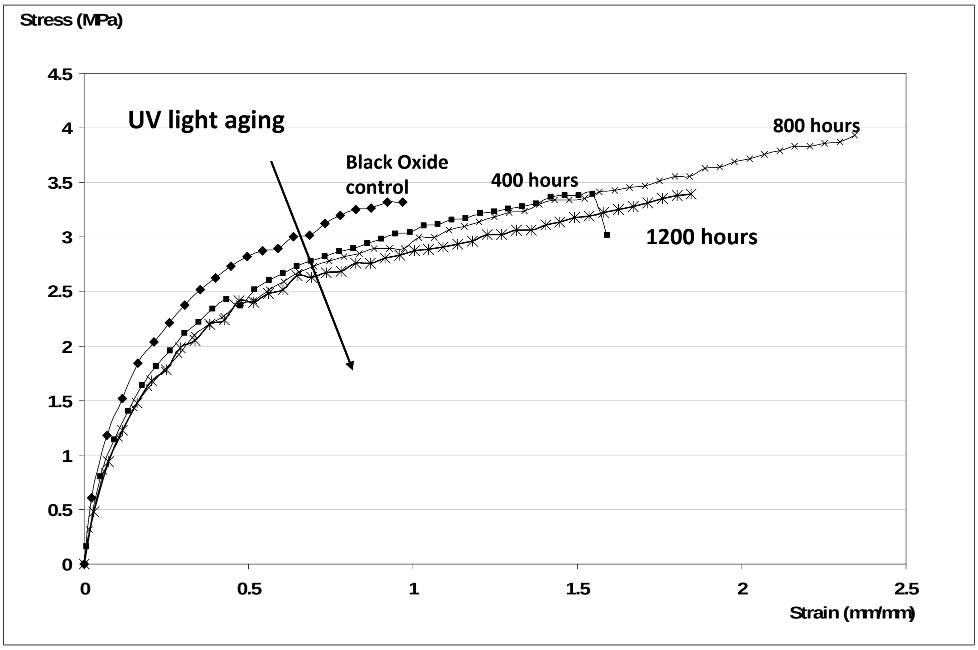


Figure B. 18: mechanical properties of Talens® Black Oxide that show consistent results to the previous samples. This sample also showed an increase in elongation which may be due to film formation processes that keep developing with aging. This sample was not tested for the daylight aging program.

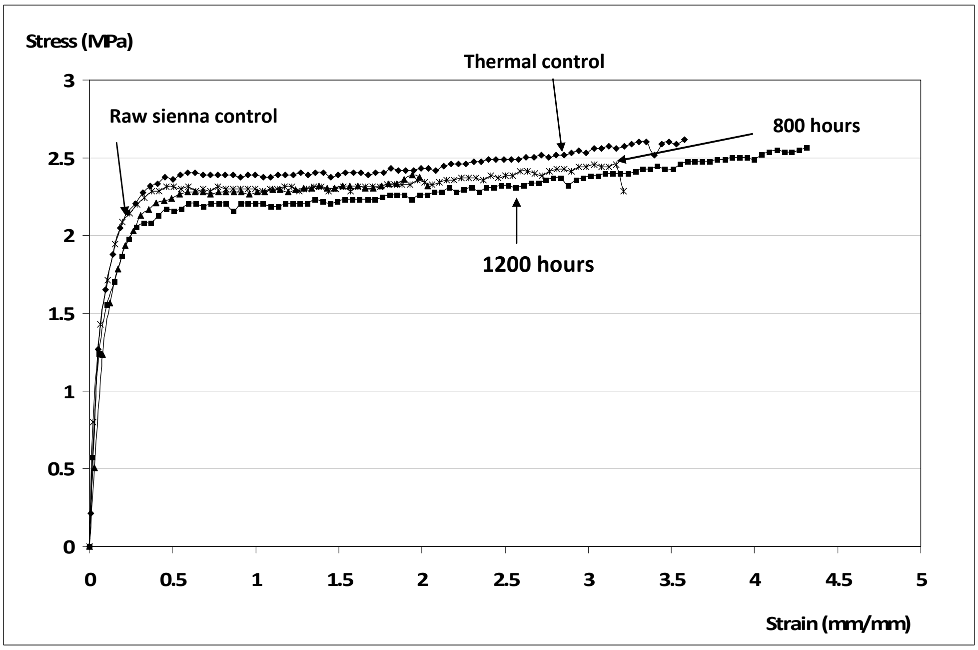


Figure B. 19: mechanical properties of Talens® raw sienna obtained after UV light aging. These results are complementary to those discussed in the main text for the Daylight aging trials.

B.2.3- Vallejo® paint samples subjected to both aging trials

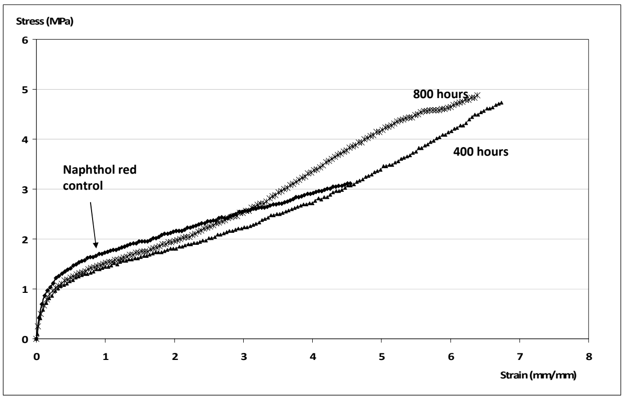


Figure B. 20: mechanical properties of Vallejo® naphthol red aged with the daylight program. This figure shows similar results to the data discussed for phthalocyanine blue shown in the text.

B.2.3- Flashe® paint samples subjected to both aging trials

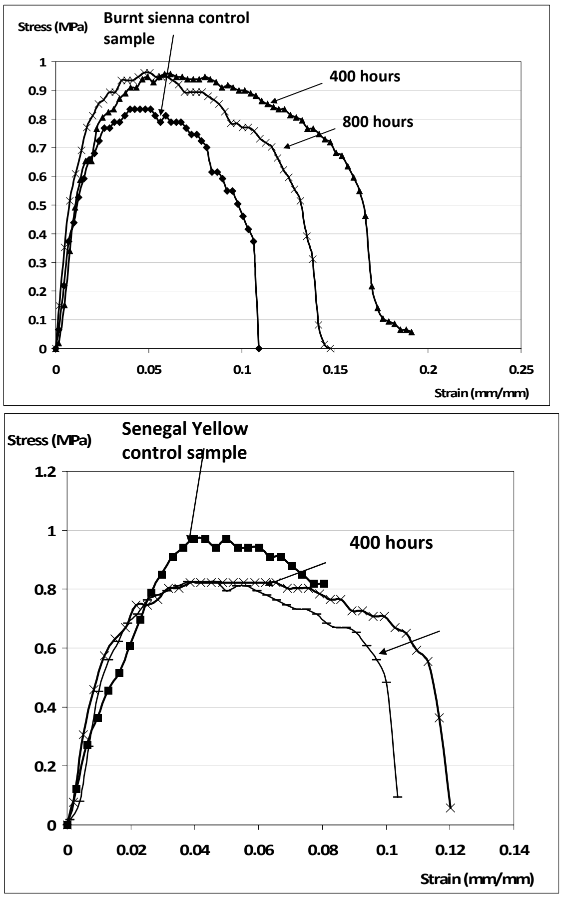
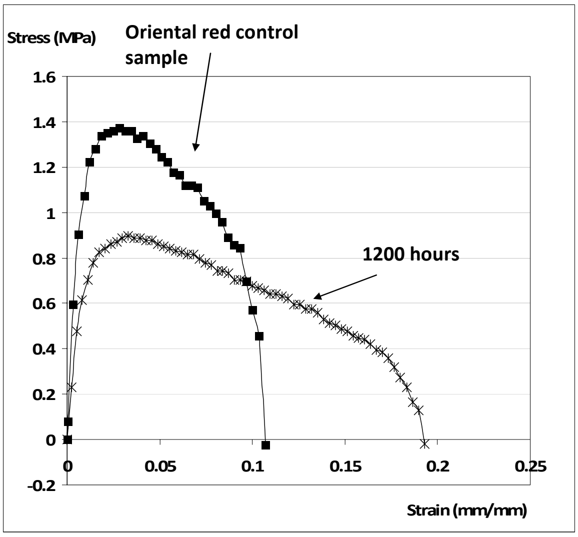


Figure B. 21: the mechanical properties of aged Flashe® paint films under the daylight regime.



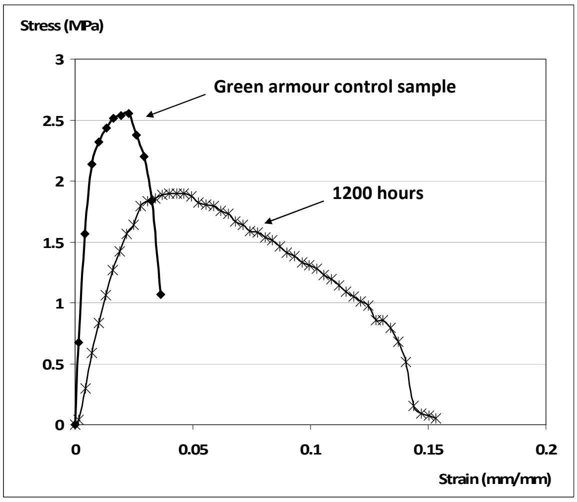


Figure B. 22: the mechanical properties of aged Flashe® paint films under the UV light regime.

APPENDIX C – Other results of interest obtained from the Cleaning trials that have not been shown in the text

C.1- A study on immersion tests as simulations of water-based surface cleaning treatments

The validity of immersion tests as representative or comparable tests to cleaning treatments is often questioned among conservators. For obtaining insight into this subject, the effects of 5 and 20 minutes immersions tests were compared to 5 and 20 minutes swabbing tests on a Talens® raw sienna acrylic paint films.

In Figure C. 1 are the absorption-drying curves for the 20 minutes immersion and 20 minute swabbing as well as amount of leached materials during these trials. It is interesting to notice that both films absorb similar amounts of water during the trials, whereas the swabbing test caused more leaching. This is related to the mechanical action applied with the cotton swab. However, macroscopically, the immersion tests clearly caused a more pronounced swelling effect than swabbing.

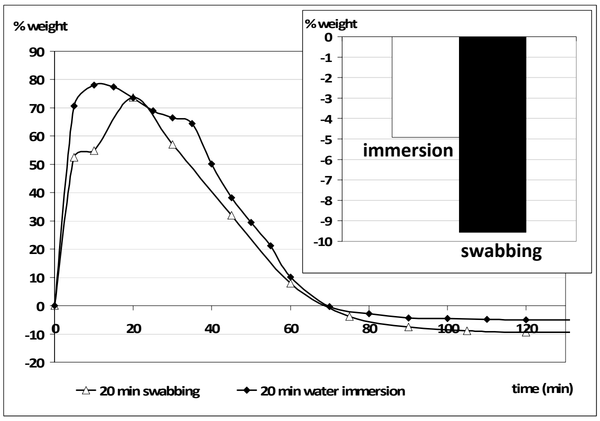


Figure C. 1: the absorption-drying profiles obtained for a Talens® raw sienna paint sample subjected to a 20 minute immersion and swabbing tests.

Below, in Figure C.2 are the mechanical properties of the films swabbed and immersed films for 5 and 20 minutes. It is clear that, in the first 5 minutes, the immersion tests cause a more pronounced alteration in the mchanical properties of the films. After 20 minutes, both swabbed and immersed films exhibit similar mechanical properties. In any case, the effects of water in these films, either in the immersion or swabbing form, caused similar alterations, i.e. a stiffening effect. It is fair to say that immersions can be representative approaches to a water-based surface cleaning treatments, where the purpose of the study is to detect and characterize the possible damage caused by such treatment.

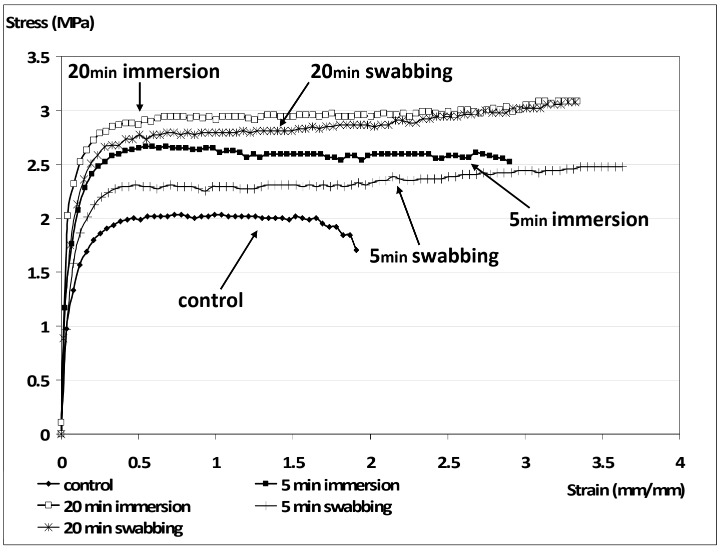


Figure C. 2: stress-strain curves obtained for Talens® raw sienna samples after 5 and 20 minutes immersion tests and 5 and 20 minutes swabbing tests. It is shown that the effects in the mechanical properties of both immersion and swabbing tests are comparable.

C.2- A study on the effects of short water immersions and swabbing tests

A comparison between the materials extracted from a series of swabbing tests and short immersions on a Liquitex® burnt umber paint film are shown in Figure C. 3 along with the effects of the swabbing tests on the mechanical properties of the same paint films. The results show a clear trend, with short swabbing tests the films loose some strength and become more flexible. This is prone to be related to the washing of additives from the surface and bulk film, which allows further coalescence of the film. The results obtained for swabbing are exactly the same as those obtained for short immersion tests. At five minute immersion, i.e. the burnt umber films experience a decrease in stiffness. However, with longer immersion times, these films rapidly gain stiffness and at 20 minutes there is a considerable stiffening effect and decrease in elasticity. This can be seen inFigure C. 6. Similar results were obtained for Liquitex® phthalocyanine blue, shown in Figure C. 7. In the case of phthlocyanine blue, the films were stiffer but maintained elongation.

In any case, it is also clear that these results differ from those obtained for Talens® raw sienna, which increase in stiffneff soon after the first 5 minutes immersion and swabbing. This confirms that each brand (and colour within such brand) may react differently to these tests.

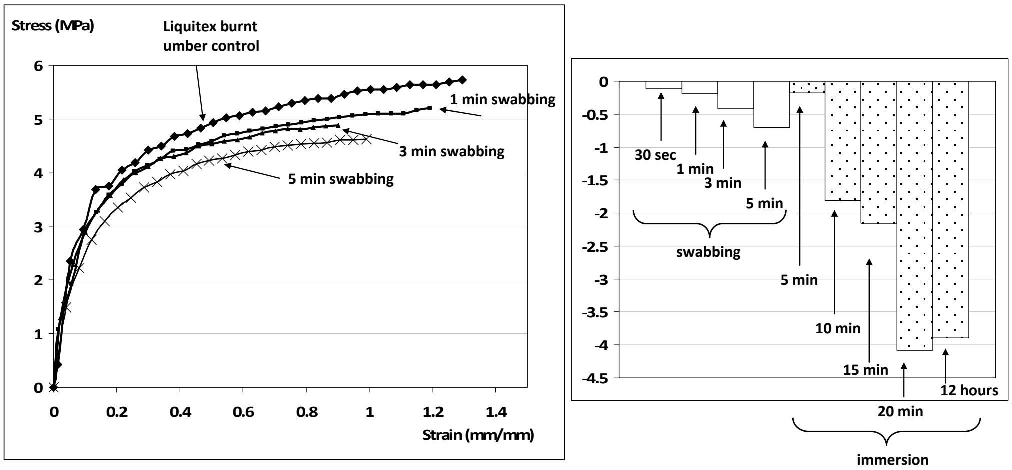
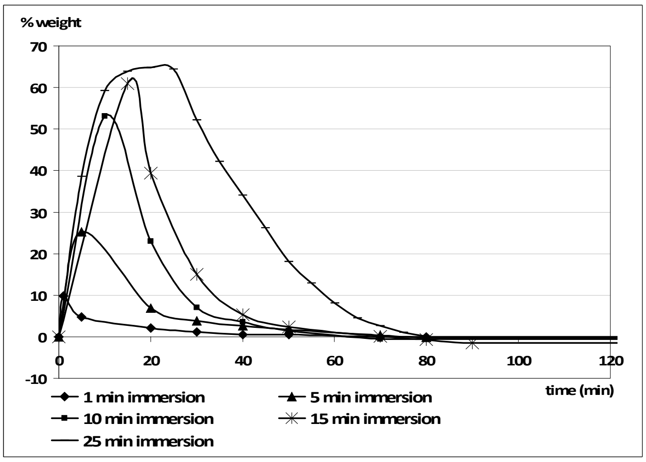


Figure C. 3: leaching of liquitex® burnt umber films subjected to swabbing and immersions. The mechanical properties of the swabbed films are shown in the left image.

C.3- A study on the cumulative effects of water immersion tests as simulations of water-based surface cleaning treatments

The effects of short immersion tests in the leaching of additives were tested for Liquitex® burnt umber and phthalocyanine blue paint samples. The scope of these tests is to bring some insight into the effects of cleaning treatments where water is in contact with the painted surface only for a short period of time. In Figure B.3-B.4 are shown the different water absorption and drying profiles for Liquitex HB burnt umber at immersion tests at 1, 5, 10, 15 and 25 minutes. The leaching effects of these immersions are also presented.

According to these results, the leaching of additives depends on the water penetration into the bulk film and may vary with the film sensitivity to water. In the case shown in Figure B.3-B.4, the phthalocyanine blue sample, which absorbs faster than burnt umber, accuses leaching sooner.



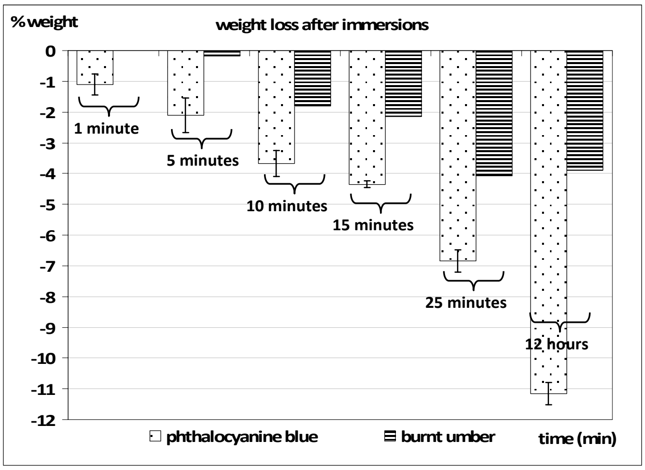


Figure C. 4- C. 5: (Above) absorption and drying profiles for 1, 5, 10, 15 and 25 minute immersion tests of Liquitex® burnt umber. The figure shows (Below) the weight loss measured for Liquitex® burnt umber and phthalocyanine blue for short immersion tests (1, 5, 10, 15 and 25 minutes). The results obtained for 12 hours immersion tests have been included for comparison purposes.

The mechanical properties of these paint films are shown in Figure B.5-C.6.

Both paint samples lost strength after the first 1 to 15 minutes of immersion tests. This is probably due to the elimination of excess of additive content around the non coalesced polymer particles and pigments, and thus it allows further coalescence processes, after the immersions. In contrast, the samples immersed for more than 15 minutes showed an increase in stiffness, which as been described priorly in this work. This data indicates that prolonged or multiple cleaning treatments in the long run may have negative effects in some acrylic paint formulations.

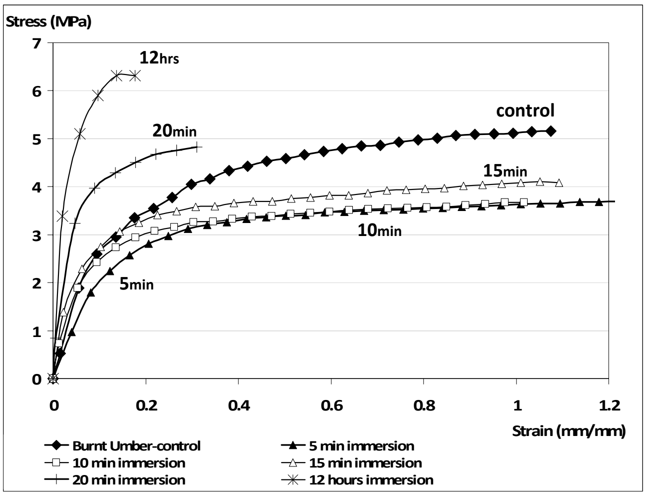


Figure C. 6: the effects of short immersion tests in the mechanical properties of Liquitex® burnt umber. The immersions comprised 5, 10, 15 and 20 minutes. The results obtained for 20 minutes and 12 hours immersions tests have also been included for comparison purposes.

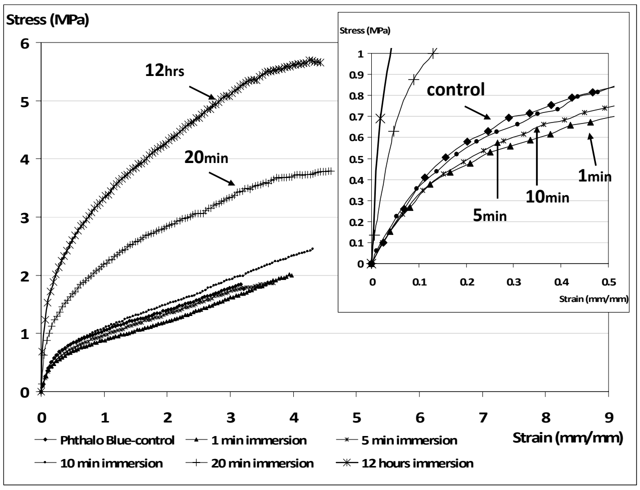


Figure C. 7: the effects of short immersion tests in the mechanical properties of Liquitex® phthalocyanine blue. The immersions comprised 1, 5 and 10 minutes (coincident with 15 minutes). The results obtained for 20 minutes and 12 hours immersions tests have also been included for comparison purposes. In the upper right corner is the magnification of the initial part of the curves.

To prove the cumulative effects of water based treatments in acrylic paint films, a Liquitex® phthalocyanine blue film was immersd six times, for 20 minutes, and compared to a film immersed for 120 minutes (equivalent to six times 20 minutes immersions). The data collected is worth commenting. The absorption-drying profiles of the paint film in the different immersion tests is shown in Figure C.8-C.9, as well as the amount of materials leached after each immersion. Along with the weight measurements from the absorption-drying curves, the variation in length, which correspond to the free swelling of the films, was also registered.

The figure suggests that the paint film progressively loose water sensitivity with increasing number of immersions, which is accompanied with a loss in free swelling response, with good correlation. The additive leaching after each immersion is also present in figure, and shows that most additive loss occurs in the first two immersion tests, corresponding to the immersions where the film swells the most. The sum of this data clearly suggests that acrylic paint films will grow somewhat less responsive to water with repeated cleaning treatments that cause leaching. However, and even without a significant amount of additives present in the bulk, these films will swell and respond to water.

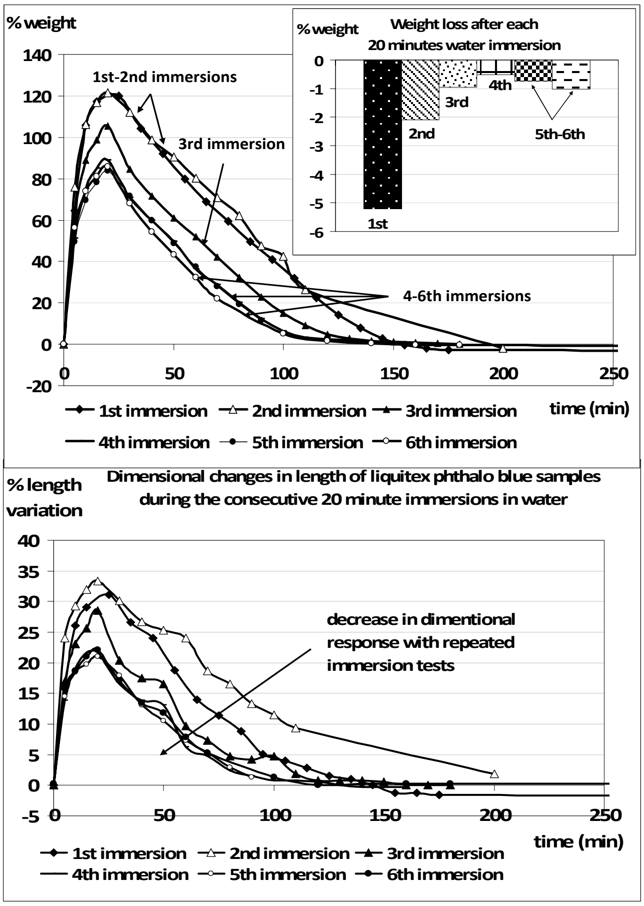


Figure C. 8- C. 9: (Above) aborption and drying profiles obtained for consecutive immersion tests performed with a Liquitex® phthalocyanine blue. The weight loss after each immersion test is also presented. (Below) the free length variation measured as consequence of the immersion and drying of the samples. The samples become less responsive to water after the first two immersion tests.

The mechanical properties of the six 20 minutes immersion tests are contrasted to the sample immersed for 120 minutes in Figure B.9. The scope of this test is to confirm the cumulative damage water can cause over time. The results show that the damaged caused by both trials is comparable, suggesting that repeated immersions can have a similar effect than a long immersion for the same amount time. It also confirms that the results obtained for longer immersion times, such as 12 hours, can be a good preview of the damage that can occur during the lifetime of repeated cleaning treatments of an acrylic paint film.

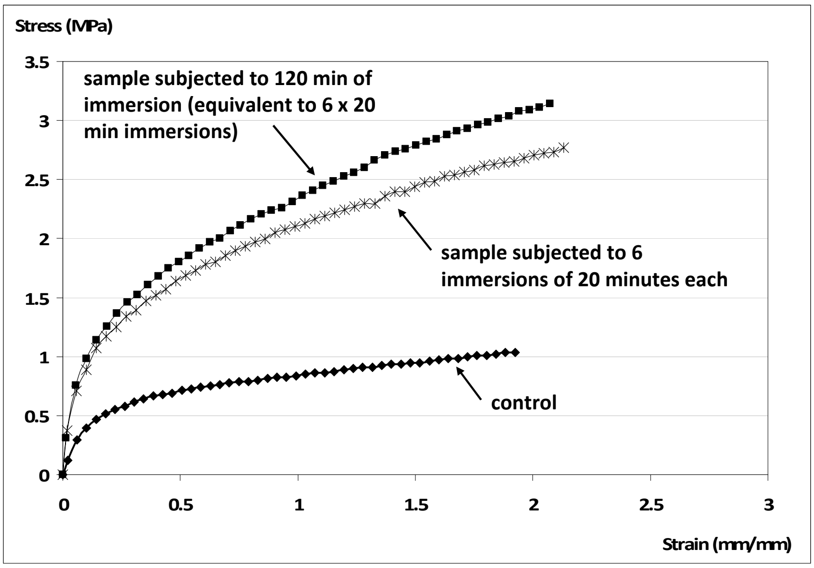


Figure C. 10: the effects of repeated 20 minutes immersion tests in the mechanical properties of a Liquitex® phthalocyanine blue paint sample. The results are compared to a sample immersed for an equivalent 120 minute immersion test.

C.4- Absorption-drying profiles and leaching of other acrylic paint samples: Talens® and Vallejo®.

The results obtained for 30 minutes immersions for several Talens® paint samples are reported in Figure B.10. A similar trend to that of Liquitex® series was observed where the synthetic organic pigments showed higher water absorption and additive loss. The weight loss measured for Talens® colours ranged from 3 to 7 %, corresponding to additive loss with 30 minutes immersion tests, and 5 to 8.5 % with 12 hours immersions.

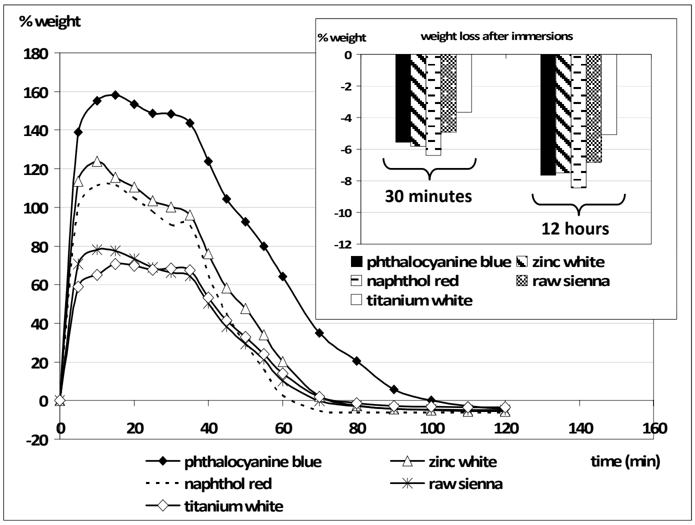


Figure C. 11: absorption and drying profiles obtained for 30 minutes immersion tests of several Talens® acrylic samples. In the right upper corner is presented the amount of material extracted from each paint film after 30 minutes and 12 hours immersions.

The stress-strain data obtained for Talens® raw sienna immersions after 5, 20 minutes and 12 hours immersions are shown in Figure C. 11. A progressive increase in stiffness is observed with immersion time. An initial increase in flexibility is also evident after the first 5 and 20 minutes immersions and this is ascribed to the elimination of residual surfactants around the polymer particles that were impeeding full coalescence of the film. After the 12 hours immersion tests there was a significant decrease in flexibility, when compared to the other immersions. However, the strain to brake is comparable to that of the original control sample, which can deform up to almost 200 % its original length prior to failure.

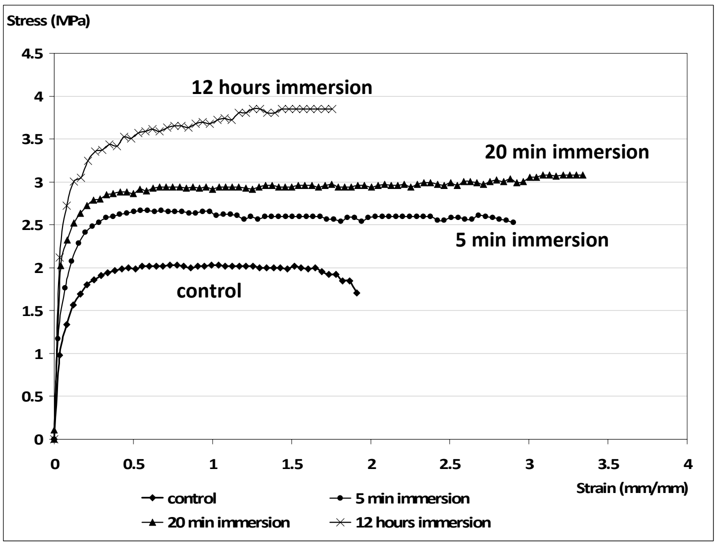


Figure C. 12: the effects of water immersion tests in the mechanical properties of Talens® raw sienna paint samples. Raw sienna samples have been subjected to 5, 10, 20 minutes and 12 hours immersions.

The Vallejo® paint brand demonstrated the largest water absorption during the immersion tests. The maximum water absorption in % weight for immersions of 80 minutes and 12 hours are shown in Figure C. 13, as well as additive loss. It is evident that organic pigments are associated with films that are more responsive to water, as observed for all the previous brands tested.

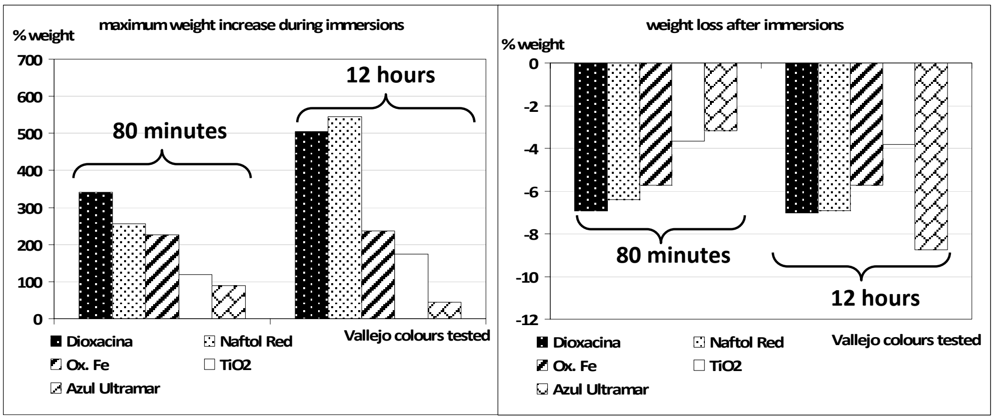


Figure C. 14: (Left) maximum weight increase during 80 minutes and 12 hours immersion tests. Vallejo® samples can present a noticeable amount of water absorption, specialy colours formulated with organic synthetic pigments. (Right) additive leaching measured by weight loss after the same immersion tests.

The Vallejo® brand presents similar results to those obtained for Liquitex® and Talens®. The immersion tests lead to a strong swelling effect and deformation after drying. The mechanical properties show a clear increase in stiffness after 80 minutes of immersion, but the samples still retain flexibility and deform up to 400 % their original length. After the 12 hour immersion, the films loss some flexibility and became slightly stiffer. However, the samples showed deformation capacity of 240 %.

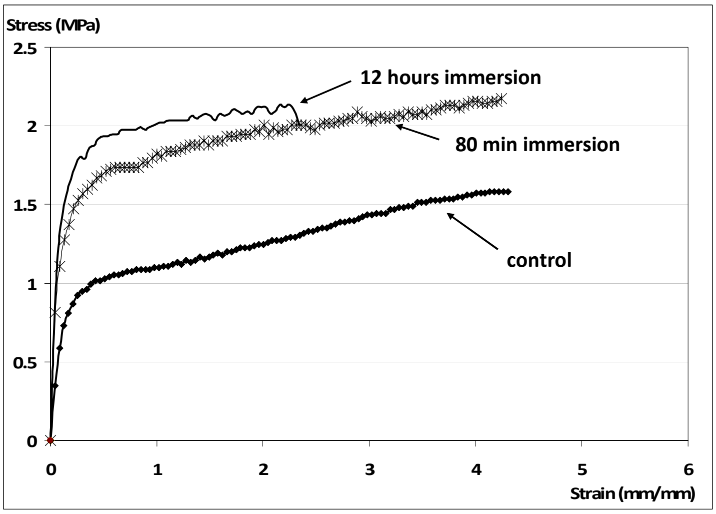


Figure C. 15: the effects of water immersion tests in the mechanical properties of Vallejo® iron oxide paint films. The samples were subjected to 80 minutes and 12 hours immersions tests. The data shows consistent trends with those shown for the previous studied brands.

C.5. The effects of water immersions in Liquitex® Heavy Body paints: variations in mechanical behaviour according to the pigments present in the formulation

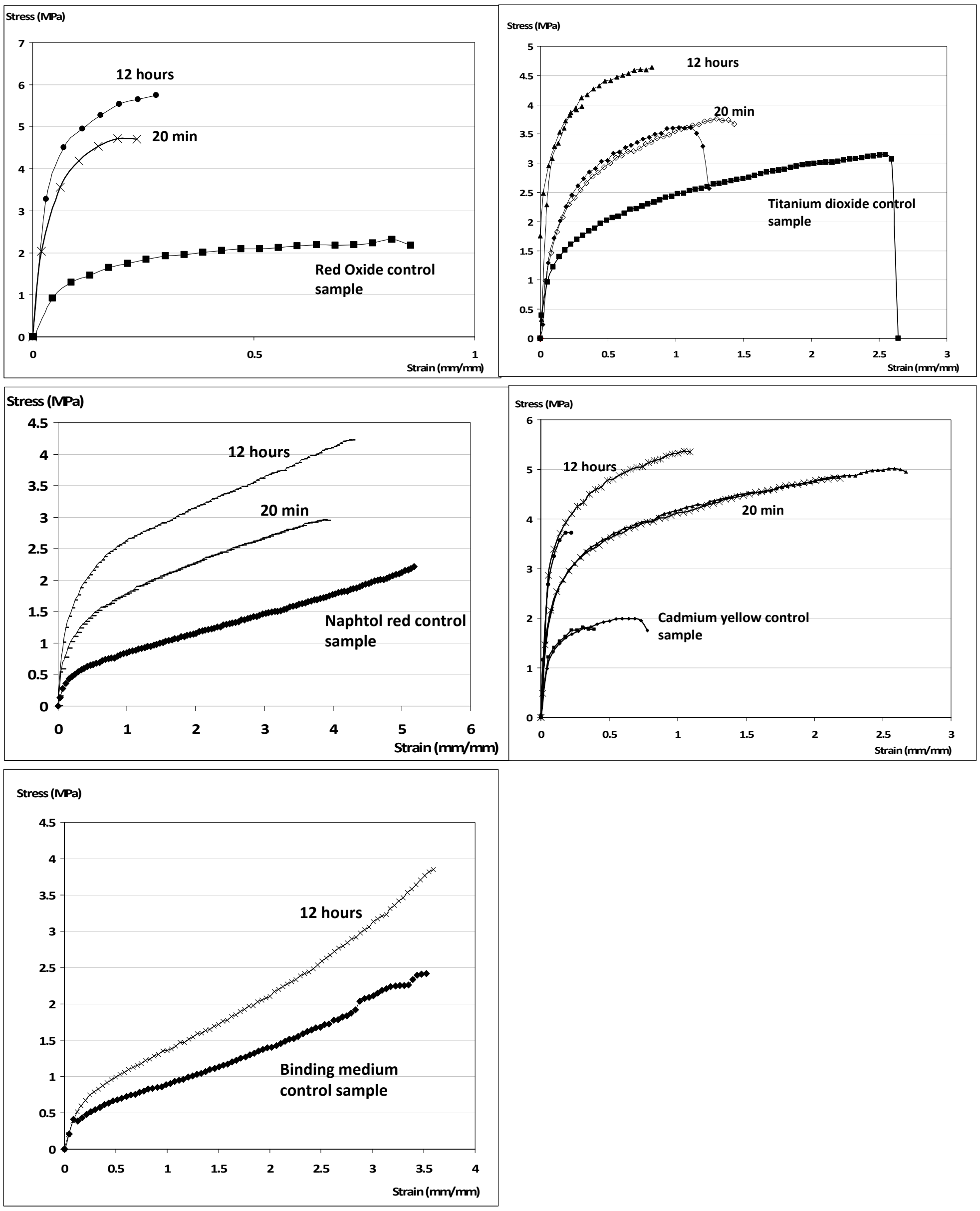


Figure C. 16: mechanical properties of several Liquitex® Heavy Body films immersed in water. The results are discussed in the main text. It is interesting to notice that the binding medium, even though not very sensitive to water also presents an increase in stiffness after long immersions. However, the medium films become tougher but not brittler.

C.6- Images of water immersion tests and other cleaning treatments

Some images obtained during the cleaning trials are included in this section for illustration purposes. Figure C.17-18 are examples of the swelling effects of water immersions on some acrylic paint films. And figures C.16-19 show examples of water-based gels and emulsion systems tested in the course of this study.

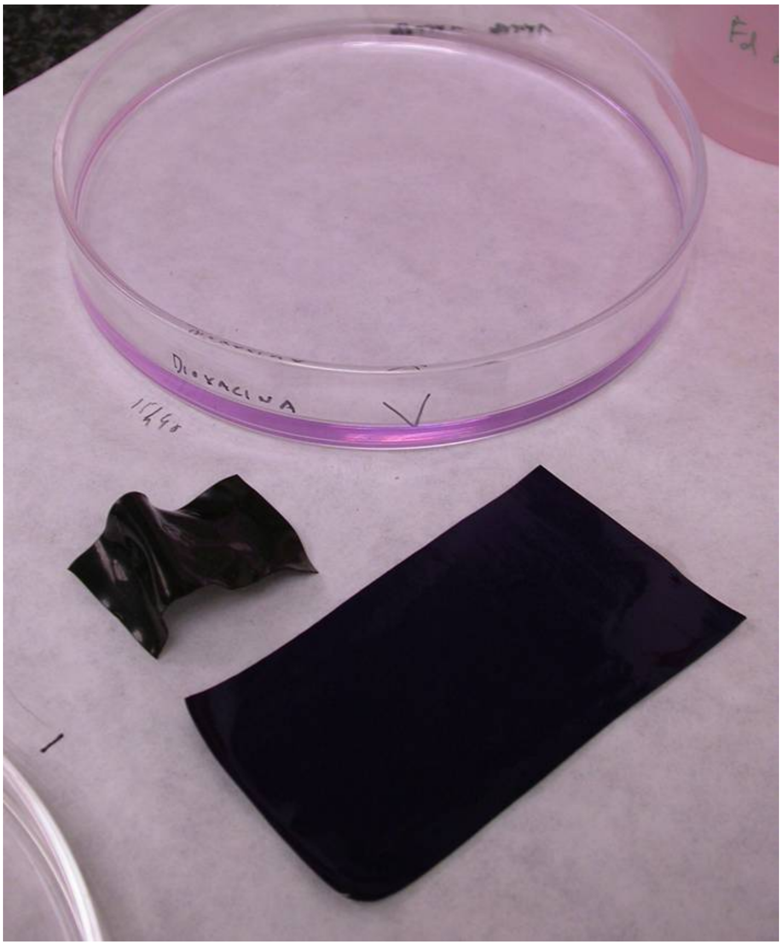


Figure C. 17: the effects of awater immersion in a Vallejo® dioxacine purple sample. Both films were the same size before the immersion. The film in the left is swollen from the 12 hour immersion test. Also visible in the figure is the solubilization of pigment in the water.

Figure C. 18: The effects of water immersion tests on Pébéo® pthalocyanine blue and naphthol crimsom paint samples. The resulting films were brittle and changed appearence.Pébéo® was the only paint brand tested in this work that showed such results.

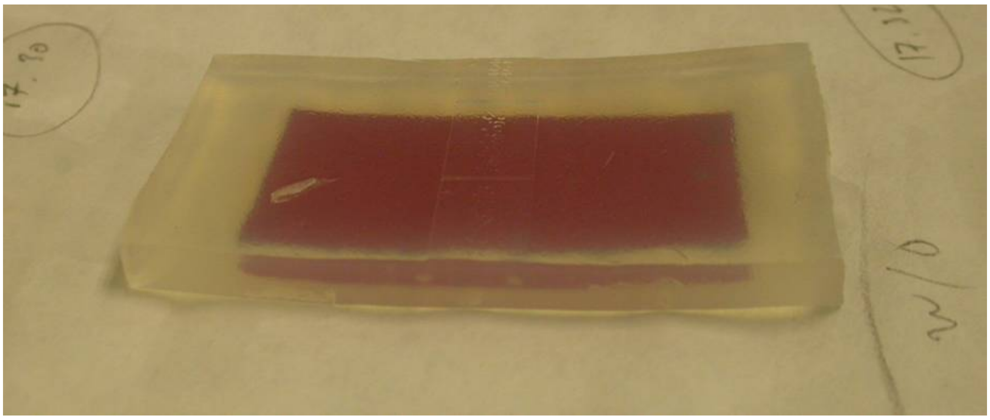


Figure C. 19: The application of an Agar-agar® (2g/100ml) rigid gel on Pébéo® naphthol crimsom surface. The paint samples exhibited a discrete swelling effect and no evident change in colour was seen. This contrasts with the images shown in the figure above.

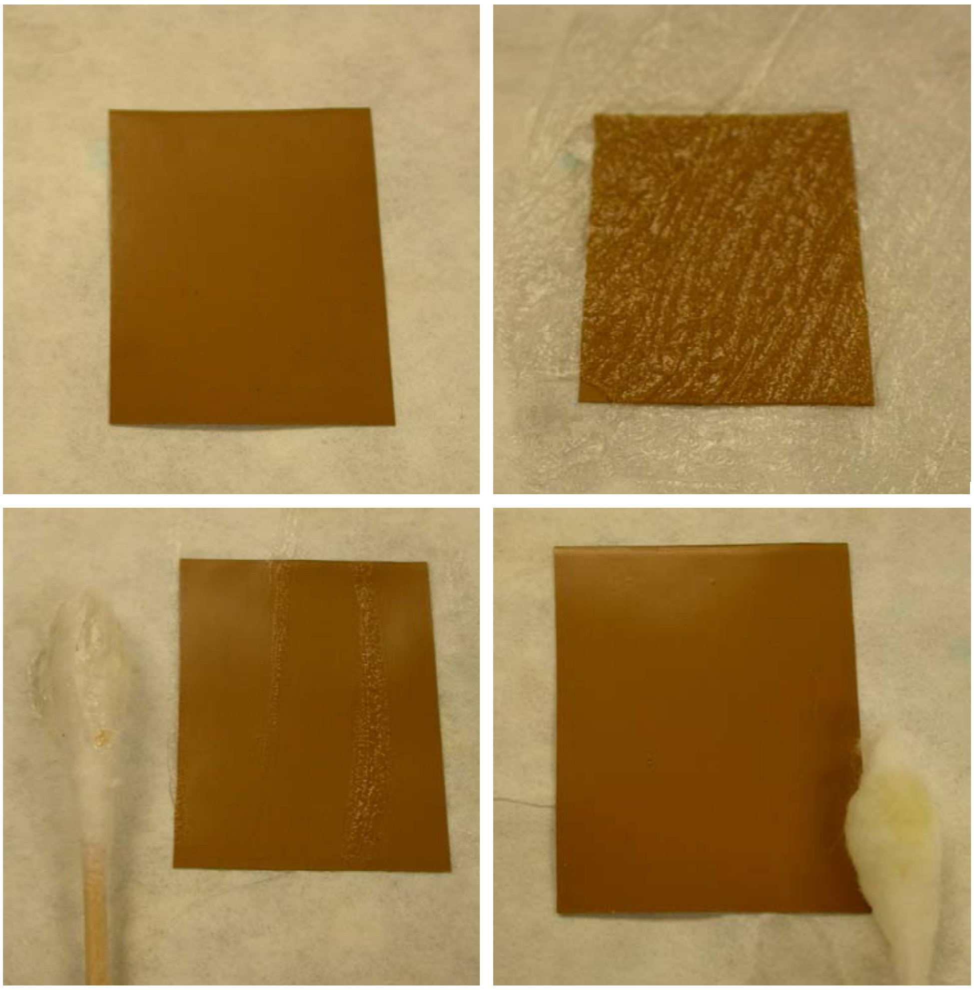


Figure C. 20: application of a Carbopol® Ultrez 21 water based gel neutralized to pH 6.5 with a NaOH [1M] solution on a Talens® raw sienna paint sample. The acrylic was exposed to the gel for 30 minutes. After the application of the gel, the films exhibit little swelling effect and appear unaffected.

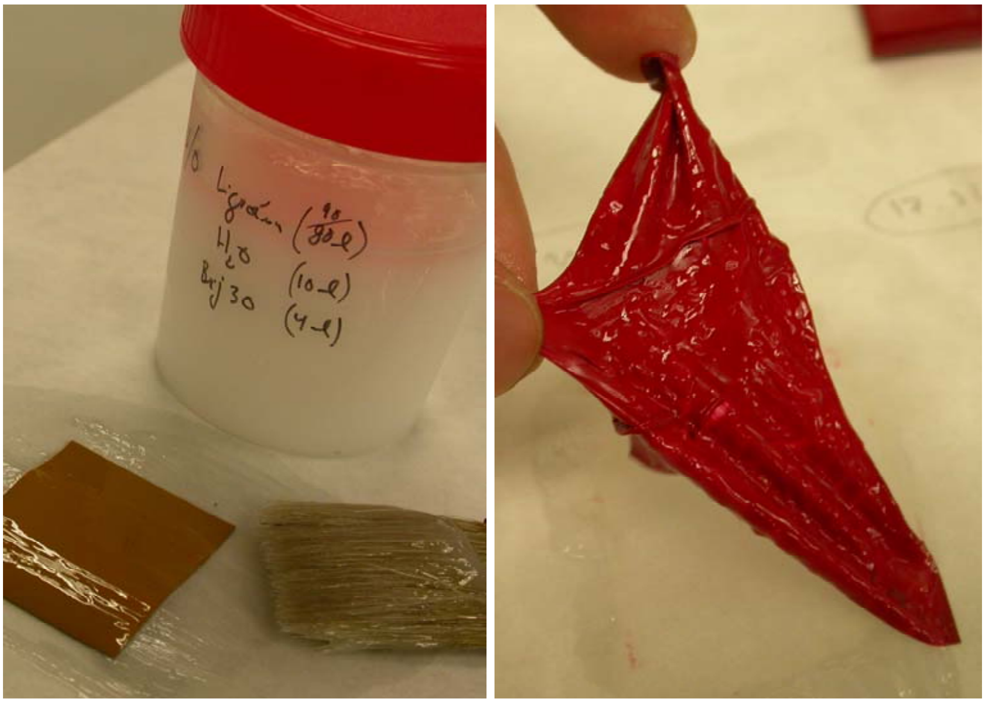


Figure C. 21: the application of a W/O (ligroin) system in two test samples. On the right Talens® raw sienna did not exhibit any changes with the application of the emulsion, whereas the Pébéo® naphthol crimson film was destroyed after a few minutes in contact with the emulsion system.

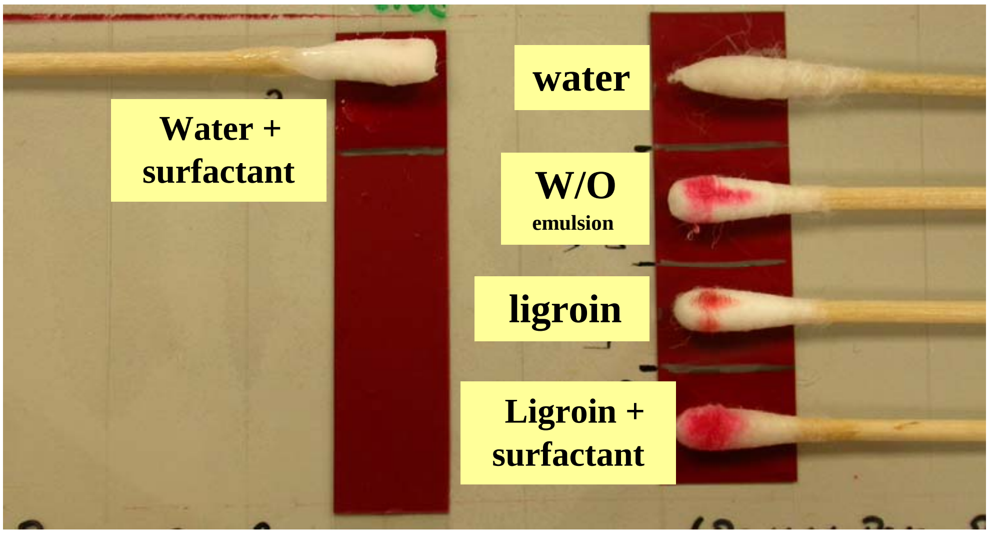


Figure C. 22: solubility tests performed in a Pébéo® naphthol crimsom with the different components of a W/O emulsion system. The effects of the emulsion seen in the previous figure are attributed to the ligroin and surfactant mixture that enhancD.1 e the solubilization of the acrylic (increase Fd value) medium already shown by ligroin in the free form.

C.7- Additional information on alternative cleaning treatments

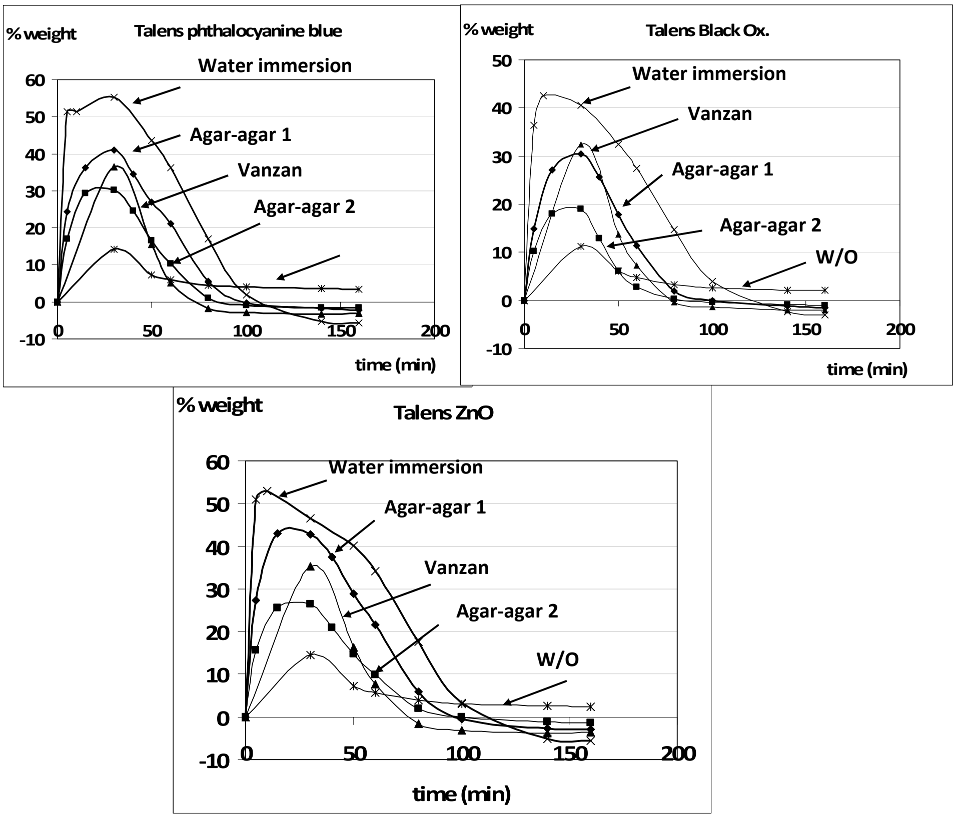


Figure C. 23: absorption and drying curves of other Talens® paint films tested. In each figure is shown a 20 minutes immersion in water, Vanzan® NF-C and Agar-agar® gels as well as a W/O emulsion in ligroin. It is interesting to notice that all colours retained ligroin in the bulk film, which contrasts to the results obtained for the Talens® raw sienna paint sample.

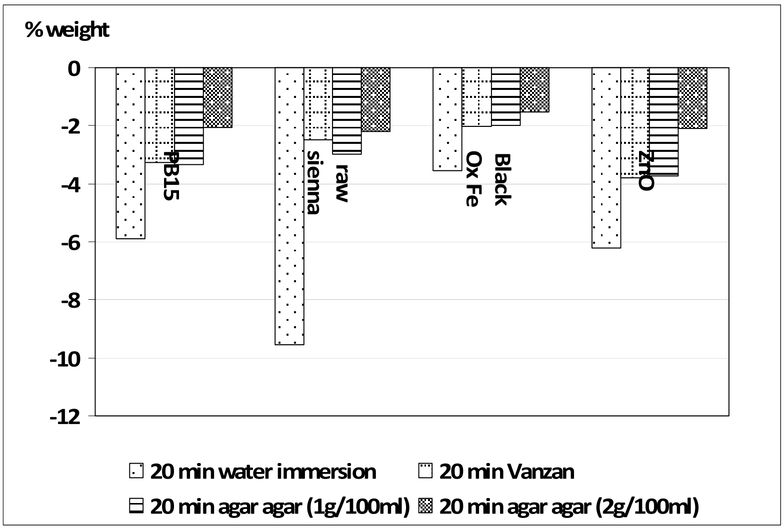


Figure C. 24: weight loss registed after each trials. Data on W/O emulsion can be consulted in the main text (Table 6.3.7).

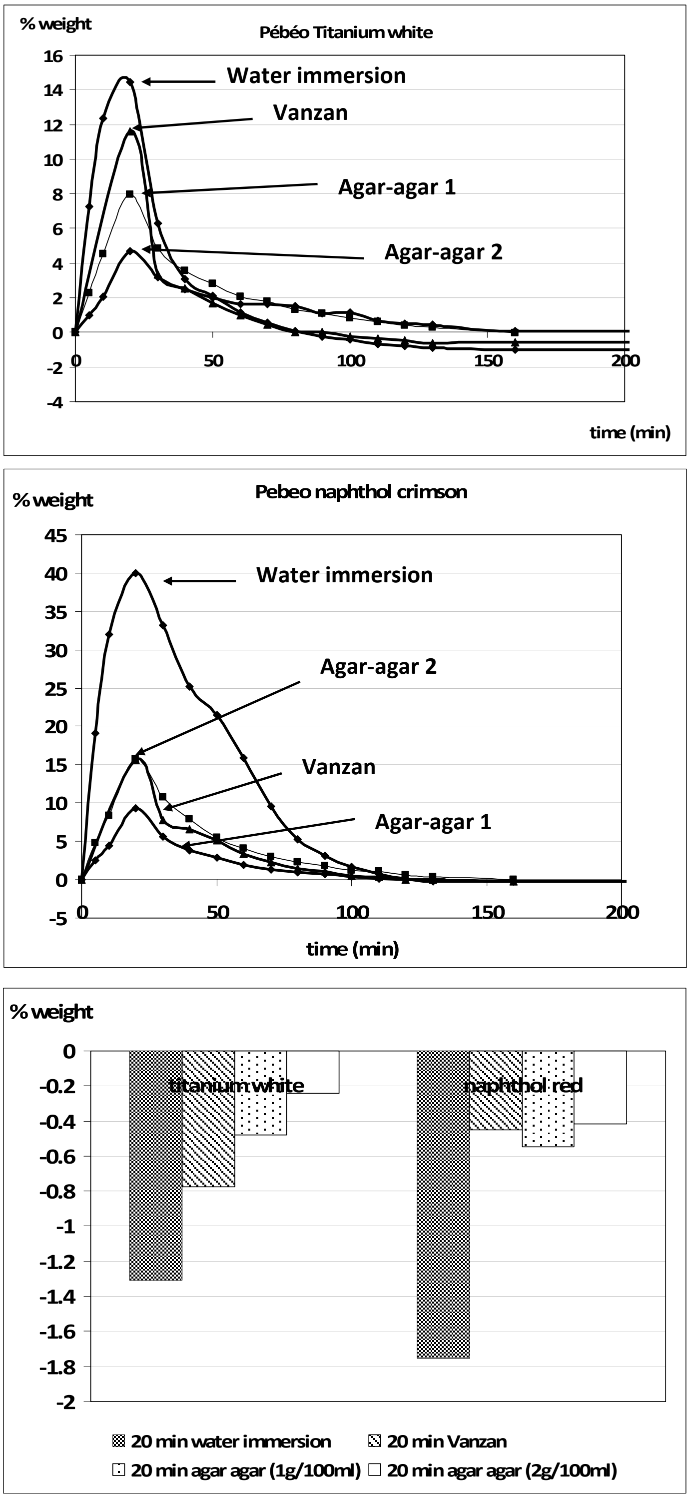
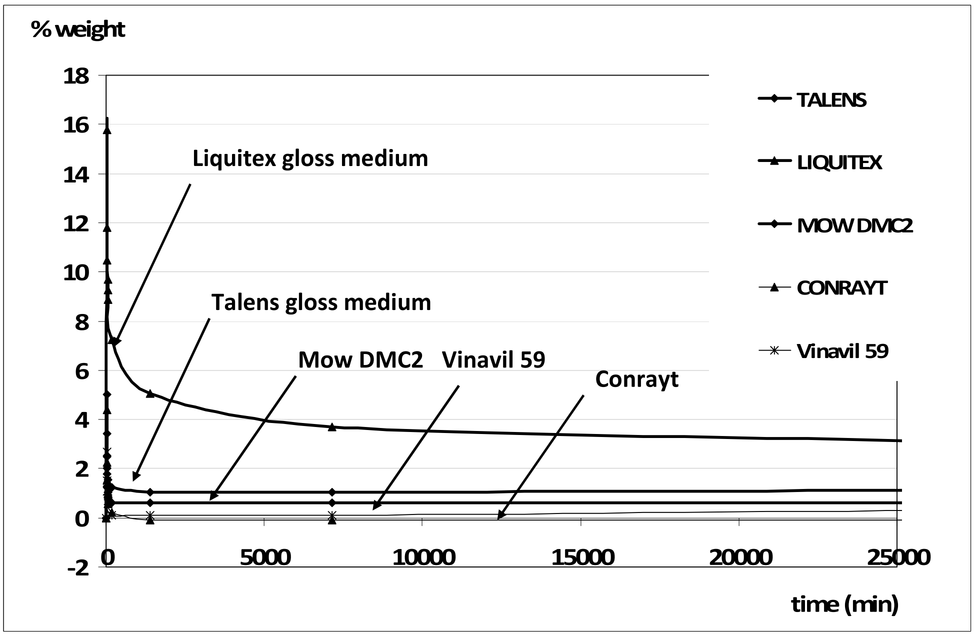


Figure C. 25: absorption drying curves of Pébéo® Titanium white (Top) and Naphthol crimson (Middle), and weight loss after the cleaning trials (Bottom).



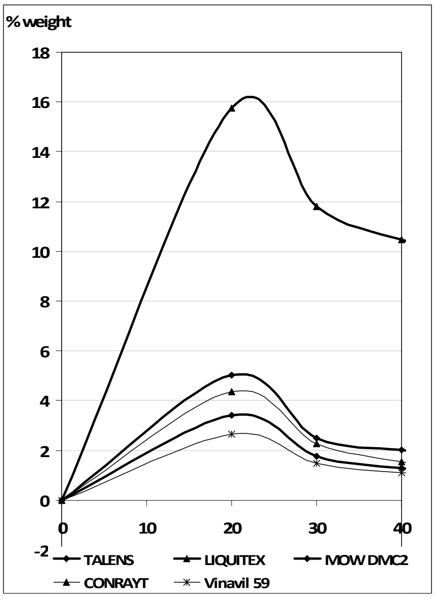


Figure C. 26: (Top) the drying and absorption of W/O emulsions in a series of binding media (Below a detail of the first 20 minutes): Liquitex gloss medium and varnish, Talens gloss medium, Vinavil 59, Mowilith DMC2, and Conrayt. The Liquitex film was reactive to the emulsion and absorbed ligroin very rapidly from the emulsion, and the film became very tacky and difficult to handle. The solvent was retained for a long time in the paint film (about 1 month). Talens gloss medium was less reactive to the emulsion, but the film was softer after the treatment, with retention of the solvent similar to that measured for Liquitex. The PVAc based films were not as affected by the emulsions as the acrylics. This was especially true for Conrayt.

APPENDIX D – Experimental protocol adapted to the study of the mechanical properties of acrylic/PVAc paint samples with high elongation at brake

D.1- Adaptation of the stress-strain tests protocols to the materials studied in this thesis

Acrylics and PVAc media[43] present high elongation values at 20-25ºC, which could not reached by means of the testing protocols used by Mecklenburg and Fuster (for studying materials such as oils, animal glues, starches and filling materials) with the same tensile strength testers [1-6]. This is because the initial sample dimentions are too big (100 mm x 5 mm x 0.2 mm (length, width and thicknes respectively) and allow a small gage separation, which was not enough for acrylic or PVAc samples to brake.

In the studies carried out here, the scope is to obtained as much information as possible from the samples (Modulous and strain/strength to brake) and avoid significant time dependent effects of the testing protocols. This has been adressed in the introduction of this thesis. Thus, studying the strain to brake values is very useful for determining trends in degradation with aging, or damage with a particular cleaning treatment. For this, and foreseing that these materials may stretch more than 100% their original size [1-15], the tensile tests have been adapted to the objectives pursuited.

In Figure D. 1 is shown the results of a series of stress-strain tests for Liquitex® burnt umber at 25ºC, 50% RH with low strain rates 0.1inc/30sec, sample size 100mm x 5mm x 0.2 mm.

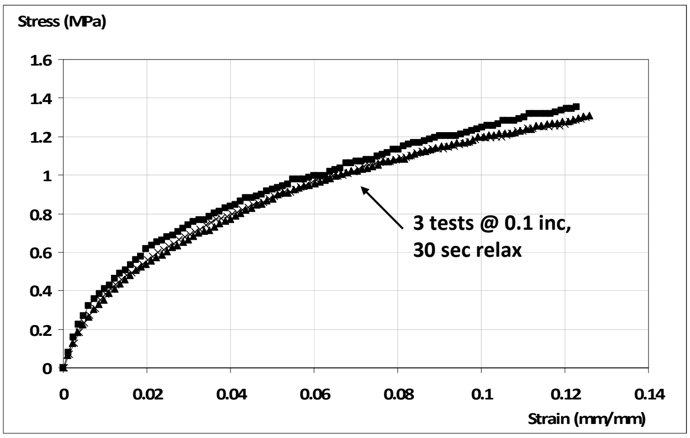


Figure D. 1: stress-strain tests of Liquitex® burnt umber at 25ºC, 50% RH with low strain rates 0. 1inc/30sec, sample size 100mm x 5mm x 0.2 mm. The results show a very good reproducibility of these tests, but the gage opening is not enough to samples to fail. The tests were stopped at 12 % deformation.

In order to keep semi-equilibrium conditions, the tests were run with 30 seconds relaxation after each strain application. The reason why this is done has been discussed in the introduction of this work and related to the time dependent properties of viscoelastic materials. Moreover, measuring each 30 seconds allows to collect data manually within a reasonable amount of time (around 1-2

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[43] Flashe® paints do not present similar behaviour. They are britlle samples.

hours for sample, depending on ultimate strain to brake). Otherwise these tests could not have been done, since it could take weeks to measure a set of samples at reals equilibrium conditions [3-5]. Another series of stress-strain tests were run changing strain rates and maintaining sample size, in order to test the effects of the strain rates in these samples. Samples rates chosen were 0.3, 0.4 and 0.5 inc maintaining sample size and environmental conditions.

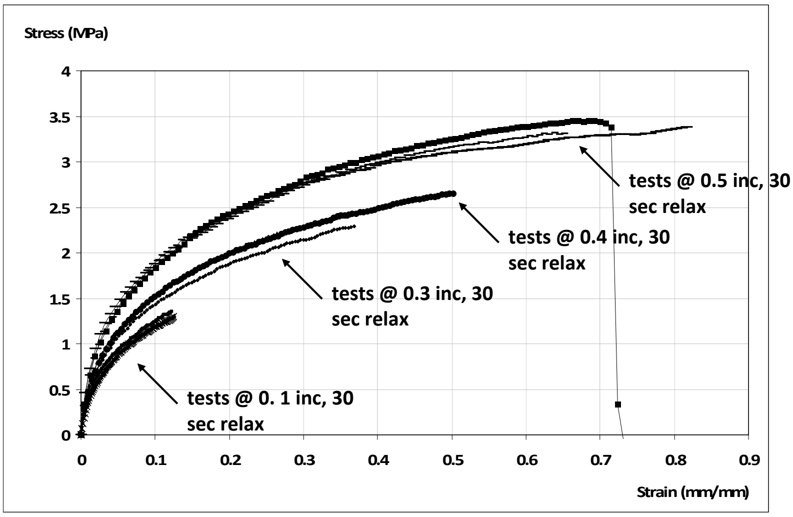

Figure D. 2: stress-strain tests of Liquitex® burnt umber at 25ºC, 50% RH at different strain rates. Only one sample broke at 70% its elongation.

Considering that this sample was the stiffest of the Liquitex® set of samples and failure was still difficult to achieve, the sample size was changed from 100 mm to 15 mm in length, maintaining the other dimentions. Tests were run at 0.5 inc, 30 seconds relaxation for burnt umber (stiff paint) and phthalocyanine film (very flexible paint). Failure was obtained for both samples (phthalocyanine blue broke very near full gage separation, around 550% deformation) and the overall mechanical properties was not compromised when compared to the protocols proposed by others. This is shown in Figure D.3. In this way a good compromise was achieved between speeds of test (without changing to a glassy behaviour) and amount of information obtained at semi-equilibrium conditions (Modulous and ultimate strain/stress).

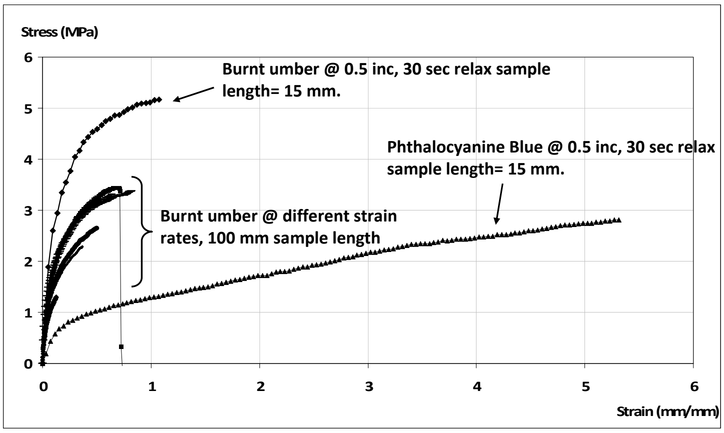

Figure D. 3: mechanical properties of burnt umber and phthalocyanine blue at 0.5 inc, 30 seconds relaxation, with reduction in the sample size. It is possible to achieve failure under these conditions.

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D.2- Monitoring the rupture of acrylic paint films: the effects of the presence of defects such as pores. Case study: Liquitex® burnt umber film before and after immersion in water.

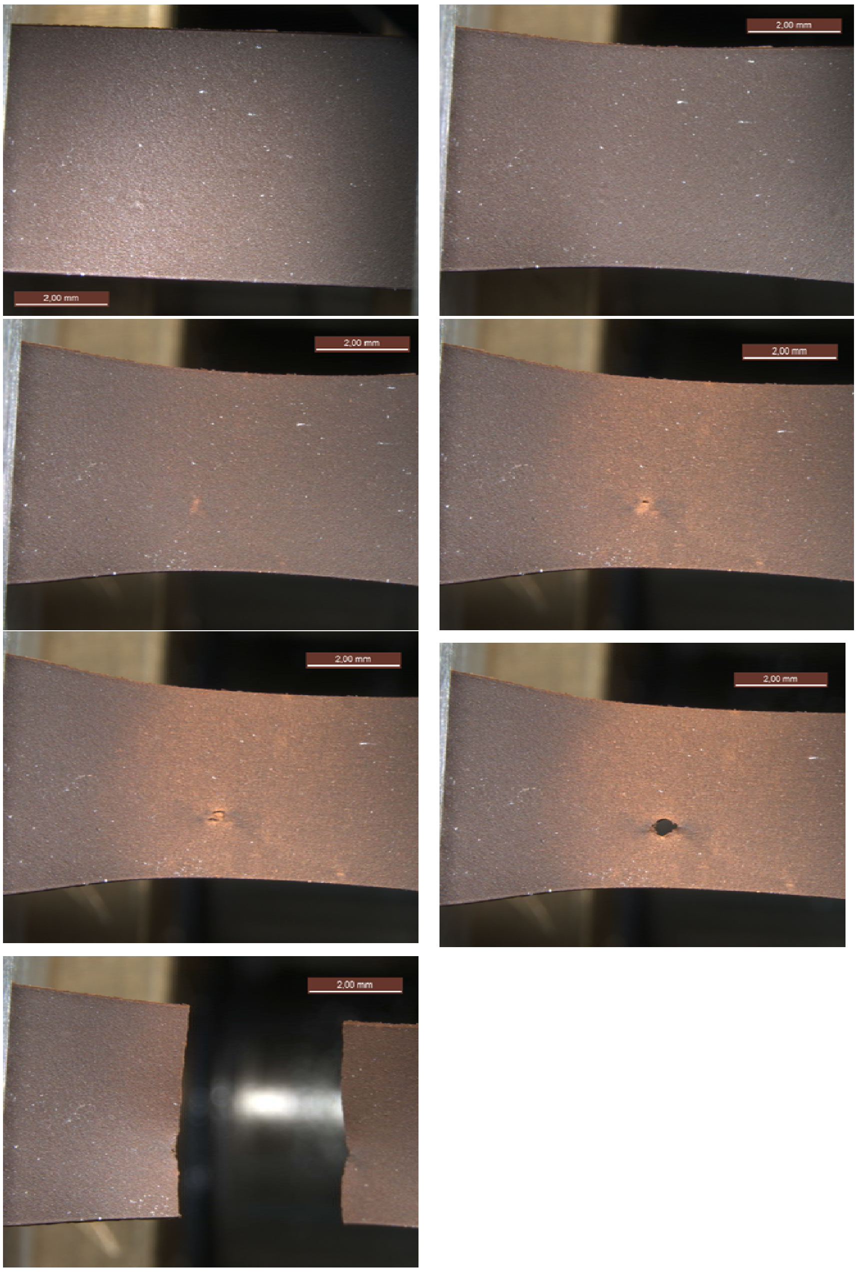

Figure D. 4: failing mechanism of a liquitex® burnt umber untreated sample. The figure shows the stree-development in a diamond shape pattern around a micropore. The stress concentration, ultimately, leads to the facture of the paint film under high strains.

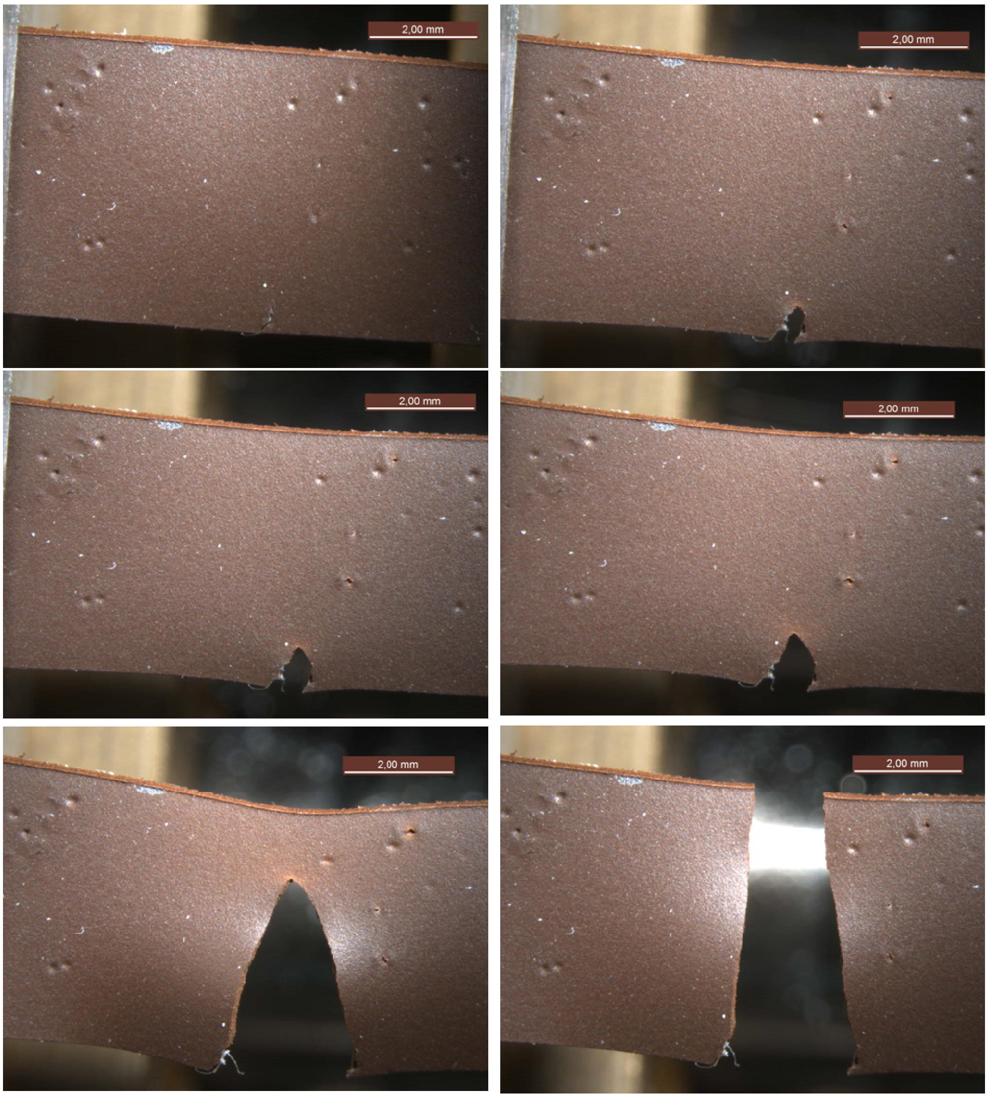

Figure D. 5: failing mechanism of a liquitex® burnt umber immersed for 12 hours in water. It is visible the profusion of pores throughout the surface of the sample created with the immersion treatments. This makes the sample much more likely to fail sooner. Indeed, the sample showed little elongation when compared to the untreated one shown in Figure D.4. The stress strain data from similar samples have been discussed in the main text and can be consulted in Figure 6.3.17.

APPENDIX E – Experimental protocol developed for Py-GC-MS: the use of HMDS for the characterisation of additives in PVAc paints.

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IDENTIFICATION OF ADDITIVES IN POLY(VINYLACETATE) ARTIST'S PAINTS USING PY-GC-MS

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Abstract

Commercial poly(vinyl acetate) (PVAc) paint formulations for artists include a number of compounds in addition to the PVAc polymer and pigments to improve the physical and chemical properties of the resulting product. Among the most common additives are surfactants, coalescing agents, defoamers, freeze-thaw agents, thickeners. These products significantly influence the behavior of the dried film. Nevertheless, they are usually difficult to detect with conventional analytical methods given their low concentration.

In order to identify these additives, present in the dried film as minor components, an analytical method based on in-situ thermally assisted pyrolysis-silylation GC-MS using hexamethyldisilazane (HMDS) as a derivatization reagent is proposed. This method improves the conventional GC-MS analysis performed by direct pyrolysis and enables the simultaneous identification of the PVAc binding medium and the additives included by the manufacturer in the commercial paint. Five different commercial PVAc paints have been analyzed, namely, armour green, burnt umber, oriental red, raw umber and white from Flashe®. Internal plastizicer VeoVa consisting of C_{10} fatty acids with highly branched chains has been recognized from the MS spectra. On the other hand, the differences found in the additive content of the studied paints, in particular the PEG (polyethylenglycol) type surfactant, are in good agreement with their mechanical properties.

INTRODUCTION

Artists' waterborne paints are prepared with a series of additives that seek the stabilization of the paint during storage, transportation, application and lifetime service.

Prior to turning into a paint, the binding medium, or latex, counts upon several additives such as initiators, chain transfer agents, buffers, surfactants, protective colloids, preservatives and residual monomers. The paint manufacturer will then add several other compounds to achieve the desired properties for the paint, and these may include wetting and dispersing agents, coalescing solvents, defoamers, preservatives, thickeners and rehology modifiers, freeze thaw stabilizers, pigments and extenders [1,2].

When the paint is applied, most of these components stay in the dried film and for conservation purposes their identification and the influence they will have in the overall properties of the dried bulk material is of the outmost relevance. It has been shown that surfactants take an important part in the film formation process, surface tackiness, water sensitivity and overall mechanical properties of the resulting films, as well as they are also associated with changes in gloss, colour and staining [3-7]. Nevertheless, the way these additives will interact and influence the aging of these materials is quite unknown to date, since the development of the paint industry has been very much based on practical experimentation [1].

The identification of additives is also of critical importance for conservation science when plannig conservation treatments such as cleaning and consolidation, since solvents and water may have a direct effect in the overall paint film due to removal of possible additives.

Several analytical techniques and methods have been applied and developed in view of the identification and characterization of additives in synthetic polymers. Nevertheless, most references found concern general industrial applications, and mainly tend to focus their studies in one type of additive. The more specialised papers on waterborne paints are generally focused on acrylic and PVAc type resins and focus in the detection of pigments, surfactants and/or plasticizers. A good review of analytical techniques applied for the characterization of coatings has been provided by Andersen [8].

Thus, several authors have presented studies on the identification of surfactants, mainly poly(ethylene glycol) type (PEG) surfactants, by means of Fourier Transformed Infrared Spectroscopy (FTIR) and Attenuated Total Reflectance (FTIR-ATR) [4-7,9-11]. Alkylaryl polyethoxylate type surfactants, have also been sucsessfully identified by means of Size-Exclusion-Chromatography combined with FTIR spectroscopy (SEC-FTIR) [12]. And also the use of chromatographic techniques, such as high performance liquid chromatography (HPLC) coupled with MS and Diode Array Detector (DAD), and Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) have been reported to detect this non-ionic type of surfactant (alkylaryl polyethoxylate) used to stabilize acrylic formulations. These techniques have the analytical advantage of having high sensibility and reduce considerably the size of the samples tested [12,13].

Recently, MALDI-MS and nanospray-ESI-MS have also proved to be sucsessful in determining the structures of poly(ethylene glycol) additives from both test specimens and paint microsamples [14,15].

The identification of plasticizers present in artist's commercial paints and binding media has been performed by spectroscopic techniques such as FTIR spectroscopy [16]. Nevertheless, Py-GC-MS has obtained much importance in the identification of these compounds, since it can discriminate with accuracy the type of plasticizer present in the paint's formulation [16-23].

In general studies, for industrial applications, Wang has published articles concerning the study of lubricants, antioxidants and flame retardants by means of Py-GC-MS [24-26]. Py-GC-MS has also been used by Blaszó for the study of the thermal decomposition of hindered amine light stabilizers (HALS), as well as liquid chromatography–ultraviolet absorbance detection–evaporative light scattering detection [27,28]. Temperature-Programmed Pyrolysis Hyphenated with Metastable Atom Bombardment Ionization Mass Spectrometry (TPPy/MAB-MS) has also been used to detect light stabilizers in car paints [29].

Hexamethyldisilazane (HMDS) as derivatization reagent for thermally assisted pyrolysis in GC-MS has already been applied successfully in the analysis of a number of organic compounds such as proteins, polysaccharide, lipids, terpenoid, acrylic and poly(vinyl) resins [30]. In particular, this method efficiently converts carboxylic and hydroxyl groups into their less polar TMS derivatives from fatty acids present in lipids [31]. Notable reduction of side reactions during pyrolysis is the main advantage of this method and, as consequence, simpler pyrograms than those from thermally assisted hydrolysis methylation (THM) are obtained. In this paper, use of *in-situ* thermally assisted pyrolysis-silylation GC-MS using HMDS is discussed for the identification of additives present in Flashe® waterborne armour green, burnt umber, oriental red, raw umber and white PVAc based paint colors. In a first step, this method has been tested in a set of paint samples and has been compared with results obtained for the same samples analysed with direct pyrolysis. In a second step, water extractions of the paint samples have been analysed in order to detect minor water soluble components present in the paint films and their corresponding peaks, retention times and mass fragmentation patterns.

EXPERIMENTAL

Analytical reagents and reference materials

Five different commercial PVAc paints have been analyzed, namely, armour green, burnt umber, oriental red, raw umber and white from Flashe®. The paints were supplied by LeFranc & Bourgeois.

Preparation of test specimens

Film specimens were prepared by casting commercial Flashe® vinyl paints colours over mylar® sheets. The colours prepared consisted of armour green, burnt umber, oriental red, raw umber and white. The products were left to dry for a year before testing, and the resulting films exhibited an average thickness of 0.15 mm.

Preparation of extractions

Samples weighting approximately 0.4-0.5 g were immersed in deionized water for 24 hours. The films were then removed and the water was dried at 50ºC in a laboratory oven. A waxy extract was obtained for analysis by Py-GC-MS.

Preparation of samples for Py-GC-MS

Samples and extracts were scrapped with a scalpel and introduced in a quartz tube with a small plug of quartz wool. For samples analysed with a derivatising reagent, 1 µL of HMDS was afterwards added.

Instrumentation

Py-CG-MS

Pyrolysis–gas chromatography–mass spectrometry was carried out with an integrated system composed of a CDS Pyroprobe 1000 heated filament pyrolyser (Analytical Inc., New York, USA), and an Agilent Technologies (Palo Alto, Ca., USA) 6890N gas chromatograph coupled with an Agilent Technologies 5973N mass spectrometer and equipped with a pyrolysis injection system. An HP-5MS capillary column (5% phenyl methylpolysiloxane; 30 m, 0.25 mm i.d., 0.25 µm) was used.

In-situ thermally assisted pyrolysis-silylation GC-MS using HMDS was performed with a temperature of pyrolysis of 700°C, for 10 s using a precalibrated Pt coil-type pyrolyser (CDS Pyprobe).

The pyrolyser interface and the inlet were set at 250 °C. Samples were injected in split mode (split ratio 1:40).

The GC temperature was initially 50 °C for 2 min, and then programmed at 5° min^{-1} to 100 °C, then at 15° min^{-1} to 295 °C, held for 10 min. The electronic pressure control was set to the constant flow mode with vacuum compensation. Helium gas flow was set at 1.2 mL min^{-1}

Ions were generated by electron-impact (EI) ionisation (electron energy 70 eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was scanned from m/z =20 to m/z =800, with a cycle time of one second. Agilent Chemstation software G1701CA MSD was used for GC–MS control, peak integration, and mass spectra evaluation. Tuning and calibration of the mass spectrometer was checked using perfluorotributylamine (PFTBA). EI mass spectra were acquired in the total-ion monitoring mode and Peak area (TIC) data were used to obtain values of peak area percentage. The temperatures of the interface and the source were 280ºC and 150°C, respectively. Compounds were identified by use of the NIST and Wiley Library of Mass Spectra and a library created by the authors for PVAc compounds.

RESULTS AND DISCUSSION

Optimization of the analytical method

Temperature of pyrolysis - Derivatisation of samples

A series of pyrolysis with derivatising reagent HMDS were performed at different temperatures ranging from 50ºC to 800ºC on Flashe® oriental red samples in order to determine the most adecuate temperature conditions for the analysis of minor components for this type of paints. The pyrograms presented in figure 1(A-C) show the results obtained at temperatures of 400ºC, 550ºC and 700ºC, respectively. According to these results, a general trend can be observed that provides useful information for establishing an analytical protocol.

Thus, analyses run at temperatures below 400ºC show no major peaks that can be related to compounds of interest present in these paints. However, it is interesting to notice that there is a small trace of trimethylsilyl ester (TMS) of ethanoic acid which is a product of the decomposition of poly(vinyl acetate) polymers chains during pyrolysis [3, 21]. In analyses performed with direct pyrolysis, the peak corresponding to ethanoic acid would appear as a fronting peak in the first minutes of the pyrogram. In contrast, in figure 1-A, the peak corresponding to the TMS form of the ethanoic acid appears as a well defined peak. This result evidences the derivatising efficiency of HMDS for polar type componds such as organic acids, as presented in previously published studies [20, 21].

Above 400ºC, several compounds of interest start to appear in the pyrogram which provide good information about the polymer main chain and additives from the waterborne paint. Figure 1-B shows a pyrogram obtained at 550ºC in which a series of peaks ascribed to vinyl versatates (VeoVa) are pointed out. These products are commonly included as internal plasticizers in PVAc based resins in order to lower the glass transition temperature (Tg) of the resulting polymer. Therefore, they come as more stable substitutes for external plasticizers such as phthalate type plasticizers which tend to migrate to the surface of the polymer with time. VeoVa pyrolysis products and mass spectra

characteristic fragmentation will be adressed thouroughly in the *Analysis of Flashe® paints* section of this paper.
Additionally, the analyses performed at 550ºC show several small peaks along the pyrogram that correspond to PEG. These pyrolisates are useful for analysis since they indicate the presence of PEG type surfactants in the paint formulation. These compounds appear in the derivatised form with HMDS, and present a characteristic masses m/z = 45, 73, 116, 145, 161. The ion with m/z = 73 appears in the derivatized products as it is the mass of the TMS group.

At 700ºC the analysis performed with HMDS gives much more complete information about the overall components of this vinyl paint, including peaks from the polymer chainand also possible fragments from distinct additives. The compounds identified are discussed in the following sections of this paper.

Pyrolysis performed at temperatures above 700ºC presented similar peak profiles in the pyrograms with the downside of showing increased signal for secondary pyrolysis products from the main polymer chain. Considering this, 700ºC was the working temperature chosen for the analytical protocol used in the analysis of these vinyl paints.

Analysis of Flashe® paints by in-situ thermally assisted pyrolysis-silylation GC-MS using hexamethyldisilazane (HMDS)

A set of Flashe® colors, namely armour green, oriental red, burnt umber, raw umber and white, was prepared as thin films and left to dry over a year period. These films have been analysed by *in-situ* thermally assisted pyrolysis-silylation GC-MS using hexamethyldisilazane (HMDS) at 700ºC in order to determine the overall composition of these products. The results obtained in the analyses of these samples are summarized in table 1.

In general, the pyrolysis of PVAc based polymers, at 700ºC, results in the formation of peaks corresponding to ethanoic acid and benzene. These are the products of side group elimination from the backbone chain of the polymer, and the brakedown and rearrangement of the polyene chain during pyrolysis, respectively [3, 21]. In the pyrogram obtained for Flashe® oriental red presented in figure 1-C, ethanoic acid in the derivatised form is detected at low retention time. However, due to the presence of the derivating reagent at early retention time, the benzene peak is undetectable. According to the literature one can still find some evidence of the formation of benzene later in the pyrogram, due to recombination and condensation reactions that occur during pyrolysis that form compounds such as 1,4-dihydronaphthalene, naphthalene and butyl benzoate [21]. Nevertheless, for the products studied in this paper, and despite being PVAc based paints, such compounds were not detected.

A further analysis of the pyrograms reveals traces of methacrylic acid (TMSMA) which is not detected with direct pyrolysis. This represents an improvement of the analysis achieved with the proposed method. Acrylic monomers are often present in PVAc formulations as co-monomers in order to improve overall mechanical properties and UV-resistance [3]. The mass spectra shows characteristic ion fragments of m/z =158, 143, 73, 69, 41.

Propanoic acid and ethanoic acid 2-oxy-TMS are also detected in the pyrograms for all samples, and may be related to recombination reactions during the pyrolysis process. Benzoic acid-TMS was also found in the pyrograms as an intense peak, with ion mass spectra m/z =194, 179, 135, 105, 77, 51.

The set of peaks that appear between 9.3 and 9.9 min in the pyrogram of the studied PVAc paints are associated to the presence of versatates used as internal plastizicer. Vinyl versatates, also named VeoVa monomers (Shell), are understood to consist of several isomers of highly branched C_9 and C_{10} vinyl esters [32]. They copolymerize with vinyl acetate by a simple addition polymerization. Peak distribution corresponding to the VeoVa fraction, that appears in the pyrogram of oriental red for flashe PVAc paint obtained with *in-situ* thermally assisted pyrolysis-silylation GC-MS using hexamethyldisilazane (HMDS), is shown in detail, in figure 2. The retention time of the six main compounds of the VeoVa fraction, which did not overlap, together with m/z values of the main ion fragments, are summarized in table 2. The close retention times suggested similar structures for these compounds.The mass spectra from all the peaks in this region are also very similar. They are dominated by m/z =73 ascribed to the fragment ion $[TMS]^+$, which indicates that these compounds have been satisfactorily trimethylsilylated by HMDS. The presence of the $[M-15]^+$ ion (m/z =229) in the mass spectra of the main compounds appearing in the VeoVa fraction, which is ascribed to the loss of a methyl group from the TMS derivatives of the compounds, suggests that the group of compounds are highly branched isomers of the decanoic acid ($C_{13}H_{28}O_2Si$) with structure close to that proposed by Learner [3,19], that is shown in Figure 3. Production on pyrolysis of C_{10} fatty acids, presumably is taking place by a similar side group elimination mechanism to that discussed above resulting in the formation of ethanoic acid and benzene from the PVAc polymer. Identification of these compounds is in good agreement to that previously found by Learner in Emultex VV536 PVAc emulsions using direct Py-GC-MS [19].

The rest of peaks that appear in the mass spectra of VeoVa compounds series exhibit low intensity if they are compared to the base peak. Nevertheless, two important processes described in general mass spectrometry treatises [33], that concern fragmentation of carboxylic acids and their derivatives, have been identified in most of the mass spectra of the compounds composing the VeoVa fraction in our experiments. First of all, the α-cleavage, which results in the formation of fragment ions $[COOTMS]^+$ (m/z = 117) and the complementary $[M-COOTMS]^+$ (m/z = 127) is observed in the mass spectra of the VeoVa series. The latter, of low abundance because this process probably is followed by a deprotonation that results in the fragment ion $[M-COOTMS-H]^+$ (m/z = 126). Secondly, γ-cleavage that results in formation of fragment ion $[CH_2-CH_2-(C=O)-O-TMS]^+$ (m/z = 145), a minor peak in the mass spectrum. Low abundance of these fragment ion is probably due to the highly branched structure of the VeoVa fatty acids.

It is not easy to explain why McLafferty rearrangement is not taking place. Most probably, it is due to the particular structure of the VeoVa compounds, which are carboxylic acids highly branched at α-, β- and γ-carbon (see Figure 3) [33].

Characteristic peaks associated to σ-bond cleavage in the aliphatic chain, resulting in carbenium ions $[C_3H_7]^+$, $[C_4H_9]^+$, $[C_5H_{11}]^+$, $[C_6H_{13}]^+$, $[C_7H_{15}]^+$, are recognized at m/z = 29, 43, 57, 71, 85, 97, 113, respectively, in the mass spectra (table 3). Characteristic accompanying pattern of peaks at m/z = $[C_nH_{2n+1}]^+ - 2$ and m/z =$[C_nH_{2n+1}]^+ - 4$ are also observed at the low-mass side of the corresponding peak of the carbenium ion, which is produced as result of dehydrogenation of these ions.

Other interesting feature in the mass spectra of the VeoVa series is that at m/z =159 that is correlated with the fragment ion $[M-C_6H_{13}]^+$. Other fragment ions that appear in the mass spectra at m/z =202, 188, 174, 160 and 126 are harder to explain but, according to Learner, [3] could result from the addition of a hydrogen atom to the charged carbon from a rearrangement reaction involving $[M-C_3H_7]^+$, $[M-C_4H_9]^+$, $[M-C_5H_{11}]^+$, $[M-C_6H_{13}]^+$ and $[M-C_9H_{18}]^+$. Peak at m/z =143, that is particularly intense in mass spectra of all compounds, has tentatively been ascribed to the formation of $[C-CH_2-COOTMS]^+$. This fragment ion at m/z 143 is found in deprotonated octanoic acid mass spectrum. This peak also appears, as a minor peak, in the mass spectra of C_{10} fatty acids associated to VeoVa fraction in Emultex VV536 PVA emulsion [3,19]. In this last case, the fragment ion considered can not be associated to a structure containing the TMS group because no trimethylsilyl derivatives are obtained by means of direct Py-GC-MS. In contrast to that, fragment ion at m/z 143 is a major peak in the mass spectra of Flashe® paints what can be attributed to the presence of the group TMS in the fragment ion. Nevertheless, it should be noted that the proposed structure [C-CH$_2$-

COOTMS]$^+$ is hardly justified on the basis of the usual rearrangements and fragmentation pathways of fatty acids.
Along the pyrogram of oriental red a series of peaks corresponding to PEG in their derivatised form with HMDS can also be identified, as explained in the previous section of this paper. These compounds have not been identified with direct pyrolysis but with the present method for every sample studied in this paper.

Besides the overall products detected in the general pyrograms, there are other compounds present in minor concentration which seem to correspond to small variations for each colour formulation.

Organic pigments are, in general, very difficult to detect directly from microsamples since they are present in very low concentrations in paints due to their strong optical properties. The pyrogram corresponding to oriental red shows a minor peak corresponding to a fragment ascribed to the pigment red 112 (PR112), an azo pigment, which is in agreement with the indications supplied by the manufacturer. The mass spectrum of this pyrolysis product exhibits fragments ion at m/z = 195, 160, 124, 97, 62 and 28, in agreement with that previously reported in literature [12]. In contrast to the behavior of oriental red, green armour paint, which is prepared mainly with a green phthalocyanine pigment, does not exhibit any peak corresponding to this organic pigment. According to that reported in literature [19], phthalocyanine compounds do not undergo any kind of scission reaction on pyrolysis to produce fragments sufficiently volatile to pass through the GC column.

Moreover, it is interesting to note that dibutyl phthalate, used commonly as an external plasticizer was also found in this paint sample, despite of the internal plasticizement discussed previously by means of VeoVa. The mass spectra of phthalate type plasticizers are typically dominated by peak at m/z = 149. Phenyl phosphate has been also detected at trace levels. This product is tentatively ascribed to a pyrolysis fragment of isopropyl phenyl diphenyl phosphate, found in some paints as a flame retardant. This product has also been identified in armour green color.

A pyrogram corresponding to armour green is shown in figure 4. The results obtained from the analysis of this paint reveal the presence of styrene, a possible co-monomer for acrylic resins, which appear to have been included in this type of paint, since traces of TMSMA are also found in this sample as in oriental red. Another interesting compound is found at higher retention time, that corresponds to a sesquimer of EA-TMSMA, which appears to be also an indicator of the presence of an acrylic resin as an additive in the fabrication of this paint. It is interresting to notice that all of these compounds seem to be present exclusively in their derivatised form, whereas they have not been detected in pyrograms obtained with direct pyrolysis.

Further in the pyrogram, a phthalate type plasticizer (di-isobutylphthalate) has been identified and may have been included in the formulation in order to improve the overall physical properties of this paint.

Interestingly, relatively strong peaks corresponding to diethylene glycol dibenzoate, with characteristic ion fragments m/z =149, 105, 77, 51 and diglycol benzoate, m/z =163, 105, 77, have been found together at high retention time in the pyrogram. These compounds are used commonly in industrial applications as plasticizers for PVAc type resins and might as well have been included in this paint formulation in order to achieve desired performance properties.

Finally, a strong peak corresponding to isopropyl phenyl diphenyl phosphate, a flame retardant additive, has been detected in this paint sample. Marker ion fragments detected are m/z =368, 251, 118, 77.

The analysis of raw umber and burnt umber colours exhibited similar pyrogram profile to these previously described.

Analysis of Flashe® paint extractions by Py-GC-MS with HMDS

A series of deionized water extractions from Flashe® oriental red, armour green, raw umber, burnt umber and white films were prepared in order to separate possible minor water soluble additives that may be hindered in the pyrogram due to the presence of major compounds such as polymer pyrolisates or secondary reactions that take place during pyrolysis. The waxy-like residues obtained from the extraction process for each colour of Flashe® paint films were analysed by Py-GC-MS with HMDS. The results obtained from the extractions of Flashe® vinyl paint samples are summarized in table 4.

A pyrogram obtained for armour green extract is presented in figure 5. It can readily be observed the presence of several peaks which have not been detected in the general pyrogram obtained from the corresponding paint sample. Well defined peaks corresponding to styrene, m/z = 104, 78, 63, 51 and methyl styrene are found early in the pyrogram, and complement the results obtained previously for the paint samples. These compounds are also present in the extracts from the rest of paint samples. Interestingly, the analysis ran for armour green also revealed peaks corresponding to o-xylene, α-methylstyrene, methylnaphthalene that may be related to recombinations reactions promoted during pyrolysis.

Two intense peaks are found in the pyrogram that correspond to butanedioic acid and pentanedioic acid, both in the silylated form.

The water extraction of these paint films appears very useful to enhance the peak signal of PEG type compounds in the pyrogram as signed in figure 5. Mostly all PEG type products appear in their derivatised form, which proves the eficiency of HMDS in the derivatization of –OH functional end groups. It is interesting to notice that, in the case of the analysis of the extract from white paint sample, it has been possible to detect the presence of PEG-type products with C=C double bond and C-C bond end groups. This might be an indicator of different cleavage pathways that occur during the pyrolytic process which would be in good agreement with previous studies found in the literature [34].

Mechanical properties of Flashe® paints

Representative stress-strain curves obtained for the paints studied are presented in figure 6. For each sample, three replicates were obtained to confirme the consistency of the results. It is interesting to point out that the replicates of each colour exhibit similar characteristics in the elastic region but are somewhat discrepant in the elongation at brake values. This is probably related to somewhat heterogeneous film formation properties of these paints, which has also been reported in the literature [35]. The results presented correspond to the replicates which exhibited most plastic deformation.

Between the different colours there is an evident variation in the mechanical behaviour of the samples. Nevertheless, all samples showed the formation of cracks soon after the first strain increments were applied, and started to brake soon after (see figure 7). Oriental Red exhibits an elongation of 14%, whereas Raw Umber reaches about 5% elongation. This implies a major difference between these vinyl paints and acrylic paints which are reported to elongate about 400% before braking [36], at similar experimental conditions.

Regarding the ultimate elongation at brake values, white and oriental red samples present similar mechanical behaviour, showing more flexibility, and this interestingly correlates with the overall pyrograms that present relatively less intense peaks correlated with PEG derivatives. In contrast, raw umber and green colours appear to have been formulated with a higher amount of PEG type compounds which may be related to the stabilization of the pigment in the formulation. Considering these colours present higher stiffness, when compared to other colours, it appears these additives might be influencing the film formation process of the paints. The existence of external plasticizers and acrylic-styrene additives may possibly be attributed to an attempt to improve the overall mechanical properties of these films.

CONCLUSIONS

In this paper, an analytical method consisting of the use of HMDS as a derivatising reagent in Py-GC-MS for analysis of PVAc paint samples and additives has been used. The optimization of the method allowed to improve the extraction of data on additives and polymer analysis when compared to direct pyrolysis.

The method was tested on Flashe® PVAc type paints and their corresponding water extracts, and the results indicate the presence of several monomers different from vinyl acetate. The presence of TMSMA and styrene can be related to the addition of co-monomers in the emulsion process, or can rather be related to the presence of more than one emulsion in the elaboration process of these colours.

Moreover, several additives have been identified, such as phenyl phosphate-type flame retardant products, glycol benzoates and phthalate type plasticizers, preservatives such as methenamine. This indicates that the manufacturer includes a variety of products in search of desired properties of the paint.

The study of the mechanical properties of several paint samples allowed characterizing the tensile properties of these films as a function of the pigments and additives present in their composition. Interestingly, there appears to be a correlation between mechanical properties and the presence of PEG type additives present in the formulations, as these compounds might be influencing the stiffness and plastic behaviour of the paint films.

Figures:

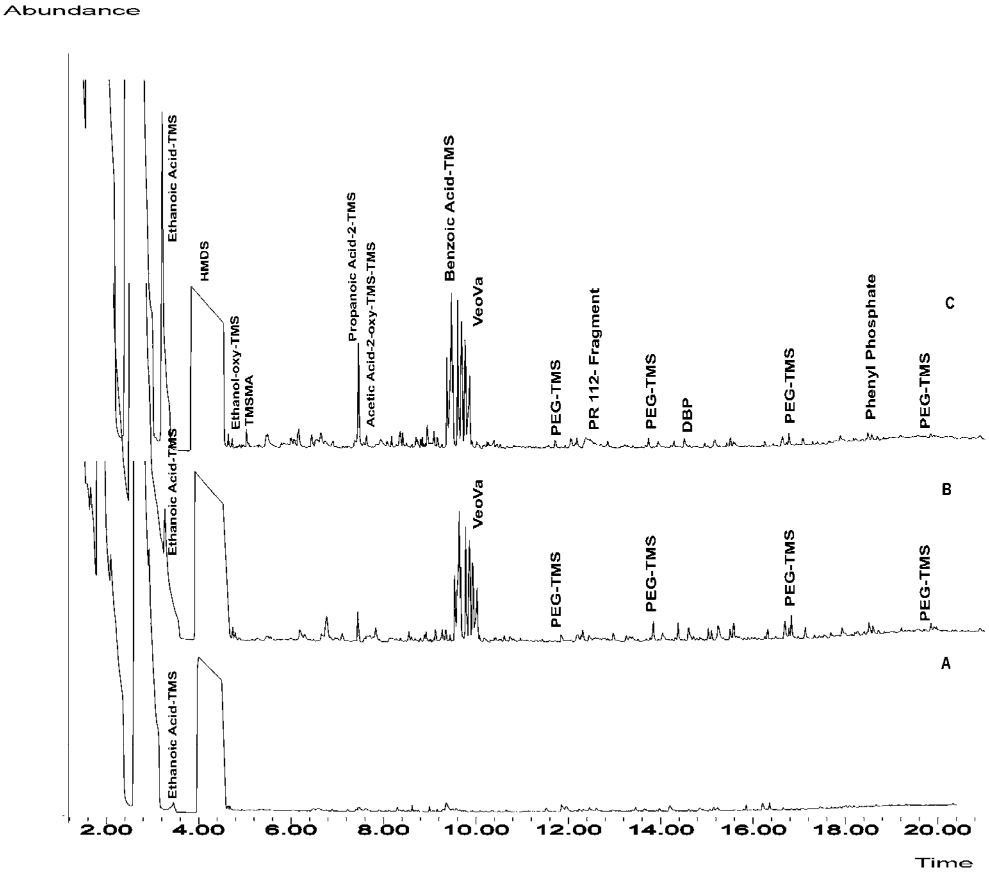

Figure 1 pyrograms corresponding to Py-GC-MS with HMDS of oriental red at different pyrolysis temperatures: A) 400ºC; B) 550ºC; C) 700ºC. These preliminary trials have revealed that pyrolysis conditions were optimized at 700ºC on what the identification of the polymer chain, pigment fragments and main additives concerns

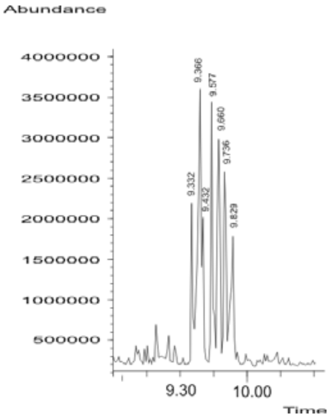

Figure 2 detail of the oriental red pyrogram which highlights the VeoVa fraction. Pyrolysis was performed with HMDS

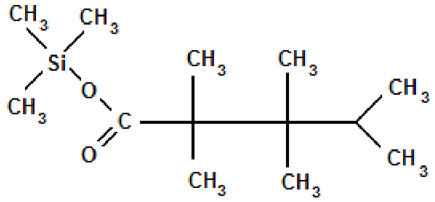

Figure 3 proposed structure of an isomer of the trimethylsilylated-C_{10} fatty acid appearing in the VeoVa fraction of Flashe® paints

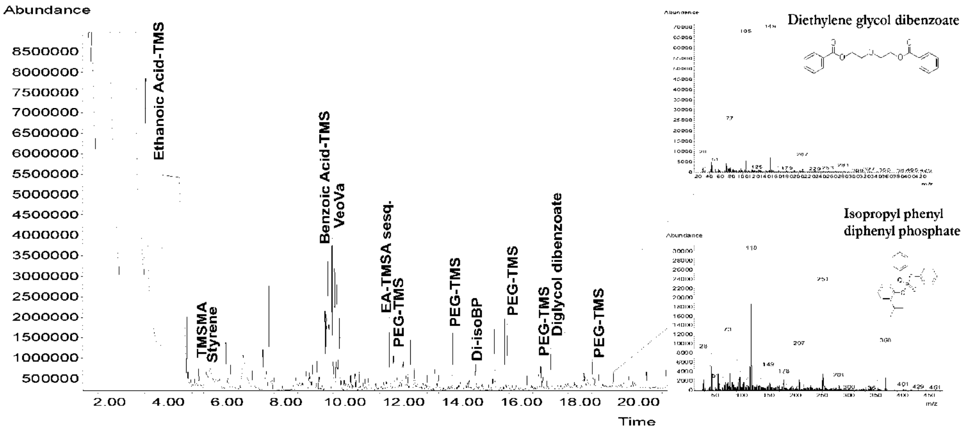

Figure 4 pyrogram corresponding to Flashe® armour green obtained at 700ºC with HMDS. In this figure, the main compounds found in the paint samples are signed, which correspond mainly to acetic acid from the polymer main chain, VeoVa internal plasticizers, i-isobutyl phthalate (Di-iso-BP) external plasticizers and PEG type surfactants. Interestingly, it has been detected the presence of styrene and methyl acrylate. Later in the pyrogram, diethylene glycol and isopropyl phenyl diphenyl phosphate have also been found

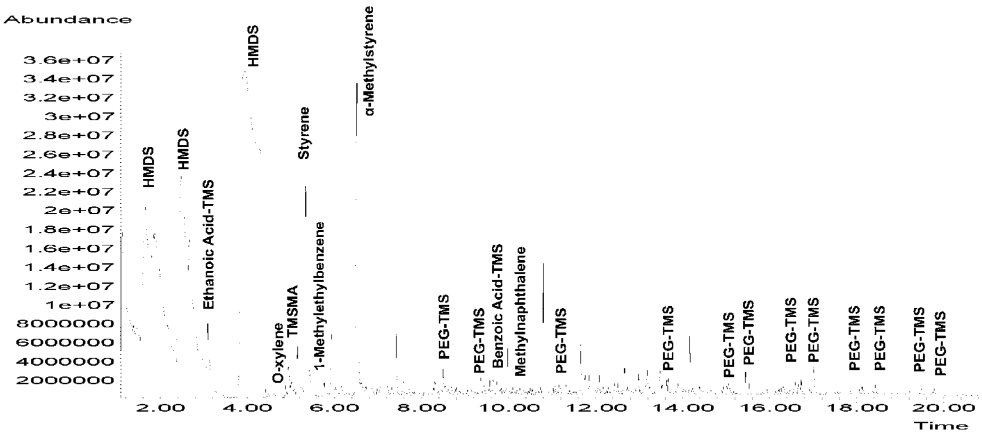

Figure 5 pyrogram obtained for Flashe® armour green extract. Peaks peaks assigned correspond to ethanoic acid-TMS, o-xylene, styrene, methylethylbenzene, α-methylstyrene, methylnaphthalene. PEG type compounds were also identified

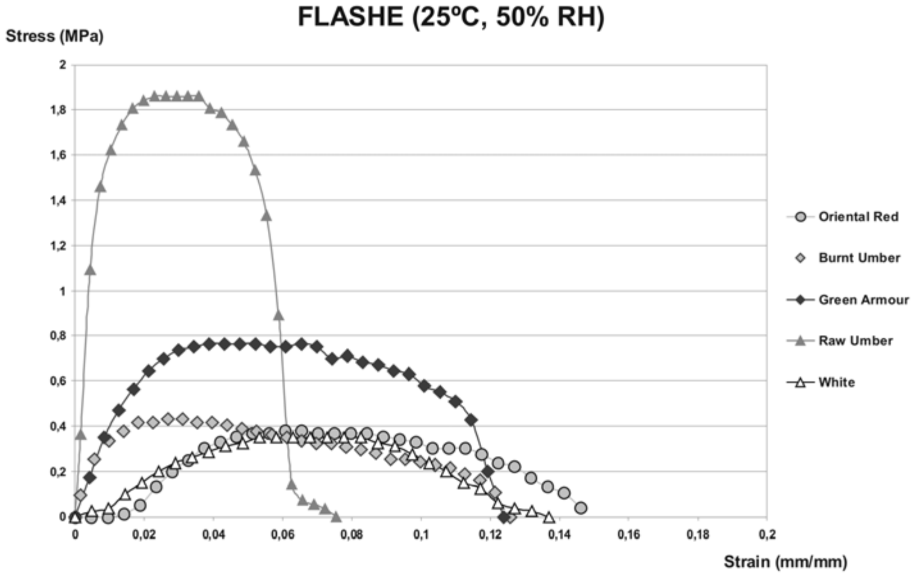

Figure 6 stress-strain curve obtained for the Flashe® samples studied: oriental red, burnt umber, green armour, raw umber and white

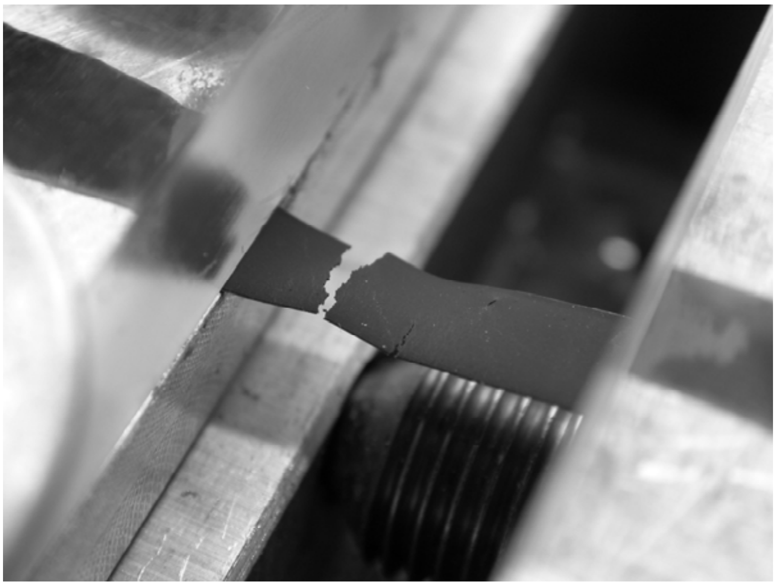

Figure 7 picture of armour green Flashe® paint sample brakeing in the mechanical tester's gage. The foto evidences the type of brake these samples experience. Rather than a clean brake, the sample experiences several simultaneous fractures with a sawtooth like pattern

Tables:

Colours		Flashe® Oriental Red	Flashe® Armour Green	Flashe® Raw Umber	Flashe® Burnt Umber	Flashe® White
Supplier		Lefranc & Bourgeois				
Declared composition by supplier		Vinyl paints				
Compounds Identified	*m/z* ion fragments					
ethanoic acid-TMS	117, 75, 45	V	V	V	V	V
2-methoxyethanol -TMS	133, 103, 89, 73, 59, 45	-	V	V	-	-
2-TMS-oxy-ethanol	119, 103, 75, 73, 58, 45	V	-	-	V	-
propanoic acid-2-methyl-TMS	145, 117, 75, 73, 58, 45	V	-	V	V	-
methacrylic acid-TMS	158, 143, 73, 69, 41	V	V	V	V	-
styrene	104, 78, 51, 39, 27	-	V	-	V	V
phenoxy-TMS	166, 151, 77, 43	-	-	-	V	-
propanoic acid 2-oxy-TMS	234, 191, 147, 117, 73, 45	V	V	V	V	V
ethanoic acid 2-oxy-TMS	220 205, 147, 73	V	V	V	V	V
benzoic acid-TMS	194, 179, 135, 105, 77, 51	V	V	V	V	V
VeoVa	see Table 2	V	V	V	V	V
butanedioic acid- TMS	261, 147, 73, 55, 45	-	-	-	V	V
pentanedioic acid-TMS	189, 142, 115, 87, 57, 43	-	V	-	-	V
pigment traces		V (PR112: 2,3,4-trichloro Benzenamine) 195, 160, 124, 97, 62, 28)	-	-	-	-
bis(2-butoxyethyl) phthalate	366, 223, 149, 56	-	V	-	-	-
diethylene glycol dibenzoate	149, 105, 77, 51	-	V	-	-	-
diglycol benzoate,	163, 105, 77	-	V	-	-	-
isopropyl phenyl	368, 251,	V	V	-	-	

diphenyl phosphate	118, 77					
PEG-TMS	45, 73, 101-103, 116-117, 145, 161 (...)	V	V	V	V	V

Table 1 summary of the compounds detected by means of Py-GC-MS in the Flashe® paint samples. Only for oriental red paint sample was detected a fragment of an organic synthetic pigment, PR112.

Peak	**VeoVa fraction Assignment**[a]	**M_w**	**t_r** (min)	**Mass spectra data (70 eV) Characteristic ions**[b]**: m/z**
1	Unidentified decanoic acid, TMS ester	244	9.34	229, 202, 188, 173, 159, 143, 126, 117, 99, 85, **73**, 71, 57, 43
2	Unidentified decanoic acid, TMS ester	244	9.43	229, 174, 159, 143, 126, 117, 85, **73**, 71, 57, 43
3	Unidentified decanoic acid, TMS ester	244	9.57	229, 202, 188, 174, 159, 143, 126, 117, 85, **73**, 71, 57, 43,29
4	Unidentified decanoic acid, TMS ester	244	9.66	229, 202, 188, 173, 159, 143, 126, 117, 85, **73**, 71, 57, 43
5	Unidentified decanoic acid, TMS ester	244	9.74	229, 174, 160, 143, 126, 117, 85, **73**, 71, 57, 43
6	Unidentified decanoic acid, TMS ester	244	9.83	229, 174, 159, 143, 126, 117, 85, 84, **73**, 71, 57, 43

Table 2 m/z values of the characteristic ions found in the mass spectra of the TMS derivatives of the main compounds included in the VeoVa fraction appearing in the pyrogram of oriental red PVAc paint

[a]Assignment of structure based on the fragment ion pattern in the mass spectrum.

[b]base peak in bold

Compound	**1**	**2**	**3**	**4**	**5**	**6**
$M^{+\bullet}$	244	244	244	244	244	244
$[M\text{-}CH_3]^+$	229	229	229	229	229	229
$[M\text{-}C_3H_7\text{+}H]^+$	202	-	202	202	-	-
$[M\text{-}C_4H_9\text{+}H]^+$	188	-	188	188	-	-
$[M\text{-}C_5H_{11}\text{+}H]^+$	-	174	174	-	174	174
$[M\text{-}C_5H_{11}]^+$	173	-	-	173	-	-
$[M\text{-}C_6H_{13}\text{+}H]^+$	-	-	-	-	160	-
$[M\text{-}C_6H_{13}]^+$	159	159	159	159	-	159
$[C\text{-}CH_2\text{- }COOTMS]^+$?	143	143	143	143	143	143
$[M\text{- }COOTMS\text{ -}H]^+$	126	126	126	126	126	126
$[COOTMS]^+$	117	117	117	117	117	117
$[\ C_7H_{15}]^+$	99	-	-	-	-	-
$[\ C_6H_{13}]^+$	85	85	85	85	85	85
$[\ C_6H_{13}\text{-}H]^+$	-	-	-	-	-	84
$[\ TMS]^+$	73	73	73	73	73	73
$[\ C_5H_{11}]^+$	71	71	71	71	71	71
$[\ C_4H_9]^+$	57	57	57	57	57	57
$[\ C_3H_7]^+$	43	43	43	43	43	43

Table 3.- Main ion fragments identified in the VeoVa fraction.

Extractions		**Flashe® Oriental Red**	**Flashe® Armour Green**	**Flashe® Raw Umber**	**Flashe® Burnt Umber**	**Flashe® White**
Supplier		Lefranc & Bourgeois				
Declared composition by supplier		Vinyl paints				
Compounds Identified	*m/z* ion fragments					
ethanoic acid, TMS ester	117, 75, 59, 45	V	V	V	V	V
propanoic acid, 2-methyl-TMS	160, 145, 75,73, 58, 45	V	V	V	V	V
ethanol, 2-[(TMS)-oxy]-TMS	119, 103, 85, 58, 43	-	-	-	-	V
o-xylene	106, 91, 77, 65, 51, 39	-	V	-	V	V
methacrylic acid-TMS	158, 143, 73, 69, 41	V	V	V	V	V
styrene	104, 78, 63, 51, 39, 27	V	V	-	V	V
vinylcarbitolether	160, 87, 72, 59, 45	-	-	-	-	V
α-methylstyrene	118, 103, 91, 78, 51, 39	V	V	-	V	V
phenoxy-TMS	166, 151, 77, 43	-	-	-	-	V
propanoic acid-2-methyl-TMS	145, 117, 75, 73, 58, 45	V	V	V	V	V
ethanoic acid 2-oxy-TMS	220 205, 147, 73	V	V	V	V	V
vinyl ethyl carbitol	160, 85, 72, 59, 45, 31, 29	-	-	-	-	V
divinylcarbitol	158, 117, 73, 71, 57, 45, 27	-	-	-	-	V
2-pyrrolidinone, 1-ethenyl	111, 82, 68, 56, 41, 28	-	-	-	-	V
methenamine	140, 112, 96, 85, 69, 53, 42	-	V	-	-	V
benzoic acid	194, 179, 135, 105, 77, 51	-	V	V	V	V
pentanedioic acid-TMS	276, 261, 158, 147, 73,	-	V	-	V	-

	55					
butanedioic acid-TMS	247, 218, 172, 147, 129, 73, 55, 45	-	V	-	-	V
Hexanedioic acid-TMS	(290), 275, 147, 11, 83, 73, 55, 45	-	V	-	V	-
PEG-TMS	45, 73, 101-103, 116-117, 145, 161 (...)	V	V	V	V	V
Phosphate-TMS	314, 299, 73, 45	-	-	-	V	-

Table 4 main compounds detected by means of Py-GC-MS in the Flashe® extractions

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Appendix F- *In situ* study of the effects of water based cleaning treatments

In this chapter are described some practical observations on the application of water based cleaning systems in two case studies: *La Puerta de Brandenburgo* (unknown artist, late 1990's, PVAc binding medium) and *Desde la Ventana I* (Rafael Calduch, 2000, Styrene-MMA-2EHA). The scope of this study was to compare the alteration forms detected in real smaples to those described in the previous chapter for the acrylic and PVAc test specimens. Since the possibility of experimenting in real paintings is fairly limited, the cleaning trials were performed on small spot tests. Free water, Vanzan® NF-C and Agar-agar® gels were used as cleaning agents and micro-samples of the treated areas were examined by SEM microscopy. Two micro-samples were extracted from each *cleaned* area.

F.1- *La Puerta de Brandenburgo* (unknown artist, late 1990's, PVAc medium)

La Puerta de Brandenburgo (Figure F.1) is a canvas painting that was donated to the Conservation Department of the Universidad Politecnica de Valencia in 1999. This painting is being studied and subjected to Conservation treatment due to the extensive damage it suffered during storage. Some technical data on this work has been summarized in Table 7.1 and some analyses are described as follows.

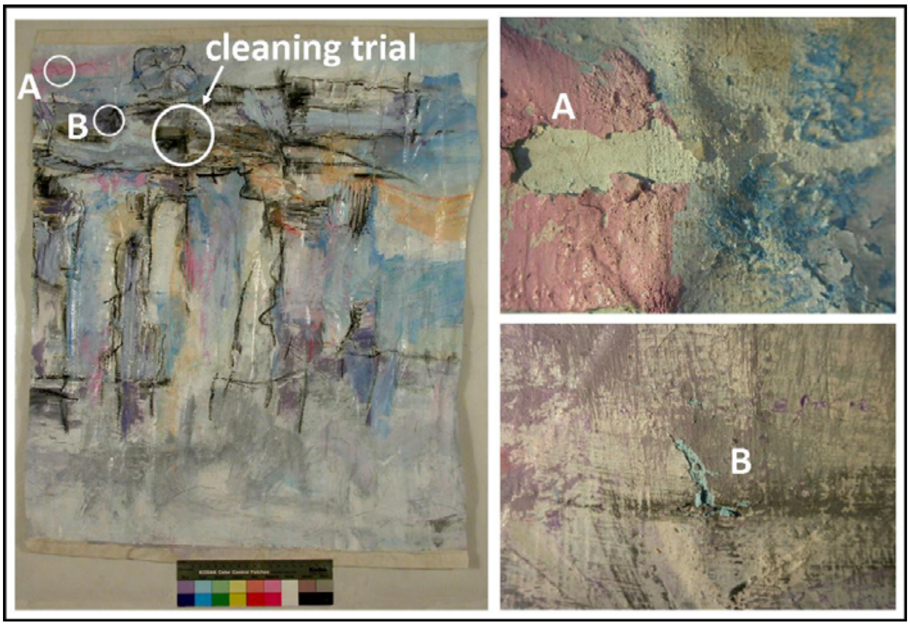


Figure F.1: *La Puerta de Brandenburgo* (unknown artist, late 1990's (?)). In the left, details from two areas of sample extraction A and B. The characterisation of the materials is discussed in the text. The other area pointed out is to the zone where the cleaning tests were performed.

Title	*La Puerta de Brandenburgo* (Brandemburg's Gate)
Author	Unknown.
Date	Presumably from the late 1990's
Type of artefact	Canvas painting. Possibly a fragment from a bigger composition.
Technique	PVAc based paint on industrial cotton canvas.
Characterisation of the support	Fine industrial canvas composed of synthetic and cotton fibers. Weave count: 32 x 28 per cm^2. No ground layer.
Strecher	Does not present a strecher. It has the format of a *standard*.
Format (size)	Rectangular shape with 60.7 x 71.5 (width and height)
Owner	Conservation and Restoration Department of the Universidad Politecnica de Valencia
History	The object was donated to the Conservation Department in 1999. The identity of the doner is not known.
Documentation	not existant

Table F.1: summary of some technical information of *La Puerta de Brandenburgo*.

The analysis of the binding medium used in *La Puerta de Brandemburgo* was carried out by FTIR-ATR spectroscopy and Py-GC-MS on microsamples extracted from different coloures areas of the painting. The characterization of pigments was done by SEM-EDX for inorganic pigments and micro-chemical tests for organic synthetic pigments. These will not be discussed in this work.

The binding medium used in all painted area was identified by FTIR-ATR as a PVAc resin, with a phthalate type plasticizer. The dark lines drawn over the painting are wax with carbon black. The analysis by means of Py-GC-MS confirmed this and also enabled to characterise the type of plasticiser as a Dibutyl Phthalate (DBP) and iso-Dibutyl Phthalate (iDBP). No other additives have been detected.

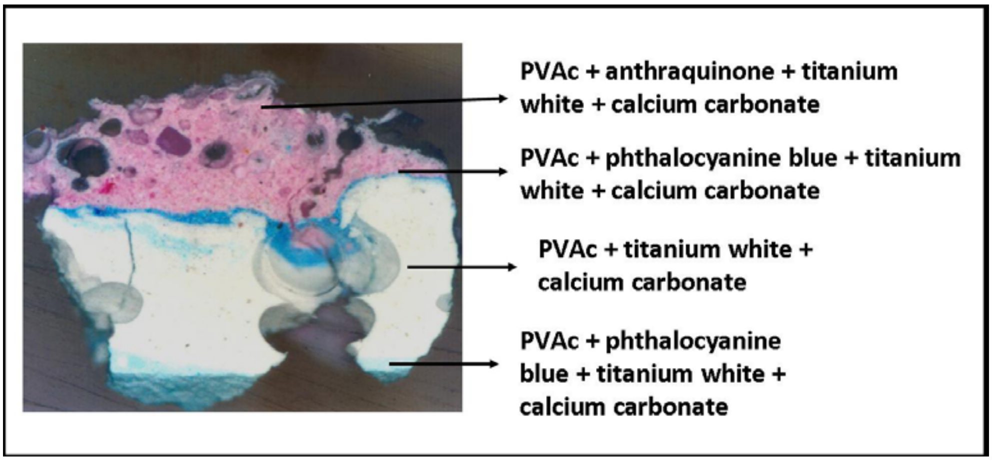


Figure F.2: cross section of a microsample A, obtained from the pink area pointed out in Figure F.1. The characterization of the materials present in the different layers is summarized in the figure. It is interesting to observe the considerable porosity of the paint layer. This was observed in all the micro samples extracted from the paint. These defects increase significantly the water absorption and swelling behaviour of the paint layer, when compared to a continuous film.

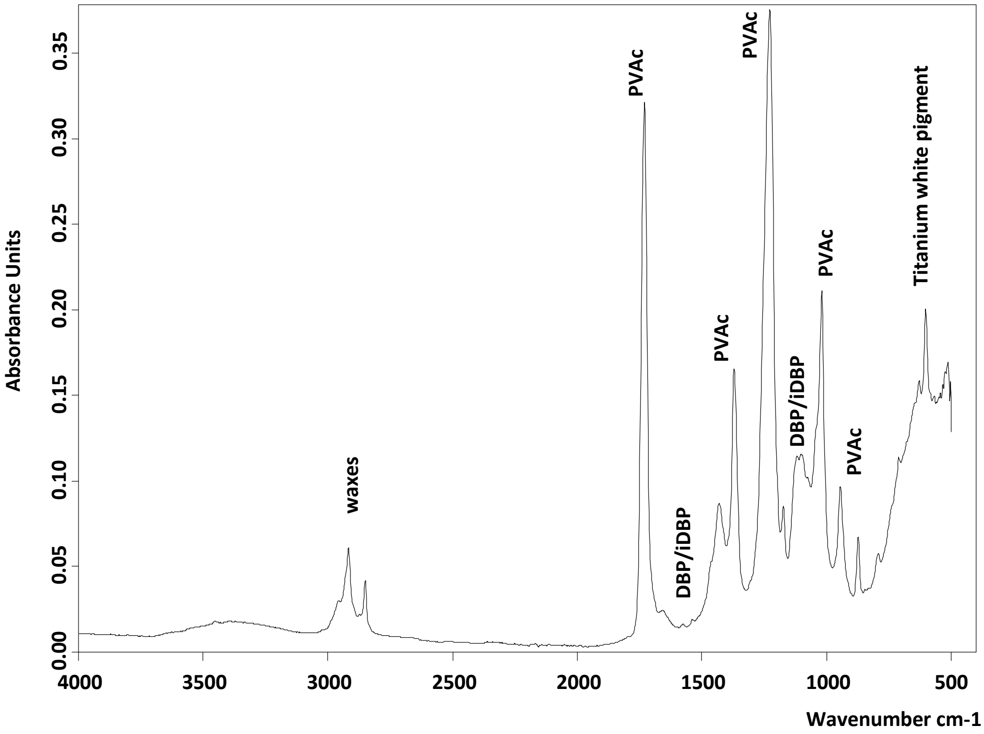
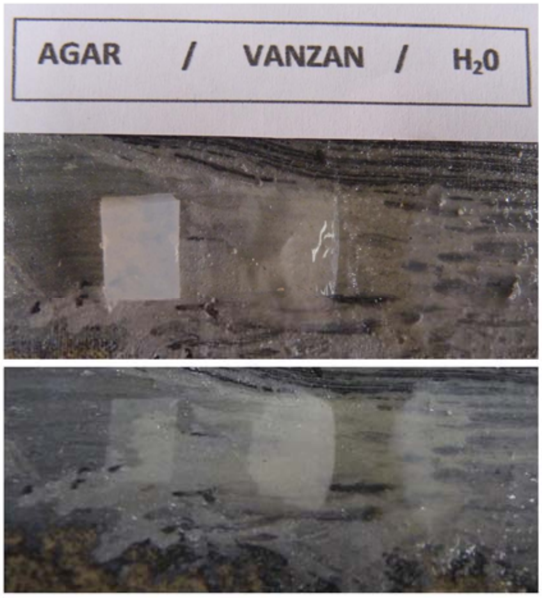


Figure F. 3: The FTIR-ATR spectrum of sample B, pointed in Figure F.1. The sample included the black line and the rest of paint layers. The binding medium is PVAc. There is evidence of a phthalate type plasticizer, which have been characterized as DBP and iDBP by means of Py-GC-MS. Waxes are detected from the black lines. The characteristic absorption of titanium white is also present.

In situ cleaning trials- ***La Puerta de Brandemburgo***

Preliminary tests were conducted in the surface of *La Puerta de Brandenburgo* to determine its affinity to water. This was done by deposing a waterdrop on the surface of the painting and examining its shape. The waterdrops showed initial high contact angles (hydrophobic surface), but the shape of the drop fastly changed and the liquid was absorbed into the film. This is due to capillarity and porosity, which visible in the cross-section shown in Figure F.2. With water absorption, the paint film swolle, and gained a whitish appearence, which is in full agreement with the swelling behaviour of PVAc test specimens described in the previous chapter of this thesis.

The cleaning trials were conducted with free water, Vanzan® and Agar-agar® gels applied for 20 minutes on a paint area of approximately 3 mm x 3 mm. The zone tested is pointed in Figure F.1, and consists of a thick layer of binding medium (PVAc) applied over the paint layers. This area was very cohese and allowed the tests to be longer than a normal conservation treatment, in order to simulate repeated treatments over time. The free water treatments consisted of adding drops of water every 2 minutes and drying the surface with a cotton swab. The gels were applied directly on the surface as shown in Figure F.4.



Application of the three water based cleaning systems: Agar-agar, Vanzan and water in the free form. The cleaning tests were conducted for long times (20 minutes) to detect possible degradation caused by water.

After the cleaning trial were stopped, the paint film was swollen, which can be seen in the image at the bottom. The gels act "locally", whereas water in the free form can easily diffuse through the paint layers.

Figure F.4: Cleaning tests performed on the upper part of *La Puerta de Brandenburgo*

The analysis by SEM of the areas subjected to the cleaning trials reveal similar results to those obtained for the PVAc based tests specimens such as Conrayt® or Mowilith® DMC2. Despite the evident swelling experienced by the paint layer, the morphology of the samples, after cleaning, is not dramatically affected (see Figure F.5). Interestingly, the non treated area and that exposed to the Agar-agar® gel exhibit similar morphology (i.e. a *rougher* surface when compared to the other spot tests). These results suggest that the rigid gel afects the surface of the samples to a less extent, conserving the surface's properties. This has also been observed for the second case study described later in this chapter.

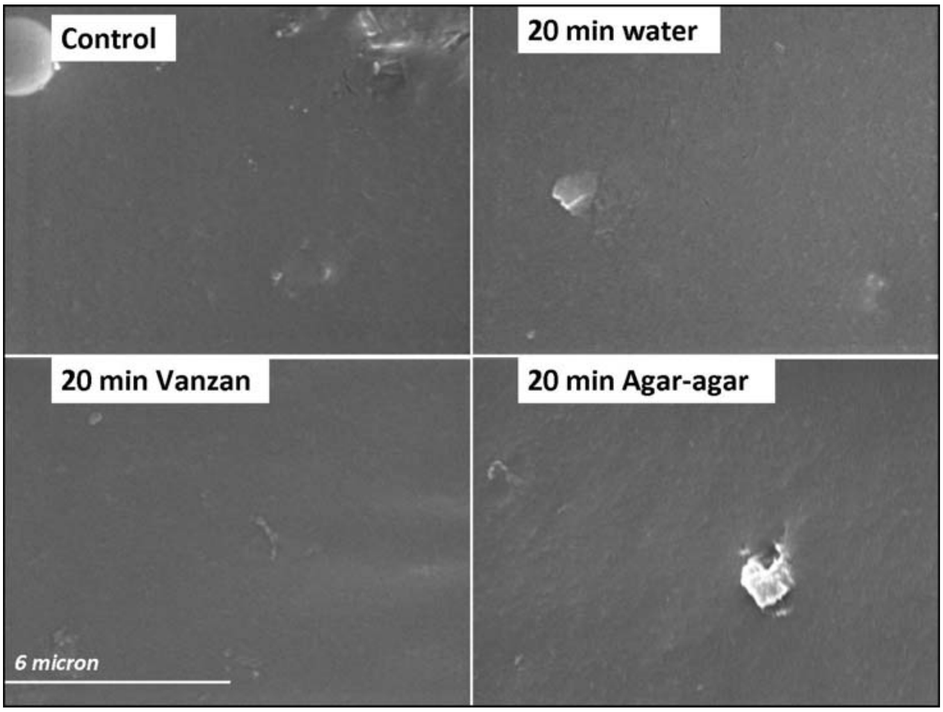


Figure F.5: Secundary electron images (x10000 magnification) of the surface of the samples extracted from the cleaning spot trials performed in *La Puerta de Brandenburgo*. The control sample and Agar-agar® cleaned surfaces show similar appearence, whereas Vanzan® and free water smoothed the surface of the film.

7.2- *Desde la ventana I* (By Rafael Calduch) –(possibly 2000)

Desde la ventana I (From the Window I) is a painting from Rafael Calduch, one of the most recognized plastic artists of the *abstract informalism* from the Valencian Comunity, Spain. The painting was brought to the Conservation Department by the artist himself for the restoration of a damaged area caused by an impact during transportation. The artist agreed with the cleaning trials proposed for this thesis, as long as they were performed in the edges.

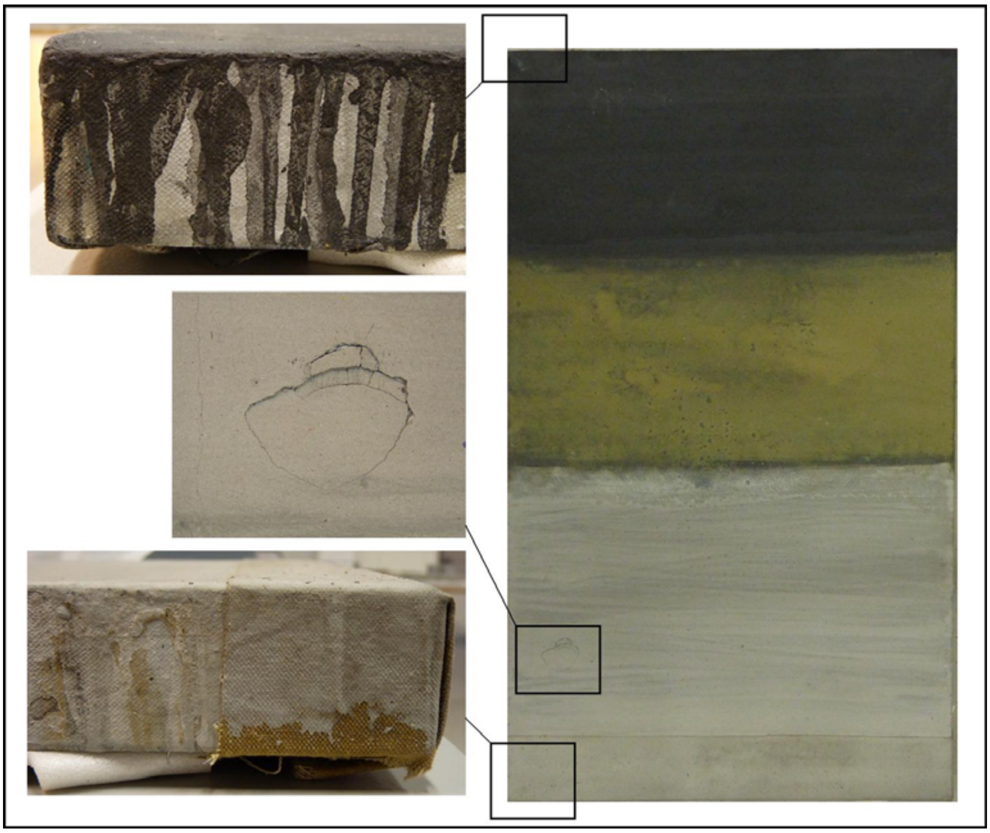


Figure F.6: *Desde la Ventana I, by Rafael Calduch (2000).* The left pictures show details of the painting as well as a damaged area that the artist caused during transportation. This artwork is currently in the Conservation Department for restoring this damage. The cleaning trials were performed in the top and bottom areas pointed in the figure.

The analysis of the binding medium was carried out by FTIR-ATR spectroscopy and Py-GC-MS. The paint layers were applied with a Styrene-MMA-2EHA type binding medium over a very diluted preparatory layer of PVAc (formulation contains DBP).

Title	*Desde la ventana I*
Author	Rafael Calduch
Date	2000
Type of artefact	Canvas painting
Technique	Styrene-MMA-2EHA and PVAc based paint on industrial canvas adhered to a wooden canvas.
Characterisation of the support	Canvas composed of cotton fibers. Weave count: 15 x 15 per cm^2.
Strecher	Wooden strecher (pine tree).
Format (size)	Rectangular shape with 40 cm x 60 cm
Owner	The artist (Rafael Calduch)
History	The canvas is on currently on conservative treatments
Documentation	not available

Table 7.2: summary of some technical information of *Desde la Ventana I*.

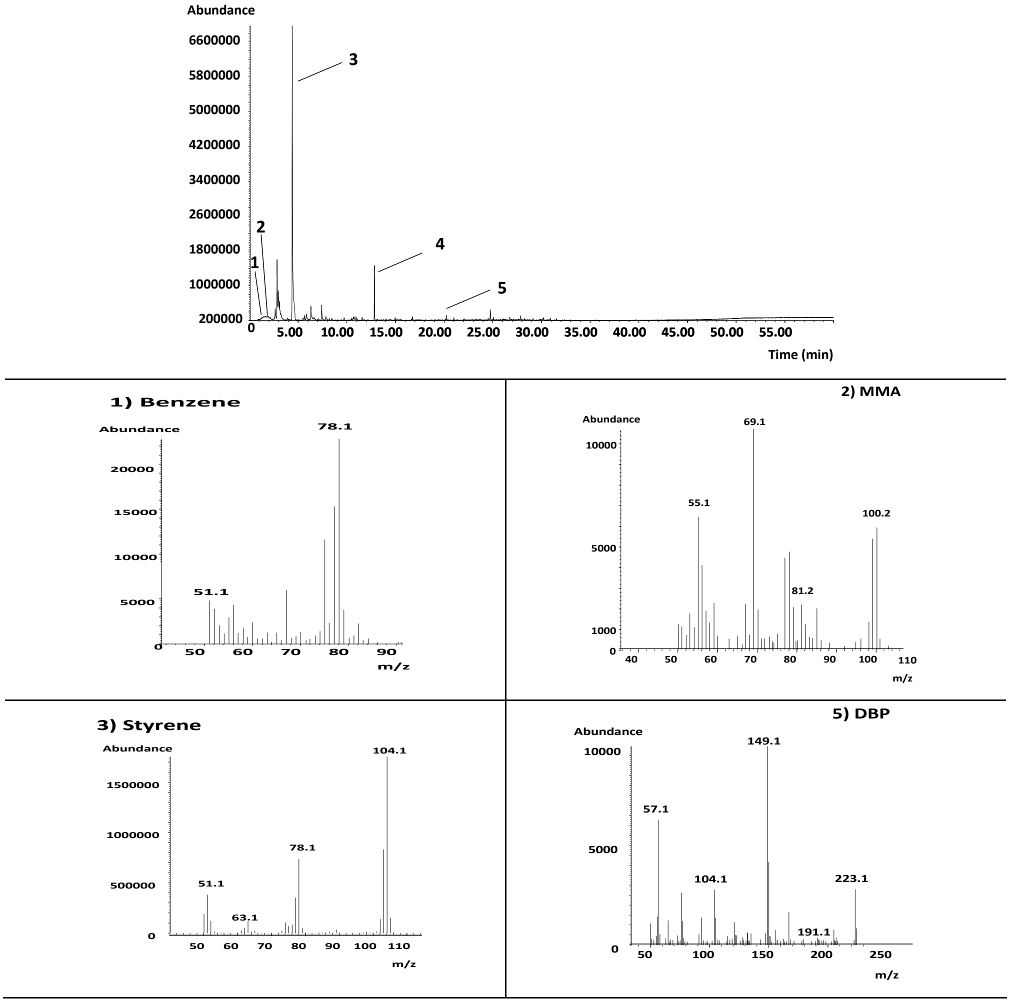


Figure F.7: Py-GC-MS analysis of a Calduch grey microsample. The analysis revealed the presence of a Styrene-MMA-2EHA type polymer over a PVAc diluted ground. DBP type plasticizer has also been identified. Peak 4 corresponds to 2EHA (mass spectrum not shown here).

In situ cleaning trials- *Desde La Ventana I*

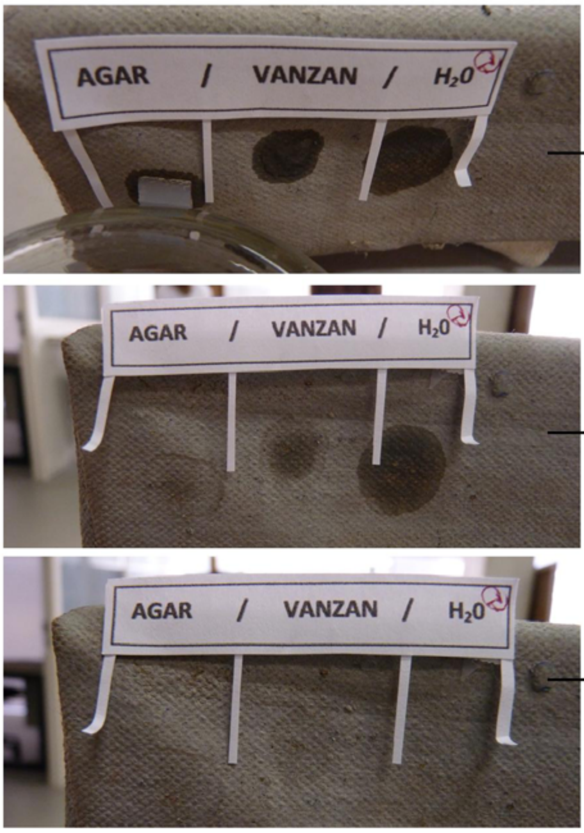
Water in the free form, Vanzan® NF-C and Agar-Agar® gels were tested to study the effects of water based cleaning treatments in the surface of *Desde La Ventana I*.

The two areas subjected to the cleaning trials are pointed out in Figure F.6. The first area consists of a solid black area (upper part of the painting); the second consists of a thin and porous paint layer applied over a stripe of fabric glued to the canvas, in the lower part of the painting. The test areas consist of 3 mm x 3 mm spot tests. The cleaning systems were applied for 5 minutes. After the paint layers were dry, microsamples were extracted and analysed by SEM microscopy.

Application of the three water based cleaning systems: Agar-agar, Vanzan and water in the free form. Tests were run for 5 minutes on the surface of one of the edges of the painting (upper left corner).

Cleaning with free water created tidelines due to diffusion of the solvent in the paint layers, which can be very inconvenient for the conservator. The creation of tidelines was limited when gels were applied, specially in the case of Agar-agar.

Figure F.8: Cleaning tests performed on the upper part of *Desde la Ventana I.*



Application of the water based cleaning systems for 5 minutes on the surface of the *Desde la Ventana I*.

After 10 minutes drying it is evident that water in the free form has wet and penetrated the surface, taking more time to evaporate.

Image taken after 30 minutes drying. Water and Vanzan gel created *tidelines*.

Figure F.9: Cleaning tests performed on the lower part of *Desde la Ventana I*. The tests were performed over a thin grey area of painting, painted directly over a stripe of fabric adhered to the canvas painting (the same fabric as the canvas). The use of the gel systems limits the penetration and diffusion of water into the paint layers, which can be seen in the different drying times.

The SEM images obtained from the samples extracted from the grey paint layer are shown in Figure F.10. These images show that the paint film has swollen and deformed considerably after the application of free water and Vanzan® gel application. In the figure, this corresponds to the *tighter* appearence of the sample. This is in good agreement with the degradation observed for the Pébéo® (acrylic-styrene) test specimens, which deform considerably with water based treatments. On the other hand, the surface exposed to the Agar-agar® gel presents similarto that of the control sample. Similar trends were seen in the samples extracted from the black area.

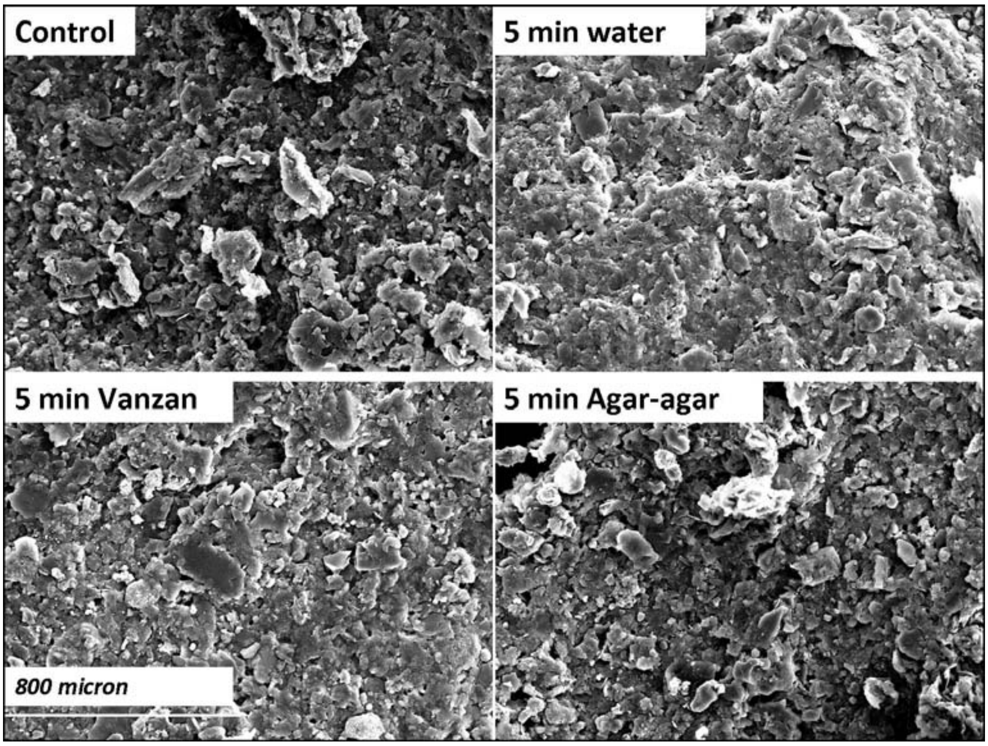


Figure F.10: Secondary electron images of the samples extracted from the grey paint layers painted over the cotton fabric of *Desde la Ventana I* (x5000 magnification).

7.3- Conclusions

It was possible to find similarities between the behaviour of the two case studies exposed here and the test specimens described in the previous chapter of this thesis that present similar chemical composition. The general observations are listed as follows:

- In contact with water (both free and gelled), the paint layers showed swelling. In the case of *La Puerta de Brandenburgo*, the PVAc based paint layer turned whitish soon after entering in contact with water. In the case of *Desde la Ventana I*, a softening of the paint layers was evident.
- The use of gels reduced the penetration of water, swelling and retention in the areas tested. This was true in very porous and poorly bounded surfaces, such as the grey area applied over the cotton fabric in *Desde la Ventana I*.
- The observations obtained macroscopically were in agreement with those revealed by SEM: The films exposed to water in the free form seem to generally suffer more alteration.