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CLEANING ACRYLIC EMULSION PAINT FILMS

Assessment of common application methods and a first approach to new proposals

Irene Cárdaba López

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Assessment of common application methods and a first approach to new proposals

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A mi padre, mi guía

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Summary

Acrylic emulsion paints comprise one of the most common medium in contemporary art. Since their introduction to the market in 1950's, their impact on art has been immense. However, despite all the advantages that this medium offers to the artists in terms of use, the conservation of these works poses a great challenge for restorers today, partly due to their high affinity to trap dirt on the surface. Airborne dust and dirt are easily attached to acrylic paint surfaces mainly due to the fact that they easily accumulate static charge and are soft at room temperature, hence surface cleaning is broadly required in most of these artworks. The conservation field has faced challenging problems associated with the cleaning of acrylic emulsion paintings throughout the last decades. Despite the several studies carried out by the most important conservation-restoration institutions worldwide, the complexity of the medium itself and its high sensitivity towards existing methods, together with the insufficient knowledge and the need for further research, have led to an immense gap in the preservation of these type of artworks. Therefore, there is a need to carry out further in-depth studies on these type of works and their materials, in order to establish more accurate guidelines for tailored treatments. To do that, besides evaluating the already existing methods in order to assess their suitability for the different acrylic paint brands and colours, we have also developed a new easy to make rigid gel which could be tailored according to specific treatment needs.

This thesis revolves around the properties and behaviour of three different acrylic paint brands and colours, which have been subjected to several cleaning tests and consequent analysis to evaluate the efficacy and side effects such as, chemical modifications of the paint film, of several cleaning treatments such as water based cotton swab cleaning, hydrogels and the use of emulsifying particles. FTIR-ATR, SEM-EDX and AFM were employed to evaluate the surface after treatment, and Termogravimetric analysis was applied to analyse changes in the binder, induced by the cleaning action. These analysis are mainly focused on checking the efficiency of the

treatments in terms of cleaning performance and capacity to carry out a residue free and harmless selective action. In addition, a comparison between brands and colours was carried out in order to identify the behaviour of the different acrylic medium against each treatment. The results obtained from this comparative study allowed us to establish appropriate lines of action for each specific case. For instance, it was observed that the brands suffering the biggest alterations in the bulk of the film after cleaning treatments, are not those showing the greatest alterations on the surface. This is a decisive issue when rethinking the monitoring and validation of appropriate cleaning methods.
Finally, in addition to evaluating the existing cleaning methods, a new rigid gel was designed and synthesized to increase the cleaning performance and improve the controlled release of water during the cleaning process. This gel besides being efficient is also easy to synthetize and customize by the restorers themselves, making this type of cleaning methods more accessible to the final users.

The structure of this thesis is divided in 7 chapters. Chapters 1, 3, 4 and 5 report the adapted versions of 4 publications derived from this thesis while, chapter 2 describes the methodology used throughout the work, and chapters 6 and 7 are devoted to discussion and conclusions.

Chapter 1 Presents a general introduction, dealing with the main aspects regarding the conservation of acrylic paint artworks and the latest cleaning methods at the date of publication. This chapter covers the theoretical framework and it contains a throughout review of the bibliographic resources that have supported the research work carried out in this thesis. It addresses the main properties of acrylic emulsion paints and the concerns regarding the degradation of this kind of paintings. The work gathered in this first chapter is an adapted version of the article "Gelled cleaning systems for acrylic emulsion paints: a scientific literature review" published in *GE-conservación* journal in 2021.

Chapter 2 describes the methodology used in the development of this thesis. It details the materials used in the sample preparation and the cleaning solutions tested, as well as their preparation and application conditions. It also makes a general introduction to the analytical methods used throughout the thesis, while the specific parameters are detailed in the following chapters.

Chapter 3 focuses on studying the chemical and physical properties of acrylic paintings. Three colours of the acrylic commercial paint brand Liquitex® (USA) are characterized by using different analytical techniques, before and after cleaning with traditional and novel aqueous cleaning methods, for comparison purposes.

A mock-up based research is performed in order to analyse paint properties, using Fourier Transform Infrared spectroscopy (FT-IR) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Samples were artificially soiled and aged under controlled conditions and the removal of artificial soil from these paint films was carried out using novel highly retentive PVA-based cryogels to avoid the uncontrolled wetting of these water-sensitive paint surfaces. Cleaning test were also performed using cotton swab as being the most common method used by restorers. The cleaning efficiency and changes induced by different water solutions were evaluated using Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). Finally, an ATR-FTIR and 2D FTIR Imaging study of the residues left by the gels was carried out for comparing the effect of novel cryogels with the effect of using Velvesil Plus® emulsions, a gel-like silicone polyether copolymer used to create a stable water-in-oil emulsion, widely used among restorer due to its high hydrophobicity and ease to prepare. Results showed that cryogels are able to clean in a more efficient and safer way than cotton swabs mainly because they reduce the mechanical action and are efficient in completely removing the soil. In fact, AFM results demostrated that the sole gentle rolling of swabs on the paint surface induces morphological changes. Moreover, it was found that cryogel is a residue-free method unlike Velvesil Plus®, which leaves siloxane residues even after rinsing the treated surface. This chapter concludes that cryogels grant a safe, satisfactory, and residue-free soil removal from acrylic paint films, overcoming some of the main drawbacks of commonly-used cleaning methods. The results gathered in this chapter are adapted from the article "Assessment of aqueous cleaning of acrylic paints using innovative cryogels" published in the *Microchemical Journal* in 2021.

Chapter 4 focuses on extending the previous study on the effect of water based cleaning treatments to other commercial paint brands, such as Titan Arts – Acrílico extrafino (Spain) and Hyplar Acrylic Colors® (USA). Those brands were specifically selected for comparative reasons due to the differences in their binding medium compositions, in order to prove the universality of the method. A pH 5 buffered aqueous solution was tested using cotton swab cleaning as well as confined in cryogel. A comparative study of both application methods was carried out by studying their effect on the surface stability of both paint brands and different colours. Paints were characterized by using Fourier Transform Infrared spectroscopy (FT-IR), pyrolysis – gas chromatography - mass spectrometry (Py-GC-MS), Thermal Gravimetric Analysis (TGA) and Atomic Force Microscopy (AFM). Different aging and degradation tendencies, according to brands and pigments, could be observed. Thus, different pigment and brand dependant additive migration patterns were reported. For instance, Titan paint samples showed an earlier migration of additives than Hyplar. Moreover, remarkable differences were observed in the effect of the cleaning methods depending on the paint composition and the cleaning application procedure used. These differences were observed both at the surface level and in the bulk of the paint film. The use of cryogels for cleaning proved to be more respectful than swab cleaning. Overall, Hyplar organic colours for instance have demonstrated a considerable sensitivity towards colour removal while Titan inorganic colours showed higher sensitivity to surfactant removal. AFM confirmed again that swab causes roughness changes on the paint surface due to the mechanical action. This chapter concludes that it is no possible to define a common cleaning system for all the acrylic brands and pigments even if, in general terms cryogels show more respectful cleaning results compared to cotton swab. TGA-DTG provided the most remarkable results for this study since it revealed the chain-scission of the polymer binder as a result of the cleaning treatment of certain mockups. Thus, paints that suffer bigger changes on their surface after treatment, are not necessarily those that have undergone major changes on the bulk of the paint film. Leading to conclude that in some cases, the stability of the paint surfaces does not always guarantee an innocuous effect of water based or gel cleaning systems, since bulk changes can lead to diminish the thermal stability of the paint film. These results were published in the *Journal of Cultural Heritage* ,"Extension study of the assessment of aqueous cleaning of acrylic paints: evaluation of Titan and Hyplar acrylic brands", year 2024.

Chapter 5 presents the development of a new easy-to-make polymer hydrogel, made by UV-photopolymerization, that exhibits excellent cleaning properties. The formulation of hydrogels obtained by UV-curing and their performance as dry cleaners for acrylic paints was investigated. Different functional acrylic monomers were used to formulate a series of UV cross-linked hydrogels by fast UV photopolymerization. Their effectiveness on surface dirt removal was assessed by SEM microscopy and colorimetry. The hydrogels showed good performance as efficient and safe cleaning tools for water-sensitive paint surfaces. Their performance is similar to that of other chemical gels proposed before, with the advantage of not needing a complex laboratory process to create them. The obtained UV-hydrogels were compared to the well-known agar gel, which is a non pre-formed and easy to prepare widely used physical gel, showing benefits in terms of reducing unwanted excess of water. Results showed that UV hydrogels did not present wet residue problems after cleaning. In addition, water release is under control due to the good retaining properties of the hydrogel, which showed a reduction of moistening compared to other commonly used easy-to-make gels.

This chapter aims to prove that easy-to-make UV-cured hydrogels are an efficient tool for the cleaning of surface dirt from water-sensitive paintings, overcoming the limits of traditional cleaning methods: easy to make and tuneable. These results were published in *Polymers* journal, under the title "Easy-to-Make Polymer Hydrogels by UV-Curing for the Cleaning of Acrylic Emulsion Paint Films", in the year 2021.

Chapter 6 addresses a general discussion of the work developed in this thesis as well as the prospects for conservation of acrylic painted artworks and concerns about the development of more accurate cleaning methodologies.

Finally, **Chapter 7** summarizes the most relevant conclusions drawn from the evaluation of the results analysed in the previous chapter.

Resumen

Las pinturas de emulsión acrílica son uno de los materiales pictóricos más comunes en el arte contemporáneo. Desde su introducción en el mercado en la década de 1950, su impacto en el arte ha sido inmenso. Sin embargo, a pesar de que este medio pictórico ofrece grandes ventajas para los artistas, su conservación plantea hoy en día un gran reto para los restauradores. La elevada acumulación de carga estática en superficie y su tendencia a reblandecerse a temperatura ambiente, hacen que el polvo y la suciedad ambiental se adhieren con facilidad a las películas de pintura acrílica. Esto provoca a su vez que las superficies pictóricas requieran limpieza de forma recurrente. En las últimas décadas, el campo de la conservación se ha enfrentado a problemas complejos relacionados con la limpieza de pinturas de emulsión acrílica. A pesar de los diversos estudios llevados a cabo por las instituciones de conservación-restauración más relevantes a nivel internacional, la complejidad del propio soporte y su gran sensibilidad frente los métodos de limpieza existentes, hacen que la información disponible resulte aún incompleta, generando una inmensa laguna de conocimiento en la conservación de este tipo de obras, y haciendo así indispensable el desarollo de investiganesadicionales en este ámbito. Es necesario profundizar en el estudio de este tipo de obras y sus materiales, con el fin de establecer directrices más precisas para el establecimiento de tratamientos específicos. Para ello, en esta tesis, además de evaluar los métodos ya existentes, valorando su idoneidad frente a diferentes marcas y colores de pintura acrílica, también hemos desarrollado un nuevo gel rígido fácil de fabricar y que permite su modificación en función de las necesidades específicas de cada tratamiento.

Esta tesis se enfoca en analizar las propiedades y el comportamiento de tres de las marcas y colores más significativos de pintura acrílica. Las muestras de pintura se han sometido a varias pruebas de limpieza y al análisis consiguiente, con el fin de estudiar la eficacia y los efectos secundarios de dichos tratamientos. Entre otros factores, se han evaluado las modificaciones químicas de la película de pintura provocadas por el empleo

de diversos métodos de aplicación: disoluciones acuosas aplicadas por medio de hisopos de algodón, hidrogeles y el uso de partículas emulsionantes. La evaluación de la superficie tras el tratamiento se llevó a cabo mediante FTIR-ATR, SEM-EDX y AFM. Además, se empleó el análisis termogravimétrico para analizar los cambios químicos en el aglutinante, provocados por la acción de las limpiezas. Estos análisis se centraron principalmente en comprobar la eficacia de los tratamientos de limpieza y su capacidad para ejecutar una acción selectiva. Así mismo, se llevó a cabo una comparación entre marcas y colores para identificar el comportamiento de los distintos medios acrílicos frente a cada tratamiento. Los resultados obtenidos de este estudio comparativo permitieron establecer líneas de actuación adecuadas para cada caso concreto. En este sentido, se observó que las marcas y colores que sufren mayores alteraciones químicas a nivel de aglutinante no se corresponden con aquellas que presentan las mayores modificaciones morfológicas a nivel superficial. Esta cuestión es decisiva a la hora de replantear el seguimiento y la validación de los métodos de limpieza mediante la monotorización exclusiva de las superficies.

Por último, además de evaluar los métodos de limpieza existentes, se diseñó y sintetizó un nuevo gel rígido, con el fin de lograr un mayor rendimiento en la limpieza y mejorar las condiciones de control en la liberación de disoluciónes acuosas durante el tratamiento. Este gel, además de eficiente, es fácil de sintetizar y adaptar a las características deseadas por los restauradores, haciendo que este tipo de métodos de limpieza sean más accesibles para los usuarios finales.

La estructura de esta tesis se divide en 7 capítulos. Los capítulos 1, 3, 4 y 5 recogen las versiones adaptadas de 4 publicaciones derivadas de esta Tesis. Por otro lado, el capítulo 2 describe la metodología utilizada a lo largo del trabajo. Finalmente los capítulos 6 y 7 están dedicados a la discusión y a las conclusiones.

El **capítulo 1** presenta una introducción general en la que se abordan los principales aspectos sobre la conservación de las obras de arte realizadas con pintura acrílica y los métodos de limpieza más recientes a fecha de publicación del artículo. Este capítulo abarca el marco teórico y contiene una amplia revisión de los recursos bibliográficos que han servido de apoyo al trabajo de investigación realizado en esta Tesis. Aborda así las propiedades principales de las pinturas de emulsión acrílica y cuestiones relativas a la degradación de este medio pictórico. El trabajo recogido en este primer capítulo es una versión adaptada del artículo " Sistemas de limpieza gelificados para pinturas acrílicas en emulsión: una revisión de la literatura científica " publicado en la revista GE-conservación en 2021.

El **capítulo 2** describe la metodología empleada en el desarrollo de esta Tesis. Se detallan los materiales y métodos utilizados en la preparación de las muestras y las soluciones de limpieza testadas, así como sus condiciones de preparación y aplicación. También hace una introducción general a los métodos analíticos utilizados a lo largo de la Tesis, mientras que los parámetros específicos se detallan en los capítulos siguientes.

El **capítulo 3** se centra en el estudio de las propiedades físico-químicas de tres colores de la marca comercial de pintura acrílica Liquitex® (EE.UU.). Asimismo, se testaron ciertos métodos de limpieza acuosos aplicados con medios tradicionales y otros más novedosos, con fines comparativos. Para llevar a cabo la caracterización de las muestras se aplicaron diferentes técnicas analíticas antes y después de realizar las limpiezas. El estudio de la composición y de las propiedades intrínsecas de la pintura se se llevó a cabo mediante espectroscopia infrarroja por transformada de Fourier (FT-IR) y cromatografía de gases-espectrometría de masas por pirólisis (Py-GC-MS). Para testar la eficacia de los métodos de limpieza, se aplicó una mezcla de suciedad artificial sobre las superficies de las muestras y se envejecieron en condiciones controladas. La eliminación de la suciedad se llevó a cabo empleando criogeles con base de PVA altamente retentivos, que permiten humectar de forma controlada las superficies pictóricas sensibles al agua. También se realizaron pruebas de limpieza con hisopos de algodón, por ser el método más popular entre los restauradores. La eficacia de la limpieza y los cambios inducidos por las diferentes soluciones acuosas se evaluaron mediante espectroscopia infrarroja con transformada de Fourier - Reflectancia total atenuada (ATR-FTIR), microscopia electrónica de barrido (SEM) y microscopia de fuerza atómica (AFM). Por último, se llevó a cabo un estudio de residuos en superficie mediante ATR-FTIR e imagen FTIR 2D para comparar la diferencia entre emplear los criogeles o las emulsiones de Velvesil Plus®, un copolímero de poliéter de silicona en forma de gel utilizado para crear una emulsión estable de agua en aceite, muy utilizada entre restauradores debido a su alta hidrofobicidad y facilidad de preparación. Los resultados mostraron que los criogeles son capaces de limpiar de forma más eficaz y segura que los hisopos de algodón, principalmente porque reducen la acción mecánica y son eficaces eliminando la suciedad. De hecho, los resultados de AFM demostraron que el incluso el suave rodamiento de los hisopos sobre la superficie de la pintura induce cambios morfológicos. Además, se comprobó que el criogel es un método que no deja residuos, a diferencia del Velvesil Plus®, que deja residuos de siloxano incluso después de aclarar la superficie tratada. Este capítulo concluye que los criogeles garantizan una eliminación segura, satisfactoria y sin residuos de la suciedad de las películas de pintura acrílica, superando algunos de los principales inconvenientes de los métodos de limpieza utilizados habitualmente. Los resultados recogidos en este capítulo son una adaptación del artículo "Assessment of aqueous cleaning of acrylic paints using innovative cryogels" publicado en la revista Microchemical Journal en 2021.

El **capítulo 4** se centra en ampliar el estudio anterior testando el efecto de los tratamientos de limpieza acuosos sobre otras marcas comerciales de pintura, como Titan Arts - Acrílico extrafino (España) e Hyplar Acrylic Colors® (EE.UU.). Dichas marcas se seleccionaron específicamente por motivos comparativos debido a las diferencias en la composición de sus aglutinantes, con el fin de demostrar la universalidad del método. Se realizaron tests de limpieza con una disolución acuosa tamponada a pH 5, aplicada mediante hisopo de algodón y criogel. Se realizó un estudio comparando ambos métodos de aplicación y evaluando su efecto en la superficie de las dos marcas de pintura y los diferentes colores. Las pinturas se caracterizaron mediante espectroscopia infrarroja con transformada de Fourier (FT-IR), pirólisis - cromatografía de gases - espectrometría de masas (Py-GC-MS), Análisis Gravimétrico Térmico (TGA) y Microscopía de Fuerza Atómica (AFM). Se observaron diferentes tendencias de envejecimiento y degradación, según las marcas y los pigmentos. Así, se observaron diversos patrones de migración de aditivos en función del pigmento y de la marca. Por ejemplo, en las muestras de pintura Titan se detectó una migración de tensoactivos más temprana que en las pinturas Hyplar. Además, se observó que el efecto de la limpieza era diferente dependiendo del método de aplicación utilizado y de la composición de la muestra de pintura. Estas diferencias se identificaron tanto a nivel superficial como en el núcleo de la película de pintura. El uso de criogeles para la limpieza resultó ser más respetuoso que la limpieza con hisopos. En general, los colores orgánicos de la marca Hyplar, por ejemplo, demostraron ser más inestables a nivel de eliminación de pigmento, mientras que los colores inorgánicos Titan mostraron una mayor sensibilidad a la eliminación de tensioactivos. EL AFM confirmó de nuevo que el hisopo provoca cambios de rugosidad en la superficie de la pintura debido a la acción mecánica. Este capítulo concluye que no es posible definir un sistema de limpieza común para todas las marcas y pigmentos acrílicos aunque, en términos generales, los criogeles muestran resultados de limpieza más respetuosos en comparación con los hisopos de algodón. Los análisis TGA-DTG proporcionaron los resultados más notables de este estudio, ya que revelaron la escisión de la cadena polimérica que conforma el aglutinante, como resultado del tratamiento de limpieza de ciertas muestras. Por ello, las pinturas que sufren mayores cambios en su superficie tras el tratamiento, no son necesariamente las que han sufrido mayores alteraciones en el núcleo de la película de pintura. Lo que lleva a concluir que: pese a que tras un tratamiento de limpieza acuoso, la superficie pictórica resulte inalterada, esto no siempre garantiza un efecto inocuo a nivel de estructura interna de la pintura, ya que esta puede haber sufrido alteraciones que provoquen la disminución de su estabilidad térmica. Estos resultados se publicaron en Journal of Cultural Heritage "Extension study of the assessment of aqueous cleaning of acrylic paints: evaluation of Titan and Hyplar acrylic brands", año 2024.

El **capítulo 5** presenta el desarrollo y propuesta de un nuevo hidrogel polimérico fácil de fabricar, obtenido por fotopolimerización ultravioleta, que presenta excelentes propiedades de limpieza. Se investigó la formulación de hidrogeles obtenidos por fotopolimerización UV y sus prestaciones como limpiadores "en seco" de pinturas acrílicas. Se utilizaron diferentes monómeros acrílicos funcionales para formular una serie de hidrogeles reticulados por medio de una rápida fotopolimerización UV. Su eficacia en la eliminación de la suciedad superficial se evaluó mediante microscopía SEM y colorimetría. Los hidrogeles mostraron un buen rendimiento como herramientas de limpieza eficaces y seguras para superficies de pintura sensibles al agua. Su rendimiento es similar al de otros geles químicos propuestos anteriormente, con la ventaja de no necesitar un complejo proceso de laboratorio para su elaboración. Los hidrogeles UV obtenidos se compararon con el conocido gel de agar, que es un gel físico no preformado y fácil de preparar, ampliamente utilizado y que presenta ventajas en cuanto a la reducción del exceso de agua no deseada. Los resultados mostraron que los hidrogeles UV no liberaban un exceso de humedad en las limpiezas. La liberación controlada se logra gracias a las buenas propiedades de retención del hidrogel, que mostró una reducción de la humectación reseñable en comparación con otros geles de uso común fáciles de preparar. Este capítulo pretende demostrar que estos hidrogeles, fáciles de fabricar mediante luz UV, son una herramienta eficaz para la limpieza de la suciedad superficial de pinturas sensibles al agua, superando los límites de los métodos de limpieza tradicionales: fáciles de fabricar y adaptables. Estos resultados se publicaron en la revista Polymers, con el título "Easy-to-Make Polymer Hydrogels by UV-Curing for the Cleaning of Acrylic Emulsion Paint Films", año 2021.

El capítulo 6 aborda una discusión general sobre el trabajo desarrollado en esta tesis, así como las perspectivas de conservación de las obras de arte realizadas a base de pintura acrílica y cuestiones relacionadas con el desarrollo de metodologías de limpieza más adecuadas.

Por último, el **capítulo 7** resume las conclusiones más relevantes extraídas de la evaluación de los resultados analizados en el capítulo anterior.

Objectives

Despite the successful projects carried out by internationally relevant institutions in the field of conservation and the variety of studies published to date proposing different cleaning systems for acrylic paint surfaces, the search for a more suitable, efficient and respectful system for this type of artworks remains under research. Therefore, the main objective of this thesis was to carry out a comparative study of available cleaning methods for acrylic paint surfaces toward assessing their potential application in the cleaning of acrylic paints, with special focus on confined methods, in orther to provide possible ways to overcome the inherent drawbacks.

The specific objectives undertaken to achieve the main goal were:

1- Assessment of state-of-the-art cleaning methods applied on acrylic paint surfaces
2- Selection and setting up of representative mockups and artificial ageing procedures for different acrylic paint brands and colours.
3- Characterization of samples and identification of differences in properties and behaviour according to brand and colour.
4- Identification of aqueous methods' effect on acrylic paint samples, according to different brand and colours.
5- Assessment of the surface residues question, in relation to cleaning methods.
6- Assessment on the influence of the application method on the success of the cleaning treatment.
7- Optimisation of an easy to make gel system able to offer safer and more efficient cleaning results.

Chapter 1.

GENERAL INTRODUCTION AND THEORETICAL FRAMEWORK

An adapted version of

Gelled cleaning systems for acrylic emulsion paints: a scientific literature review

I. Cárdaba and A. Solbes

Ge-Conservación, 20(1): 337-351 **2021**

SJR, Q1, IF: 0,18 , 117/669, Visual Arts, Performing Arts

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1. General Introduction

Scientific research in the field of contemporary art conservation raised due, in part, to the growing awareness of the need to preserve our heritage through the application of accurate practices, based on a thorough knowledge of the materials that are part of the artistic objects. The incorporation of different materials and techniques used by artists since the 20th century, forces conservators and restorers to face unknown problems caused by the use of new and unfamiliar materials, for which there are no previous examples of behaviour to refer to. As in the case of industrial products, paint formulations are almost never described in detail, and the composition of a given product may change many times during its production without ever changing its brand. Sometimes, works that appear to be created with the same material may show different aging behaviour, so the origin of the products used must be identified [1].

Among contemporary painting media, acrylic paint is one of the most important given its widespread use among artists as an alternative to oil paint. Acrylic paints have been widely used by artists since the early 1960s [2, 3]. While there is no indication that acrylic paints are less stable than oil paints, they require different conservation treatments due to their different composition and therefore further research has been necessary to understand their behaviour and aging. For instance, after a short period of exposure to the environment, conservation specialists observed that the artworks accumulated surface dirt for different reasons associated with their composition [4]. This phenomenon has been a severe problem for conservation since the application of any cleaning method is constrained by the acrylic film's delicate morphology and its high sensitivity to organic solvents and water. In this sense, the literature has widely reported [5] that the most relevant problems are associated with the presence of certain hydrophilic additives such as wetting and dispersing agents [6-8], which can be washed away during aqueous cleaning.

Works of art made with acrylic paints pose a difficult challenge for conservator-restorers when it comes to cleaning. Despite the amount of research work published to date on the preservation and treatment of these type of paints, there is still much uncertainty regarding the effects of cleaning treatments on the original paint components.

To address this situation, since the early 2000s, a significant body of science-based research has been conducted on the properties of acrylic paints, including exploration of the effects of surface cleaning treatments. The book ***The Impact of Modern Paints*** **[9]** was published in that year, based on a research conducted by Jo Crook and Tom Learner on techniques and materials used by well-known contemporary artists. ***Modern Paints Uncovered*** **(MPU) [2] and** ***Analysis of Modern Paints*** [3] are among the most remarkable publications that address the conservation of this type of artworks. MPU proceedings were published in 2007 after the Symposium held at the Tate Modern in London, organized by the Getty Conservation Institute, the Tate Modern and the National Gallery of Art. This book gathers contributions from diverse authors regarding conservation issues of different contemporary paint materials. Some works are focused on analysing and characterizing the paints themselves; others focus on their behaviour and aging properties; and others, on cleaning treatment assessment. *Analysis of Modern Paints*, instead, is a research in conservation publication, by the conservation scientist Thomas J.S. Learner. This book, published in 2004, focuses on describing the analytical methods suitable for the identification of modern paint materials.

The **Tate Axa Art Modern Paint Project** (TAAMPP) [10, 11], is one of the most noteworthy project in the field and dealt with the conservation of the acrylic emulsion paints. It was developed at the Tate Modern in London between 2006 and 2009, through the AXA Art Research Grant, and its main objective was to assess and improve the conservation strategies towards acrylic emulsion paintings, with a special focus on the effects of wet-cleaning treatments. In addition, some of the artworks analysed in the TAAMPP project were (re)assessed in 2019 as a part of a collaborative project between the Tate Modern and the HIPERION Molab European Platform. In this regard, the absence/presence of migrated surfactants on the the works [11] was determined in order to evaluate the long-term behaviour of the paint surfaces after the cleaning treatment. Moreover, the Getty Conservation Institute (GCI), initiated the **CAPS (Cleaning Acrylic Emulsion Paints)** project in 2009, consisting on a workshop series integrating scientific research with latest perspectives on cleaning technology in art conservation. This project aims to stimulate the development of problem-solving frameworks, facilitate dialogue on the application and evaluation of new treatments, and guide future research on acrylic painted surfaces.

Over the course of this twenty-year period, in parallel with the development of these big projects, several authors have published works that contribute to the state of the art of the conservation of acrylic emulsion paints. Many of the existing investigations on conservation of acrylic emulsion paints in the field of modern and contemporary art are focused on the identification of the main constituents of the paint formulations [2, 9]. Other studies concentrate on the aging tendencies and their behavior under diverse environmental conditions [12]. However, the most studied issue is the effect of surface cleaning on acrylic painted artworks, with the focus on searching for accurate methods to remove dirt without compromising the integrity of the paint films. Thus, some researchers have the aim to improve the analytical techniques towards the characterization and study of the behaviour of the acrylic paintings [13, 14]. For instance, some authors propose to refine the already used analytical techniques to achieve more accurate identifications [15] while others propose to incorporate new techniques, less common in the study of acrylics[16, 17]. The aim of many investigations has also been to deepen the knowledge about the components that are present in this type of paints, in order to better refine the proposed treatments [18]. One of the most recurrent issue is the study of the additives present on these films, which are rich in surfactants [19-21]. The investigation of the effect that pigments have on the stability and behaviour of the acrylic paints [22-24] is also an important issue. Other authors have carried out studies about the aging of these paints, including the effect of light and humidity on the degradation processes of the acrylics [25-27]. In some cases, accelerated aging is performed in order to predict the possible trend in the aging of certain acrylic paints [28, 29].

In addition to investigating the characteristics of the materials and their aging, many researchers have worked on developing and testing cleaning methods for aqueous sensitive surfaces, as is the case of acrylics [30, 31]. It is safe to say that cleaning is probably one of the most complex and delicate tasks to undertake on a contemporary work of art, due to the large amount of variables that conservators may have to deal with, such as, for example, the absence of a protective coating. Moreover, the aqueous sensitivity of acrylic paintings makes it very difficult to find harmless efficient treatments for removing dirt from these surfaces. Therefore, a hot topic for conservation scientists is the development of new cleaning systems and methods, able to bring aqueous cleaning agents into contact with artefacts in a safe and accurate way. pH and conductivity adjusted aqueous solutions [32-39]are the most studied cleaning systems due to their ability to remove dirt while providing some kind of control over the side effects on acrylic paint surfaces, such as swelling of the paint film and solubilisation of paint additives, like surfactants [33, 36, 40, 41]. Some authors have thoroughly studied the use of non-polar solvents, since they are safer with respect to swelling capacity and surfactant removal [42], however, they are weak agents for soil removal and leave surfaces poorly cleaned [39].

The application mode of the cleaning methods also seem to play an important role. Thus, gelling agents have been proposed both as thickening agents for the cleaning solutions and as rigid containers, such is the case of the hydrogels, that allow a controlled release of the confined aqueous cleaning solutions.

Our research group has published several articles in this field, mainly focused on studying the application of adjusted aqueous cleaning treatments on acrylic paint surfaces by employing diverse application methods, such as cotton swab, silicone based emulsifiers, rigid physical gels and chemical hydrogels [43]. All these methods were studied for comparative reasons, in order to analyse their advantages and drawbacks in terms of induced compositional changes and surface modification on the acrylic paints. Although there is not much literature focused on this type of comparative studies, there are previous works dealing with comparing the use of swab rolling versus rigid gel, in terms of their influence on surface roughness changes [44 - 46].

All the studies carried out so far have provided important steps towards safer cleaning systems, although there is still work to be done in order to optimize universal systems, adaptable to specific needs. This task requires reviewing the results and continuing researching towards application methods that allow even greater control and ease of preparation than those proposed so far. To this end, the last chapter of this dissertation proposes the incorporation of an easy to make UV-cured hydrogel [43], which is commonly used in other scientific and technical fields such as optics and medicine, in order to explore its feasibility in this type of cleaning treatments.

2. Acrylic paint properties

Acrylic emulsion paints are complex fluids made up of a binder (acrylic resin or latex), pigments, and many additives that favour their stability in the aqueous medium [47]. Additives are essential for the paint to be preserved in optimal conditions and to have specific properties of use, rheology or curing process [48]. Both wetting agents and dispersants are introduced in considerable quantities to blend fillers and pigments in the aqueous phase and also during the resin polymerization process [49]. Due to their amphiphilic nature, wetting agents allow emulsifying solid particles of polymers and pigments in water. At the same time, dispersants prevent these particles from flocculating or forming aggregates, maintaining a homogeneous dispersion of the emulsion [50]. Like other components, both additives remain in the dried film, retaining their inherent sensitivity to water.

As wetting agents, the industry usually uses a combination of ionic and non-ionic surfactants [21]. Within the non-ionic surfactants, the polyethene glycol (PEG) type surfactants are considered the most problematic regarding preservation, and they can significantly affect the film's optical and mechanical properties [51]. Surfactants have high mobility and can migrate from inside the acrylic film to the surface by different mechanisms associated with their glass transition temperature (Tg) and the type of copolymer or curing process among other physicochemical phenomena [52]. This additive can be grouped in the surface in localized zones or in a continuous manner, modifying the saturation and gloss of the paint and, at the same time, trapping environmental dirt [53]. During the drying and film formation process, surfactants accumulate mainly near the surface, close to the support or inside the polymeric matrix and can form hydrophilic aggregates with high absorption capacity by capillarity [54]. These surfactants added as resin stabilizers can account for 2 to 6% of the dry film total weight [3].

Similarly, dispersants remain in the film while retaining all their properties and hydrophilic capacity. Acrylic paints use high molecular weight polymers such as polyacrylic acids (PAA) to perform this function [30]. These macromolecules exhibit an amorphous helical structure that can increase up to 1000-fold and absorb water at higher pH values. Although PAAs maintain a low hydration state with acidity, they rapidly ionize when exposed to an alkaline environment, transitioning to an expanded and absorption-sensitive state [33]. Acrylic paints are usually buffered to a pH between 9 and 10, thus favouring the swelling of PAAs and giving the paint a creamy texture and rheology suitable for use [3]. From a physicochemical point of view, the addition of an alkaline solution to the system displaces the hydrogen atoms of the carboxylic groups (-COOH), transforming them into carboxylate groups (-COO-) repelling each other [55]. The electrostatic repulsion of these groups produces the elongation of the PAA chain in the matrix, considerably increasing the volume of the dry film and modifying its mechanical properties irreversibly.

2.1. Swelling and extraction of materials

Concerning the conservation of acrylic paints, the literature considers the phenomena of swelling due to water absorption [7, 56, 57] and the subsequent extraction of constituent materials [8, 44, 58-59] as the most damaging effects on their survival over time. Both can occur naturally by absorbing ambient humidity, accidentally by any external deterioration agent, or due to different restoration processes, especially cleaning.

Acrylic film swelling by absorption occurs by capillarity from the first minute of contact [36] with an organic solvent or any type of aqueous solution. The absorption capacity depends, as noted, on the different water-soluble materials present (surfactants and dispersants), but also their quantity, the elasticity of the polymer, the particle size of the resin and the curing and ageing processes [58-59]. Absorption occurs to saturation within 5 to 10 minutes after contact and may be influenced by the coalescence degree of the film or by water-soluble material degradation. Ploeger [60] observed that this phenomenon differed between pigmented and unpigmented films, noting that pigments and other additives can affect the process. In this sense, certain compounds such as thickeners and aluminosilicate type pigments are noteworthy for their hydrophilic capacity [8].

Other authors such as Whitmore, Morris and Colaluca [59] point out that solution absorption and diffusion is reduced by 25-50% for treated films, which have already significantly reduced their water-soluble materials, extracted by desorption. In general, paints with organic pigments tend to absorb and swell to a greater extent than those containing inorganic pigments [Figure 1], possibly due to a more significant presence of hydrophilic additives in their composition [52]. The convention says that the greater the absorption of a solution, the greater the swelling and extraction of materials.

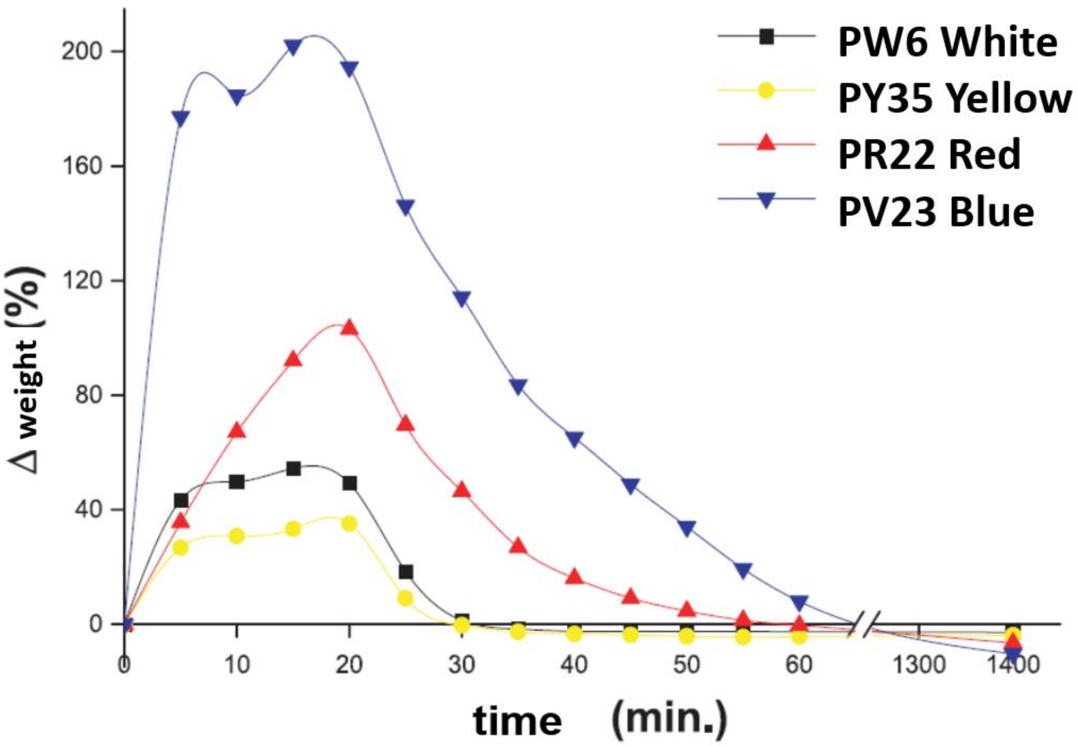

Figure 1 Absorption-desorption tests of four Hyplar acrylic films in deionized water. Inorganic: PW6 white and PY35 yellow. Organic: PR22 red and PV23 blue. A 200% weight increase for a blue paint with dioxazine organic pigment stands out (Solbes García, Á. 2017). [61]

Regarding the extraction of materials, two main aspects should be considered; the natural exudation of surfactants to the surface and the adsorption-desorption phenomena resulting in the loss of critical compounds or their relocation in the polymer matrix [14, 53]. Surfactant's exudation or leaching occurs, for example, with changes in temperature and relative humidity depending on the copolymer's Tg [62-63]. A temperature below Tg will generate a much stiffer and more volume-compressed film, pushing surfactants out of the matrix. On the contrary, a higher temperature will produce the opposite effect, a softer and more morbid film with a matrix that will absorb these compounds.

Something similar occurs with the relative humidity, since high humidity environmental conditions (above 40% RH) will imply a better absorption of surfactants into the paint, and lower humidity will imply a more significant presence on the surface [19].

The first acrylic emulsion paint formulations were based on poly ethyl acrylate/methyl methacrylate [p(EA/MMA)], a stiffer copolymer than its predecessor, the poly butyl acrylate/methyl methacrylate [p(nBA/MMA)][64]. Its hardness and hydrophobicity characterize the former, so the formulation is committed to a high presence of wetting and dispersing agents. Therefore, the appearance of the new copolymer responds to the need to generate a less rigid polymer, with the idea of reducing these additives during manufacturing and ensuring better surfactant absorption in the film [5].

Finally, and as mentioned before, components can be extracted by water desorption as well as by other solutions. In this process, pigments, fillers, thickeners, or other additives can be removed or relocated within the polymer matrix [8], significantly affecting optical and mechanical paint properties. At the visual level, we can speak of surface structure changes that modify the original saturation and gloss, the formation of haziness due to the accumulation of surfactants on the surface or the embedding of the environmental dirt [21, 50].

2.2. Mechanical properties

At the mechanical level, loss of adhesion and elasticity is frequent, in addition to the appearance of micropores [Figure 2]. Surfactants, for example, are compounds that favour film plasticity. Their removal can generate rigidity, leaving a more brittle film due to the presence of small voids and future breakpoints sensitive to elongation [65].

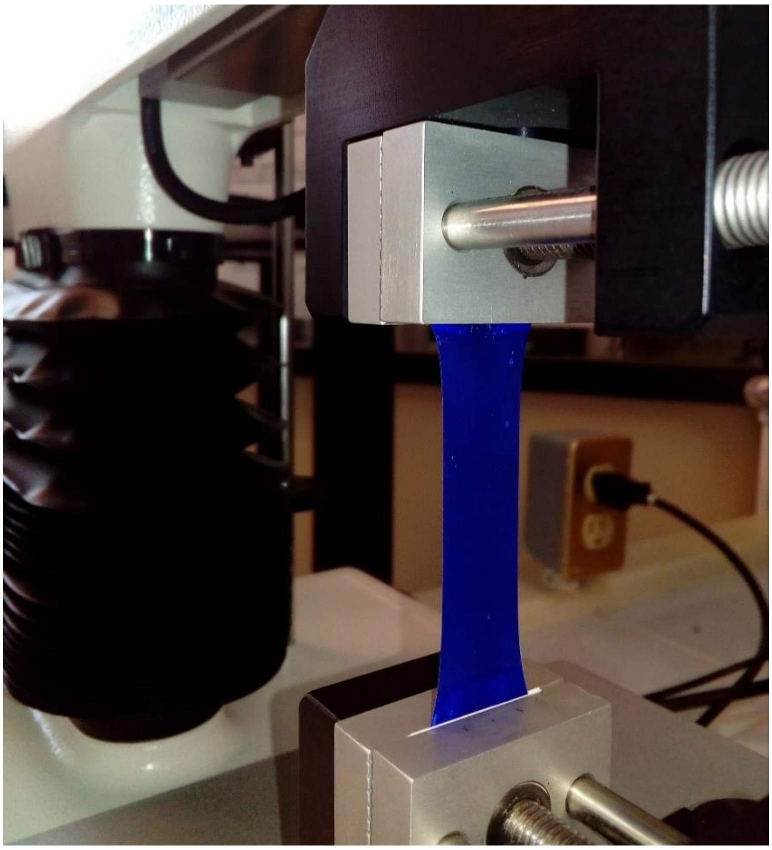

Figure 2 Tensile-strength test of a blue acrylic paint film in laboratory test (Solbes García, Á. 2017)

One of the main differences between the mechanical properties of a solid and a viscoelastic material is that solids present a stress-strain curve in which the elastic and plastic zones are easily differentiated. In acrylic films, a non-linear viscoelastic material, the elasticity varies according to the applied stress. Although it is considered that these materials will recover their size once the stress has ceased, the viscoelastic properties are irreversibly affected [66].

During tension testing, the mechanical properties of the viscoelastic materials depend on both the temperature and the speed at which the load is applied. But, in the case of acrylic paints, this will rely on other factors such as the glass transition temperature (Tg) or the volume concentration of fillers and pigments (pigment volume concentration or PVC) [67]). If a test is carried out at a very high speed, the sample will behave with high brittleness and low resistance to breakage, while at low rates; it will present good plasticity and high deformation values [68]. Similar effects have been reported in acrylic paints as a function of Tg and changes in temperature and relative humidity: the paints increase their stiffness as the temperature decreases, producing an inevitable reduction in their deformation capacity. When the temperature is reduced below the Tg, the film`s mechanical properties deteriorate significantly (lower stretching and increased stiffness), showing itself as a brittle and fragile material [69]. Regarding pigment concentration, it is considered that a high volume of solid particles in a paint can produce poorly cohesive films, with low strength and elongation to breakage. This is caused by the difficulty shown by the resin in encompassing the fillers and forming a continuous polymer matrix [62].

3. Cleaning systems and methods for the cleaning of pictorial artworks

The cleaning of pictorial works is an important treatment in the conservation of works of art. This field is under continuous study due to its complexity and importance in the correct treatment of the acrylic paintings. So far, different professionals have carried out studies to evaluate the pros and cons of available cleaning methods and systems according to the characteristics of the works on which they are applied [5, 35, 39, 43-46, 70-71]. It is essential to consider the risks involved in any cleaning intervention on a pictorial surface, such as the irreversible degradations caused by the cleaning treatments, the health risk implied in using toxic substances and the potential risk to the environment.

When selecting a cleaning treatment, the cleaning agent or system and the application method need special attention, since both are decisive in achieving the desired results. So far, the most common cleaning systems used to clean pictorial works have been based mainly on solvents and aqueous solutions. Regarding the application method, the most commonly used to date has been the cotton swab, releasing the cleaning solutions in a "free" form [70]. In the 80s, Richard Wolbers proposed the incorporation of gels and gelled systems opening a new line of methods that remains in continuous development [70]. This new contribution arises from the need to better control the action and release of liquid cleaning systems on surfaces. The surface cleaning of ancient pictorial works is often approached differently, thanks to the generally existing protective layer of varnish. However, with the emergence of contemporary art and the incorporation of new pictorial techniques, the mere removal of dust deposits on certain surfaces turned challenging. In many contemporary works, the absence of protection layers or varnishes implies the need to apply the cleaning methods directly on the paint surfaces, which are generally sensitive to most cleaning agents. Thus, acrylic emulsion paints are highly sensitive to water and polar organic solvents, which cause the swelling of the paint layer. In addition, the interaction of solvents with the acrylic film can cause the rupture of its microstructure, causing optical changes and decreasing its mechanical strength. On the other hand, solubilisation of additives can occur inside the pictorial layer, promoting additive migration to the surface, resulting in a modification of the physicochemical and mechanical properties of the film [71].

3.1. Aqueous cleaning systems applied to acrylic emulsion paints.

The sensitivity of acrylics towards aqueous cleaning can be categorized based on three main parameters: the effect of pH, the ionic strength and the impact of water on the migration of surfactants. Acrylics are slightly alkaline materials, formulated at pH 9.5 and although the paint, once dried, is insoluble in water, it still maintains the ability to hydrate, swell and soften in the presence of alkaline solutions. This causes the alteration of the pictorial layer, favours the leaching of some compounds from the painting and promotes the inlay of dirt. To minimize these effects, it is necessary to use slightly acidic solutions [30].

Conductivity is another parameter that must be controlled when preparing a cleaning solution. Conductivity measures ionic concentration in the solution and the mobility of the ions within it [72]. The film formed by an acrylic paint acts as a semipermeable membrane and the exchange of materials between the cleaning solution and the paint can occur through the surface's micro-pores due to the osmotic force. This movement of materials occurs when the relative concentration of soluble salts in both sides tend to balance. Therefore, it is necessary to formulate isotonic cleaning solutions, that is, with ionic force values similar to those of the paint, so that this ion exchange does not occur [30]. According to the research carried out by Chris Stavroudis, the most appropriate conductivity for acrylic surfaces is around 6000 S [72]. Nevertheless, it is always recommended to measure the surface conductivity before starting the cleaning and adjusting thereafter the solution's conductivity to the values of the pictorial film.

3.2. Gelled systems for the cleaning of acrylic emulsion paints

Controlled release aqueous cleaning methods improve the control of cleaning treatments. Richard Wolbers proposed the first approach to reduce excess wetting of the surface during cleaning, by using polymeric gels to thicken solvents, thus better-retaining liquids [70]. Incorporating gelled systems or the so-called "gel-like" systems minimized the inconveniences arising from applying solvents in free form. On the one hand, gelling allows the controlled and slow release of the cleaning solution, reducing its penetration into the paint and the risk of swelling. On the other hand, the increase in viscosity reduces the diffusion of the solubilized pictorial material in the cleaning system. Thus, a more selective treatment is achieved, limited to the area on which it is applied. Viscosity also decreases solvent evaporation, improving the control of the cleaning action and reducing toxicity for restorers.

Among the available systems, there are, on the one hand, the so-called thickeners or gelling agents and, on the other hand, the gels. Thickeners are substances added to a solution to increase its viscosity (methylcellulose, Carbopol, etc.). Gels can be either flexible or rigid and their main application is to keep the liquid in its inner porous structure (agar, gellam-gum and semi-interpenetrate network hydrogels). In the broadest sense, a gel is defined as a material that functions as a solid and deforms under specific stress. A polymer cross-linking system undergoes a phase transition from liquid to solid at a critical point, which is called the sol-gel transition or gel point. The change is due to the formation of an infinite grouping of networks that expands throughout the system [73].

In the borderline between the thickeners and gels, there are also the "semi-soft"' materials, the so-called highly viscous polymeric dispersions (HVPD) [73].

In addition to the aforementioned methods, it is worth mentioning the emulsifiable crosspolymer gels, as being an increasingly widespread alternative to the use of conventional emulsions and micro-emulsions. For instance, the Velvesil Plus which is a silicone-based polymeric emulsion stabilizer that is and easy to prepare system (simpler than emulsions) that can function as an apolar vehicle for emulsified aqueous solutions.

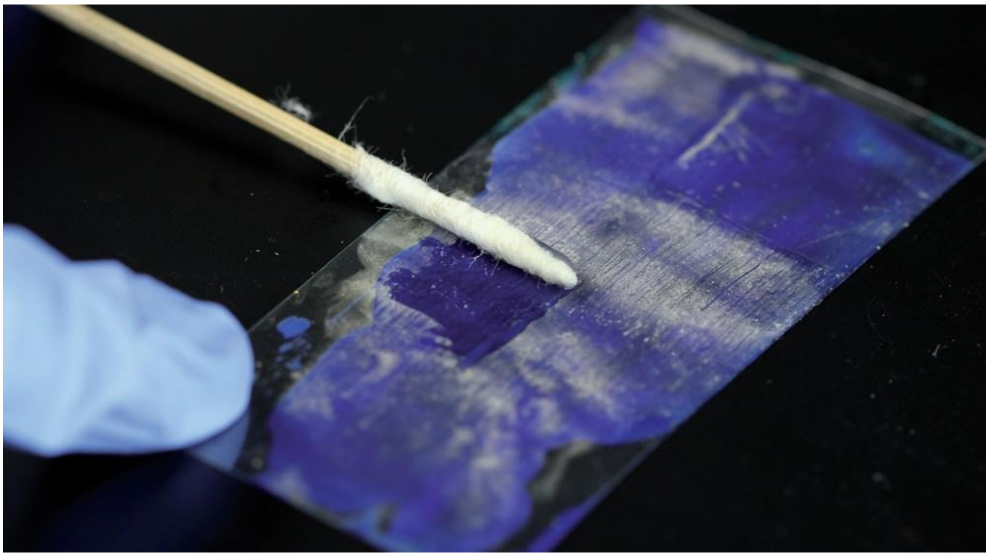

Figure 3 Application of a pH 5.0 buffer solution emusified with Velvesil Plus® for the removal of surface dirt on a layer of acrylic paint. Photograph of authors in laboratory trials (2017).

3.2.1. Gels

There are mainly two types of gels: physical and chemical gels. Physical gels undergo the transition from liquid to gel, or solid state, by a change in temperature or pH. In this case, the change is reversible, and the gel can return to its liquid state when these conditions change.

However, this transition is irreversible in chemical gels, occurring when covalent bonds between molecules create a network. These gels are used as sponges or "liquid containers", where the gel network remains stable while the embedded liquid can be modified or changed according to its intended use [73].

These physicochemical properties of the gels allow numerous applications. On the one hand, the gel can be applied to a specific artwork area without expanding. On the other hand, the liquid inside the gel behaves as if it were free between the surface of the work and the gel, solubilizing the necessary products within the surface, avoiding penetration to a great degree [73].

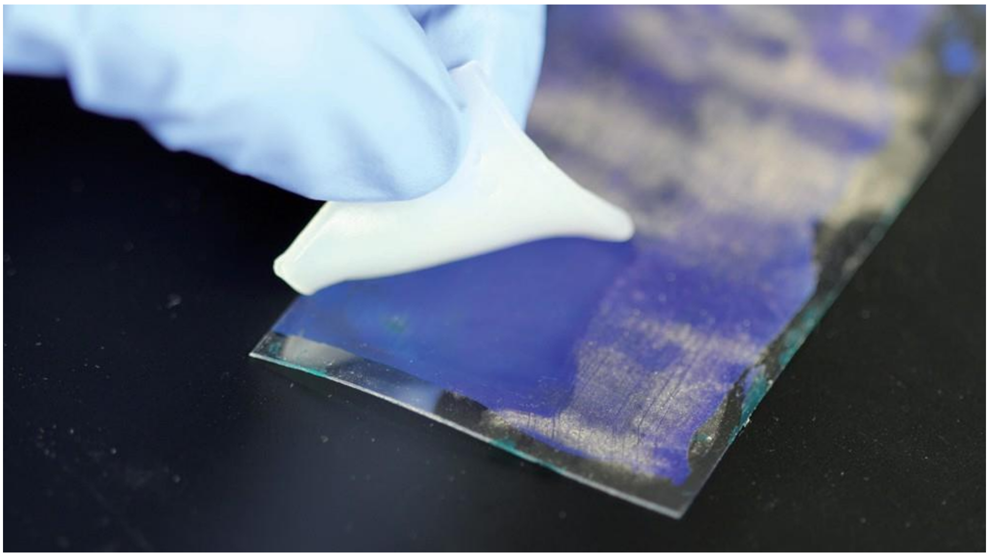

Figure 4 Example of applying a Nanorestore® hydrogel loaded with a buffer solution adjusted in pH and conductivity to remove surface dirt on a layer of acrylic paint. Photograph of the authors in laboratory trials (2017).

a) Physical gels

This category includes agar-agar gels and gums. Both form transparent rigid hydrogels that can retain large amounts of water when in contact with the porous matrix. Agar gels are thermoreversible and are created from a heating and cooling process [74]. They are easy to apply, although being semi-rigid, gels' adaptability on irregular surfaces can be complicated. Furthermore, the internal structure of these gels does not have sufficient capacity to retain and release the liquid in a controlled manner. Some researchers are studying this drawback in order to improve the controllability of agar gels [75-77] by creating gels with a higher polymer concentration.

b) Chemical gels

It is the least invasive application method used for cleaning water-sensitive surfaces, with the most outstanding advantages. They are based on cross-linked polymer networks formed by the covalent bonding of specific polymers that yield stable gels. Unlike physical gels, the internal structure and porosity of these gels can be modulated, allowing much greater control over the release of the embedded solution. In this way, a safer intervention is achieved, easy to apply and free of residue from the gel itself [78]. Poly vinyl alcohol (PVA) is one of the monomers used to form these type of gels. It is a compound with a great capacity to form hydrogels, easy to acquire, affordable and biodegradable. One of the gels derived from the PVA is the Poly vinyl alcohol–borate gel, which exhibits interesting mechanical properties since it adapts to surfaces ideally, is transparent, and is easy to manipulate. Moreover, these gels accept a range of organic co-solvents, can be stiff, spreadable, non-sticky and peelable. Certain studies claim that it is a residue- free method [73], although other research has shown that there are traces of borate left after surface application [79]. On the other hand, PVA cryogels obtained by freezing and thawing cycles of the polymer solution are a handy tool for removing dirt on irregular and sensitive surfaces[71, 80]. Moreover, they have a much greater adhesion capacity than other chemical rigid gels; they are soft and quite flexible, facilitating handling in the face of cleaning.

UV cured HEMA based chemical hydrogels are a suitable option developed by our research team. These gels can be modified depending on the needs on retention, porosity, viscoelastic behaviour and required hydrophilicity [43]. They are somewhat stiffer than PVA cryogels, so they adapt worse to irregular surfaces, but they have the advantage of not presenting wet residue problems after application. Their performance is similar to that of other chemical gels proposed before, with the advantage of not needing a complex laboratory process to prepare them.

4. Conclusions

Research on cleaning methods applied to contemporary paintings is in continuous development. New cleaning systems are formulated as knowledge on contemporary materials advances and further intervention criteria are adopted.

One of the most meaningful conclusions is the need to evaluate the surfaces individually before intervention. The adjustment of the pH and conductivity parameters of the aqueous solutions and the consideration of the residue issue are among the essential parameters when selecting the most appropriate system.

Even considering the feasibility of non-contact cleaning methods such as carbonic snow and atomic oxygen [81], this work has focused on aqueous methods and gels due to their greater accessibility by the community of restorers. The materials used in the preparation of the gels described in this work are available to most professionals. This work deepens in the use of chemical gels for their versatility as a more suitable tool for controlling the release of cleaning solutions and as a safer method in terms of residue and surface effect.

References

[1] O. Chiantore, A. Rava, Conserving Contemporary Art: Issues, Methods, Materials, and Research, Getty Publications, 2013: 195

[2] T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium. Los Angeles: Getty Conservation Institute, 2007.

[3] T. Learner, Analysis of Modern Paints, Research in Conservation, Getty Publications, 2005.

[4] E. Jablonski, T. Learner, J. Hayes, M. Golden, Conservation concerns for acrylic emulsion paints, Stud. Conserv. 48 (2003) 3–12.

[5] B. Ormsby, T. Learner, The effects of wet surface cleaning treatments on acrylic emulsion artists' paints – a review of recent scientific research, Stud. Conserv. 54 (2009) 29–41.

[6] P.M. Whitmore, V.G. Colaluca, E. Farrel, A note on the origin of turbidity in films of an astists' acrylic paint medium, Stud. Conserv. 41: 4 (1996) 250-255

[7] N. Agarwal, R.J. Farris, Water absorption by acrylic-based latex blend films and its effect on their properties, Journal of Applied Polymer Science. 72: 11 (1999) 1407-1419

[8] R. Ploeger, A. Murray, S. Hesp, D. Scalarone, An investigation of the chemical changes of artists' acrylic paint films when exposed to water, in: Materials issues in art and archaeology VII: symposium held November 30-December 3, 2004, Boston, Massachusetts, U.S.A., 2004: 49-56.

[9] J. Crook, T. Learner, The Impact of Modern Paints, Watson-Guptill, 2000.

[10] Tate AXA Art Modern Paints Project www.tate.org.uk/about-us/projects/tate-axa-art-modern-paints-project-taampp (accessed April 21, 2023)

[11] B. Ormsby, O. Lundsbakken, L. Monaco, A. Bartoletti, J. Lee, Revisiting cleaned acrylic emulsion painting surfaces 10 years on: observations and implications: Transcending Boundaries: Integrated Approaches to Conservation, ICOM-CC 19th Triennial Conference Preprints, Beijing, 17–21 May 2021, Paris, International Council of Museums, 2021.

[12] L. Pagnin, R. Wiesinger, A.N. Koyun, M. Schreiner, The Effect of Pollutant Gases on Surfactant Migration in Acrylic Emulsion Films: A Comparative Study and Preliminary Evaluation of Surface Cleaning, Polymers. 13 (2021) 1941.

[13] D. Scalarone, O. Chiantore, T. Learner, Ageing studies of acrylic emulsion paints. Part II. Comparing formulations with poly(EA-coMMA) and poly(n-BA-co-MMA) binders: ICOM –CC 14th Triennial Meeting Preprints, The Hague, 12-16 September 2005: pp. 350-357

[14] D. Scalarone, O. Chiantore, Separation techniques for the analysis of artists' acrylic emulsion paints, J. Sep. Sci. 27 (2004) 263–274.

[15] J. Peris-Vicente, U. Baumer, H. Stege, K. Lutzenberger, J.V. Gimeno Adelantado, Characterization of Commercial Synthetic Resins by Pyrolysis-Gas Chromatographjy/Mass Spectyrometry: Application to Modern Art and Conservation, Anal Chem. 81 (2009) 3180-3187

[16] E. Willneff, S. Schroeder, B. A. Ormsby, Spectorscopic techniques and the conservation of artists' acrylic emulsion paints, Herit Sci. 2:25 (2014)

[17] K. Urich, S. Centeno, J. Arslanoglu, E. Del Federico, Absorption an diffusion measurements of water in acrlic paint films by single-sided NMR, Prog Org Coat. 71 (2011) 283-289

[18] T. Fardi, V. Pintus, E. Kampasakali, E. Pavlidouo, M. Schereiner, G. Kyriacou, Analytical characterization of artist's paint systems based on emulsion polymers and synthetic organic pigments, J Anal Appl Pyrolysis. 135 (2018) 231-241

[19] I. Ziraldo, K. Watts, A. Luk, A. Lagante, R. Wolbers, The influence of temperature and humidity on swelling and surfactant migration in acrylic emulsion paint films, Stud Conserv. 61:4 (2016)

[20] A. C. Hellgren, P. Weissenborn, K. Holmberg, Surfactants in water-borne paints, Prog Org Coat. 35 (1999) 79-87

[21] F.G. Hooglands, J.J. Boon, Analytical mass spectrometry of poly(ehtylene glicol) additives in artists' acrylic emulsion media, artists' paints, and microsamples from acrylic paintings using MALDI-MS an nanospray ESI-MSInt J Mass Spectrom. 284 (2009) 72-80

[22] M. Anghelone, D. Jembrih-Simbürger, V. Pintus, M. Schreiner, Photostability and influence of phthlocyanine pigments on photodegradation of acrylic paints under accelerated solar radiation, Polym Degrad Stab. 146 (2017) 13-23

[23] V. Pintus, R. Ploeger, O. Chiantore, S. Wei, M. Schreiner, Thermal analysis of the interaction of inorngaic pigments with (Nba/mma) acrylic emulsion before and after UV ageing, J. Therma Anal Calorim. 114 (2013) 33-43

[24] V. Pintus, S. Wei, M. Schereiner, Accelerated UV ageing studies of acrylic, alkyd and polyvinyl acetate paints: influence of inorganic pigments. Microchem J. 124 (2016) 949-961

[25] V. Pintus, M. Schereiner, Characterizacion and identificacion of acrylic binding media: influence of UV light on the ageing process. Bionala Chem 399 (2011) 2961-2976

[26] V. Pintus, S. Wei, M. Schreiner, UV ageing studies: evaluation of lightfastness declarations of commercial acrylic paints, Anal. Bioanal. Chem. 402 (2012) 1567–1584.

[27] M. Cortea, A. Radvan, C. Vasiliu, N. Puscas, Preliminary results of accelerated ageing test son acrylic part paints, U.P.B. Scie Bull, Series A, 76:1 (2014)

[28] F. C. Izzo, EL. Balliana, F. Pinton, E. Zendri, A preliminary study of the composition of commercial oil, acrylic and vinyl paints, and their behaviour after accelerated ageing conditions, Conservation science in cultural heritage. (2015) 353-369

[29] M.T. Domenech-Carbó M.F. Silva, E. Aura-Castro, L. Fuster-López, S. Kröner, M.L. Martinez-Bazan, X. Mas-Barberá, M. F. Mecklenburg, L. Osete-Cortina, A. Domenech, J.V. Gimeno-Adelantado, D. j. Yusa-Marco, Study of behaviour on simulated daylight ageing of artist' acrylic and poly(vinyl acetate) paint films, Anal Chem. 399 (2010) 2921-2937

[30] C. Stavroudis, T. Doherty, The Modular Cleaning Program in Practice: Application to Acrylic Paintings, in: M.F. Mecklenburg, A.E. Charola, R.J. Koestle (Eds.), New Insights into Clean. Paint. Proc. from Clean. 2010 Int. Conf. Univ. Politec. Val. Museum Conserv. Inst., Smithsonian Institution, Washington, D.C., 2013: pp. 139–145.

[31] T. Fardi, V. Pintus, E. Kampasakali, E. Pavlidou, K. Papaspyropoulos, M. Schreiner, G. Kyriacou, A novel methodological approach for the assessment of surface cleaning of acrylic emulsion paints, Microchem J. 141 (2018) 25-39

[32] C. Stavroudis, T. Doherty, R. Wolbers, A new Approach to Cleaning I: Using Mixtures of Concentrated Stock Solutions and a Database to Arrive at an Optimal Aqueous Cleaning System, WAAC Newsletter. 27: 2 (2005) 17-28

[33] C.E. Dillon, A.F. Lagalante, R.C. Wolbers, Acrylic emulsion paint films: The effect of solution pH, conductivity, and ionic strength on film swelling and surfactant removal, Stud. Conserv. 59 (2014) 52–62.

[34] L. M. Tiedemann, A. J. Kunov-Kruse, Surface cleaning acrylic emulsion paints: evaluating conductivity adjusted aqueous solutions, CESMAR7 Colour and Conservation, Proceedings. (2015) 169-175

[35] A. Solbes-Garcia, J. Miranda-Vidales, A. Nieto-Villena, L. Salvador Hernandez, L. Narvaez, Evaluation of the oxalic and tartaric acids as an alternative to citric acid in aqueous cleaning systems for the conservation of contemporary acrylic paintings, JCult Heritage. 25 (2017) 127-134

[36] B. Ormsby, T. Learner, G.M. Foster, J. Druzik, M. Schilling, Wet-cleaning acrylic emulsion paint films: An evaluation of physical, chemical and optical changes, in: Mod. Paint. Uncovered Symp., 2007: pp. 189–200.

[37] B.A. Ormsby, E. Kampasakali, C. Miliani, T. Learner, An FTIR-based exploration of the effects of wet cleaning treatments on artists' acrylic emulsion paint films, E Preserv. Sci. 6 (2009) 186–195.

[38] B. Ormsby, T. Learner, M. Schilling, J. Druzik, Herant Khanjian, D. Carson, G. Foster, M. Sloan, The effects of surface cleaning on Acrylic Emulsion Paintings: A preliminary Investigation, Tate Papers. 6 (2006) www.tate.org.uk/research/tate-papers/06/effects-of-surface-cleaning-on-acrylic-emulsion-painting-preliminary-investigation (accessed April 21, 2023)

[39] B. Ormsby, A. Soldano, M.H. Keefe, A. Phenix, T. Learner, An Empirical Evaluation of a Range of Cleaning Agents for Removing Dirt from Artists ' Acrylic Emulsion Paints Removing, in: AIC Paint. Spec. Gr. Postprints, 2013: pp. 77–87

[40] D. Scalarone, M. Lazzari, V. Castelvetro, O. Chiantore, Surface monitoring of surfactant phase separation and stability in waterborne acrylic coatings, Chem. Mater. 19 (2007) 6107–6113.

[41] E. Kampasakali, B. Ormsby, A. Cosentino, C. Miliani, T. Learner, A Preliminary Evaluation of the Surfaces of Acrylic Emulsion Paint Films and the Effects of Wet-Cleaning Treatment by Atomic Force Microscopy (AFM), Stud. Conserv. 56 (2011) 216–230.

[42] S. Zumbühl, F. Attanasio, N.C. Scherrer, W. Müller, N. Fenners, W. Caseri, Solvent action on dispersion paint systems and the influence on the

morphology: changes and destruction of the latex microstructure, in: Mod. Paint. Uncovered Proc. from Mod. Paint. Uncovered Symp., 2007: pp. 257–268.

[43] I. Cárdaba, L Porcarelli, A. Gallastegui, D. Mecerreyes, M.I. Maguregui, Easy-to-make polymer hydrogels by UV-curing for the cleaning of acrylic emulsion paint films, Polymers. 13 (2021) 2108

[44] T.T. Duncan, B.H. Berrie, R.G. Weiss, A Comparison Between Gel and Swab Cleaning: Physical Changes to Delicate Surfaces, in: L. V. Angelova, B. Ormsby, J. Townsend, R. Wolbers (Eds.), Gels Conserv. Art, Archetype Publications, London, UK, 2017: pp. 250–256.

[45] A. Bartoletti, T. Maor, D. Chelazzi, Facilitating the conservation treatment of Eva Hesse's Addendum through practice-based research, including a comparative evaluation of novel cleaning systems, Herit Sci. 8: 35 (2020)

[46] A. Bartoletti, R. Barker, D. Chelazzi, Reviving WHAAM! A comparative evaluation of cleaning systems for the conservation treatment of Roy Lichtenstein's iconic painting, Herit Sci. 8:9 (2020).

[47] S. Croll, Overview of developments in the paint industry since 1930, in: T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007: 17-29.

[48] B. Ormsby, T. Learner, Artists' acrylic emulsion paints: materials, meaning and conservation treatment options, AICCM bulletin. 34 (2014) 57-65.

[49] M. De Sousa Ramos Félix Silva, Analytical study of accelerated light ageing and cleaning effects on acrylic and PVAc dispersion paints used in Modern and Contemporary Art, Doctoral dissertation, Universitat Politècnica de València, 2011.

[50] F. Belaroui, M. P. Hirn, Y. Grohens, P. Marie, Y. Holl, Distribution of water-soluble and surface-active low-molecular-weight species in acrylic latex films, J Colloid Interface Sci. 261:2 (2003) 336-348.

[51] R. Wolbers, A. Norbutus, A. Lagalante, Cleaning of Acrylic Emulsion Paints: Preliminary Extractive Studies with Two Commercial Paint Systems, Smithsonian Contributions to Museum Conservation. 2:3 (2012) 148-157.

[52] S. Digney-Peer, A. Burnstock, T. Learner, H. Khanjian, F. Hoogland, J. Boon, The migration of surfactants in acrylic emulsion paint films: Modern art, new museums, contributions to the Bilbao Congress, 13-17 September 2004, 49 (2004) 202-207.

[53] J. Mallégol, J. P. Gorce, O. Dupont, C. Jeynes, P.J. McDonald, J. Keddie, Origins and effects of a surfactant excess near the surface of waterborne acrylic pressure-sensitive adhesives, Langmuir. 18:11 (2002) 4478-4487.

[54] E. Aramendia, J. Mallégol, C. Jeynes, M.J. Barandiaran, J. Keddie, J.M. Asua, Distribution of surfactants near acrylic latex film surfaces: A comparison of conventional and reactive surfactants (surfmers), Langmuir. 19:8 (2003) 3212-3221.

[55] E. Hogfeldt, T. Miyajima, J. Marinsky, M. Muhammed, J. Ruiz, Application of a simple three-parameter model to titration data for some linear polyelectrolytes, Acta Chem. Scand. 43:5 (1989) 496-499.

[56]J. Snuparek, A. Bidman, J. Hanus, B. Hajkova, Water Absorption in Acrylic Latex Films, J Appl Polym Sci. 28:4 (1983) 1421-1428.

[57]R. E. Ploeger, Infrared analysis of materials leached by water from acrylic paint films, Proceedings of the Sixth Infrared and Raman Users Group (IRUG), (2004) 46-51.

[58] L.N. Butler, C.M. Fellows, R.G. Gilbert, Water sensitivity of latex-based films, IndEng Chem Res. 42:3 (2003) 456-464.

[59] P. M. Whitmore, H. R. Morris, V. G. Colaluca, Penetration of liquid water through waterborne acrylic coatings, in: T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007: 217-223.

[60] R. E. Ploeger, A. Murray, S. Hesp, D. Scalarone, Morphological changes and rates of leaching of water-soluble material from artists' acrylic paint films during aqueous immersions', in: T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007

[61] A. Solbes García, Evaluación de sistemas de limpieza acuosa, basados en ácidos orgánicos, para pinturas acrílicas, Doctoral dissertation, Universidad Autónoma de San Luis Potosí, 2017.

[62] J. Hayes, M. Golden, G. D. Smith,From formulation to finished product: causes and potential cures for conservation concerns in acrylic emulsion paints, in: T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007: 58-65.

[63] G. D. Smith, Aging characteristics of a contemporary acrylic emulsion used in artists' paints, in: T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007: 236-246.

[64] P. Smithen, A history of the treatment of acrylic painting, in: T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007: 165-174.

[65] E. Hagan, M. Charalambides, T. Learner, A. Murray, C. Young, Factors affecting the mechanical properties of modern paints, in: T. Learner, P.

Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007: 227-235.

[66] Z. W. Wicks, F. Jones, S. P. Pappas, D. Wicks, Organic coatings: science and technology, Third edition, John Wiley & Sons, Inc, 2007.

[67] E. Hagan, M. Charalambides, C. Young, T. Learner, S. Hackney, Influence of the inorganic phase concentration and geometry on the viscoelastic properties of latex coatings through the glass-transition, Polymer. 52:7 (2011) 1662-1673.

[68] M. F. Mecklenburg, C. S. Tumosa, An Introduction into the Mechanical Behavior of Paintings under Rapid Loading Conditions, in: M. F. Mecklenburg (eds.) Art in Transit: Studies in the Transport of Paintings, Washington, DC: National Gallery of Art, 1991: pp. 137-171.

[69] E. Hagan, M. Charalambides, C. Young, T. Learner, The effects of strain rate and temperature on commercial acrylic artist paints aged one year to decades», Applied Physics A. 121:3 (2015) 823-835.

[70] C. Riedo, G. Rollo, D. Scalarone, O. Chiantore, Improved PVA gels for the cleaning of painted surfaces, in: L. Angelova, B. Ormsby, J. Townsend, R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017: pp. 283

[71] I. Cardaba, G. Poggi, M. Baglioni, D. Chelazzi, I. Maguregui, R. Giorgi, Assessment of aqueous cleaning of acrylic paints using innovative cryogels, Microchemical Journal, 152: (2020) 104311

[72] T. Doherty, C. Stavroudis, Desarrollando sistemas de limpieza para pinturas sensibles al agua mediante ajuste del pH y de la conductividad, in: Conservación de arte contemporáneo: 13ª jornadas, febrero 2012, Centro de Arte Reina Sofía, Departamento de Conservación-Restauración, Madrid, 2012: pp. 39-48

[73]L. Angelova, E. Carreti, B.H. Berrie, R. G. Weiss, Poly (vinyl alcohol)-borax "gels": a flexible cleaning option, in: L. Angelova, B. Ormsby, J.

Townsend, R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017: pp. 23

[74] M. Bertasa, O. Chiantore, T. Poli, C. Riedo, V. Di Tullio, C. Canevali, A. Sansonetti, D. Scalarone, A study of commercial agar gels as cleaning materials, in: L. Angelova, B. Ormsby, J. Townsend, R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017: 11

[75] A. Sansonetti, M. Bertasa, C. Canevali, A. Rabbolini, M. Anzani, D. Scalarone, D. A review in using agar gels for cleaning art surfaces, J Cult Heritage. 44 (2020) 285-296

[76] O. Dimond, M. Barkovic, M. Cross, B. Ormsby, The role of agar gel in treating water stains on acrylic paintings: Case study of Composition, 1963 by Justin Knowles, Journal of the American Institute for Conservation. 58 (2019) 144-157

[77] P. Cremonesi, A. Casoli, Thermo-reversible rigid agar hydrogels: their properties and action in cleaning, in: L. Angelova, B. Ormsby, J. Townsend, R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017: 19

[78] P. Baglioni, D. Berti, M. Bonini, E. Carreti, L. Dei, E. Fratini, R. Gigorgi, Micelle, microemulsions and gels for the conservation of cultural heritage, Advcolloid Interface Sci. 205 (2014) 361-371

[79] C. Riedo, G. Rollo, O. Chiantore, D Scalarone, Detection and Identification of Possible Gel Residues on the Surface of Paintings after Cleaning Treatments, Heritage. 4 (2021) 304–315.

[80]N. Khandekar, A survey of the conservation literature relating to the development of aqueous gel cleaning on painted and varnished surfaces, Reviews in conservation, IIC, London, 1 (2000) 10-20

[81] J.S. Tsang, S. Babo, Soot Removal from Acrylic Emulsion Paint Test Panels: A Study of Dry and Non-Contact Cleaning, in: Preprints, ICOM-

CC 16th Triennial Conference, Lisbon, Portugal, 19-23 September 2011, 2011: 1–9

Chapter 2.

METHODOLOGY

The scientific-experimental studies carried out on the art conservation field aim to improve the knowledge on the materials of which artworks are composed and to diagnose their alteration processes or deterioration due to the action of different agents. To do that, it is essential to develop studies based on samples or mock-ups that simulate the real conditions of the works of art in order to obtain representative and reliable results that can be used to improve the conservation of this type of artworks. It is also worth mentioning the importance of analytical techniques applied to these studies in order to be able to make accurate scientific assessments.

This work, preceded by a throughout bibliographic search, is mainly developed on the basis of a sample based methodology, designed with the objective of reproducing the most common and representative conditions of artworks made with acrylic paint. To this end, this research is based on the scientific methodologies reported in previous studies, according to the bibliographic sources referenced at the end of the chapter.

The materials and methods used in the experimental section of the thesis are described below.

1. Reference materials

An accurate selection of materials and study parameters is necessary to obtain comparable and reliable results. During the phase of sample design, it is essential to rely on other reference researches and standardized norms such as ISO, so as to ensure that the results obtained are representative and comparable.

1.1 Paint samples

In this work, acrylic paints belonging to three different brands and three different colours were selected for deeper analysis. Liquitex, Titan and Hyplar brands were selected due to their widespread use in the art scene at different levels, both Liquitex and Hyplar at the international level, and Titan at a national level. Liquitex is a very popular brand widely used and analysed by other researchers. Titan acrylic paints represent a range of modest quality but widely used paints at national level. Finally, Hyplar paint, from the American company Grumbacher, was selected as representative of the older acrylic paints, whose polymeric formulation differs from that of the Titan and Hyplar. Finally, specific Red, blue and green colours were selected as being representative in colour ad composition. Thus, the organic pigments Phtalocyanine green and Naphtol red, known for their high sensitivity to light and low stability towards cleaning, were selected. On the other hand, inorganic Ultramarine blue and Cadmium red were also studied as a counterpoint, taking into account that this type of pigments tend to be more stable while requiring different additives for their stabilization in the paint.

In addition to the above mentioned colours, brown and white Liquitex acrylic samples were also included in the study reported in Chapter 5. In this case, the composition of the acrylics was not a paramount question, since the scope was set on the optical assessment of the degree of dirt removal efficiency, and therefore these colours were optimal for that purpose, regardless their composition.

Brand	**Colour**	**Pigment**
Liquitex ®	Ultramarine Blue	PB 29
	Phtalocyanine Green	PG 7
	Cadmium Red Light	PR 108
	Brown	PBr7
	Titanium white	PW6
Titan	Dark Ultramarine Blue	PB 29
	Titan Dark Green	PG 7
	Cadmium Red Light	PR 108
Hyplar ® (Grumbacher)	Ultramarine Blue	PB 29
	Phtalo Green	PG 7
	Naphtol Red	PR 112

Table 1 Identification of the studied acrylic paint brands, colours and respective pigments

2.2 Artificial dirt

To emulate the surface dirt that is usually deposited on acrylic paints, this study reproduces the formulation proposed by Ormsby et al [1]. The dirt mixture was applied directly on the surface of the samples with a brush and left to dry for one to three years.

Components	Quantities
carbon black	0,5 g
Iron oxide	0,175 g
Volcanic ash	0,4375 g
White caolin	0,5 g
Technical gelatin powder	2,5 g
Rice starch	2,5 g
Cement	4,37 g
Olive oil	2,5 ml
White mineral oil	5 ml
Tested benzine	250 ml

Table 2 Artificial dirt compositon

2.3 Reagents for preparing the aqueous cleaning solutions

The cleaning procedures described in this work were carried out by using water based cleaning solutions, adjusted in pH and conductivity. These solutions were directly applied, emulsified, gelled or confined into solid gels. The reagents used to prepare the different cleaning systems are detailed in the following table and precisely described in Chapter 3.

Reagent	Purity	Supplier
Glacial acetic acid	99.8-100.5%	Sigma Aldrich
Sodium hydroxide	>97.0%	Sigma Aldrich
Ammonium hydroxide	33%	Sigma Aldrich
Citric acid	99.5%	Sigma Aldrich

Table 3 Reagents used in the preparation of the aqueous cleaning systems.

2.4 Gels, gelling agents and emulsifiers

This work studies the performance of three commercial emulsifier, gels and gelling agents, which are tested as cleaning methods. Velvesil Plus® is a silicone-based polymeric emulsion stabilizer. Agar-agar® is the most widely used physical gel among restorers and Nanorestore Cleaning® Peggy hydrogel is one of the chemical hydrogels that have proven to be most successful in cleaning water sensible surfaces.

Commercial name	**Type**	**Supplier**
Velvesil Plus ®	Emulsifiable silicone crosspolymer gel.	CTS, Italy
Agar-agar ®	Agar-agar polysacharide	CTS España
Nanorestore Cleaning ® Peggy	PVA-based hydrogel	CSGI (Firenze)

Table 4 Identification of the tested emulsifiers and gels.

2.5 Reagents used for the preparation of UV-Cured hydrogels

In the experimental part of the thesis, a series of UV cured hydrogels were synthesized and studied. The composition of these hydrogels were based on the combination of HEMA with either VP, METAC or AMPS monomers, and the addition of PEGDMA as crosslinker and IRGAcure as photoinitiator, as shown in table 5.

Reagent	**Purity**	**Supplier**
2-(Hydroxyethyl)methacrylate (HEMA)	97%	Sigma Aldrich
Vinylpyrrolidone (VP)		Sigma Aldrich
[2-(methacryloyloxy)ehyl]trimethylammonium chloride (METAC)	75wt%	Sigma Aldrich
2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)	99%	Sigma Aldrich
Poly(ethylene glycol) dimethylmethacrylate (PEGDMA MW 550g mol^{-1})	-	Sigma Aldrich

2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (IRGAcure 2956)	-	Sigma Aldrich

Table 5 Identification of the components employed for the synthesis of the UV-cured hydrogels.

2 Sample preparation

Acrylic paints were applied on Mylar® sheets using a paint applicator (Baker Universal Applicator from Neurtek). The average thickness of films was 150 µm. Samples were then left in a dark and dust-free environment from one to three years.

2.1 Artificial soiling

A sample set, comprehending all the colours and brands, was artificially soiled using the artificial dirt mixture and according to a procedure described elsewhere [1]. Samples were naturally aged, in a dark and dust-free environment and tests were carried out at different aging intervals, as described in the following chapters.

2.2 Accelerated ageing

A set of mockups were aged under accelerated conditions. On the one hand, acrylic paints from Liquitex containing Hansa Yellow 10G (PY3) and Phthalocyanine Green BS (PG7) organic pigments and Ultramarine Blue (PB29) inorganic pigment were used to test their aging behaviour as part of a parallel research project published elsewhere[2]. On the other hand, a set of 19 phthalocyanine green mockups of both Titan and Hyplar brands were also aged under accelerated conditions, for in between brand comparison purpose. The ageing procedure consisted in exposing the reference paint films (1 x 2 cm) to artificial solar radiation under controlled temperature, humidity and irradiance conditions, as reported in a previous work [3]. For the accelerated aging we used a Solarbox 1500e RH weathering chamber (Neurtek Instruments, Spain), with a Xenon Lamp which provided radiation with wavelengths between 300 and 800 nm and a nominal irradiance of 600

W/m^2. The camera was equipped with an indoor 310 nm UV filter and it was set to a black panel temperature of 55 °C and 50% humidity. The accelerated ageing was carried out under isochronous sampling up to a maximum of 1426 h.

3. Cleaning tests

Cleaning tests were carried by using three different methods for applying the cleaning solutions: swab-rolling, gels and emulsifiable crosspolymer gels. Cleaning methods were chosen on the premises of low toxicity, ease of use and low risk of leaving residues. For this reason emulsions and micro-emulsions [4] were discarded and the research focused on gelled systems and gels [5].

3.1 Cleaning aqueous solutions

Although it is well known that when cleaning acrylic paintings the pH and conductivity of each surface need to be measured in order to adjust the cleaning solutions according to the obtained values, in this study several stock buffered solutions were prepared according to bibliography [6]. After observing that the effect of pH was negligible in terms of cleaning efficacy on the mock-up surfaces, pH 5 buffer was chosen as the standard throughout the work, both because a slightly acidic pH minimizes the swelling of acrylic emulsion paints without hampering the cleaning action and for reasons of reproducibility and comparability of the obtained results when using different application methods. The cleaning solutions used in the different parts of the research will be described in the corresponding chapters.

3.2 Immersion tests

Immersion tests were performed on the mockups in order to observe in a magnified way the swelling effects of humidity on acrylic paintings and to extract and identify the water soluble components of the paints. A sample set comprehending all the studied colours and brands, was immersed in 40 ml of deionized water during 24h. Prior to mechanical and chemical characterization the test specimens subjected to immersion were kept at laboratory conditions from one to three months. An aliquot of the liquid extract obtained during immersion was dried at room temperature in a laboratory and then analysed by means of Transmission FTIR in order to identify the extracted water soluble components.

3.3 Swabbing tests

Swab rolling tests were performed using sterilised laboratory cotton swabs. The swabs were immersed in the corresponding cleaning solution and excess of water or aqueous solution was removed with laboratory paper. The paint films were gently swabbed during 10s and this cleaning procedure was performed three times. After cleaning, a final rinse was performed with a cotton swab soaked in the corresponding rinse solution, as stated in Chapter 3.

3.4 Gel cleaning tests

Cleaning with gels was performed using different methods. On the one hand, both physical (Agar-Agar ®) and chemical hydrogels (Nanorestores Cleaning ® Peggy and a novel UV-cured hydrogel) were employed. On the other hand, a comercial emulsifiable silicone crosspolymer gel was tested (Velvesil Plus ®). The application conditions are specified in the following chapters.

2.4. Analysis methods

Imaging and chemical analytical techniques were employed to characterize and investigate the effects of cleaning systems on paint mockups. Scanning Electron Microscope (SEM) and Colorimetry were used to evaluate the cleaning efficacy of the applied treatments. Atomic Force Microscope (AFM) was employed to assess the surface after treatments, both in terms of cleaning efficacy and roughness changes. Pirolysis Gas Chromatography-Mass Spectrometry (Py-GC-MS) was used to characterize the paint binders and pigments, as well as to identify compositional changes after accelerated aging. Infrared spectroscopy (FTIR, FTIR-ATR and 2D-imaging-FTIR) was used to characterize and evaluate changes in the composition of the paint surface, in order to assess the effects and efficacy of the applied cleaning methods as well as detecting the residues left by the cleaning systems. Termogravimetric analysis were performed by means of DTG/DSC to characterize the paint binder and evaluate composition and structure changes within the paint films after cleaning treatments.

The characterization and evaluation of the novel UV-cured gel was performed by means of FTIR-ATR, SEM, dynamic mechanical analysis (DMA) and tensile tests.

Specific analytical parameters and technical data are given in the corresponding chapters.

References

[1] B. Ormsby, A. Soldano, M.H. Keefe, A. Phenix, T. Learner, An Empirical Evaluation of a Range of Cleaning Agents for Removing Dirt from Artists ' Acrylic Emulsion Paints Removing, in: AIC Paint. Spec. Gr. Postprints, 2013: pp. 77–87

[2] L. Ortiz-Herrero, I. Cardaba, L. Bartolomé, M.L. Alonso, M.I. Maguregui, Extension study of a statistical age prediction model for acrylic paints, Polymr Degrad Stab. (2020) 179

[3] L. Ortiz-Herrero, A.C. de Almeida Assis, L. Bartolomé, M.L. Alonso, M.I. Maguregui, R.M. Alonso, J.S. Seixas de Melo, OPLS multivariate regression of FTIR-ATR spectra of acrylic paints for age estimation in contemporary artworks, Chemom. Intell. Lab. Syst. (2020) 207: 104187

[4] B. Ormsby, E. Willneff, M. B. Clark, J. Lopez, M. H. Keefe, A. Phenix, Cleaning acrylic paints: Mineral Spirits-based Microemulsions and the Question of Residues, in: proceedings of 7th International Conference Colour and Conservation. Milan, Polytechnic University, November 13-14, 2015.

[5] L. Angelova, B. Ormsby, J. Townsend, R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017.

[6] C. Stavroudis, T. Doherty, The Modular Cleaning Program in Practice: Application to Acrylic Paintings, in: M.F. Mecklenburg, A.E. Charola, R.J. Koestle (Eds.), New Insights into Clean. Paint. Proc. from Clean. 2010 Int. Conf. Univ. Politec. Val. Museum Conserv. Inst., Smithsonian Institution, Washington, D.C., 2013: pp. 139–145.

Chapter 3.

ASSESSMENT OF AQUEOUS CLEANING OF ACRYLIC PAINTS USING INNOVATIVE CRYOGELS

Adapted version

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Abstract

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

Keywords: Cleaning Cryogels, Acrylic paints Velvesil Plus®, Modular Cleaning program

1. Introduction

Waterborne acrylic paints have been frequently used in modern and contemporary art. They usually feature high molecular weight acrylic polymers that are based on the esters of acrylic acid and methacrylic acid, and a broad range of additives including surfactants, stabilizers, wetting agents and viscosity modifiers, added to enhance stability, longevity, flow and film formation properties [1]. Different colors are obtained by the addition of either organic dyes or inorganic pigments. The usually low glass transition temperature of the acrylic resin, which results in films that are soft at room temperature [2–4] and the migration to the surface of hydrophilic additives, i.e. surfactants, upon drying [5] make acrylic paint films prone to attract airborne dust. Therefore, acrylic paintings need to be cleaned, even though this operation is particularly challenging [6]. The community has been searching for the safest and most effective procedure since 2003 [7,8]. The main problem of acrylic paints is their sensitivity to water and to organic solvents over a broad range of polarities. In fact, they show a swelling capacity of up to ten times higher than oil films [9]. It was observed that in 3 months old samples the interaction with solvents causes the partial disruption of films' microstructure, which, in turn, induces considerable optical changes and a decrease in the mechanical strength [9]. The cleaning of acrylic paintings can also lead to the solubilization of migrated additives on the surface and extraction of additives from the bulk of the film, and their migration to the surface, resulting in changes in the physico-chemical and mechanical properties of the film [10,11]. Even if aliphatic and low-molecular weight aromatic hydrocarbons induce the lowest swelling [9] and are less prone to interact with the hydrophilic components of the acrylic paint layer [11], the use of water for the removal of airborne dust, which is mainly hydrophilic, grants better cleaning performances.

Several strategies have been recently developed to tackle the cleaning of water-sensitive artworks. The Modular Cleaning Program (MCP) [12,13] uses pre-mixed stock solutions (pH buffers, chelators, surfactants and ionic buffers) to prepare cleaning systems with controlled pH and conductivity, so to minimize the risk of changes in the acrylic films [14,15]. However, the use of gelled systems is one of the most successful strategies to achieve highly effective and non-invasive cleaning. For instance, in order to reduce the interactions between aqueous cleaning solutions and artistic surfaces, pHEMA/PVP aqueous semi-interpenetrated polymer networks have been recently proposed [16–19]. More recently, highly retentive PVA-based cryogels have been developed for the selective removal of unwanted patinas from artistic surface [20,21]. These gels, obtained via freezing/thawing repeated cycles starting from PVA aqueous solutions, are stickier, softer and more flexible than pHEMA/PVP networks; thus, they represent a class of very promising tools for soil and grime removal from modern and contemporary paintings, which often present irregular textures and, as previously indicated, feature water-sensitive paints. A different approach involves the use of water-in-oil emulsions, where water is confined in low polarity solvents, which should be as inert as possible towards the paint layers. Among the most frequently used solvents, one can find mineral spirits [22] or low-polarity silicone-based solvents, as the continuous phase of reverse microemulsions/emulsions [23]. One commercial cleaning system that was used in recent times in cleaning case studies is Velvesil Plus®, a gel-like silicone polyether copolymer that was adopted to create stable emulsions in a silicone solvent continuous phase [24, 25]. This material was selected as a suitable reference product for our study as it is still available on the market to conservators, even if other silicone polymers, such as KSG-350 z® (Shin Etsu Chemical, Japan) [26], are now used in the restoration practice.

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

2. Materials and Methods

2.1. Materials

Glacial acetic acid (99.8-100.5%), sodium hydroxide (≥97.0%), ammonium hydroxide solution (33%), citric acid (99.5%) were all supplied by Sigma Aldrich. Velvesil Plus® and decamethylcyclopentasiloxane, also known as cyclomethicone D5 (≥97.5%) were both obtained from CTS (Florence, Italy). Poly(vinyl alcohol) (PVA) (HD 99+% with M_w=146-186000, and HD 89% with M_w=89-124000) was used for the synthesis of the PVA-based cryogels. Acrylic paint mock-ups were prepared using Ultramarine Blue (LI 29), Phtalocyanine Green (LI 7) and Cadmium Red Light (LI 108) paints from Liquitex®.

2.2. Cryogels preparation

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

2.3. Acrylic paint film mock-ups

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

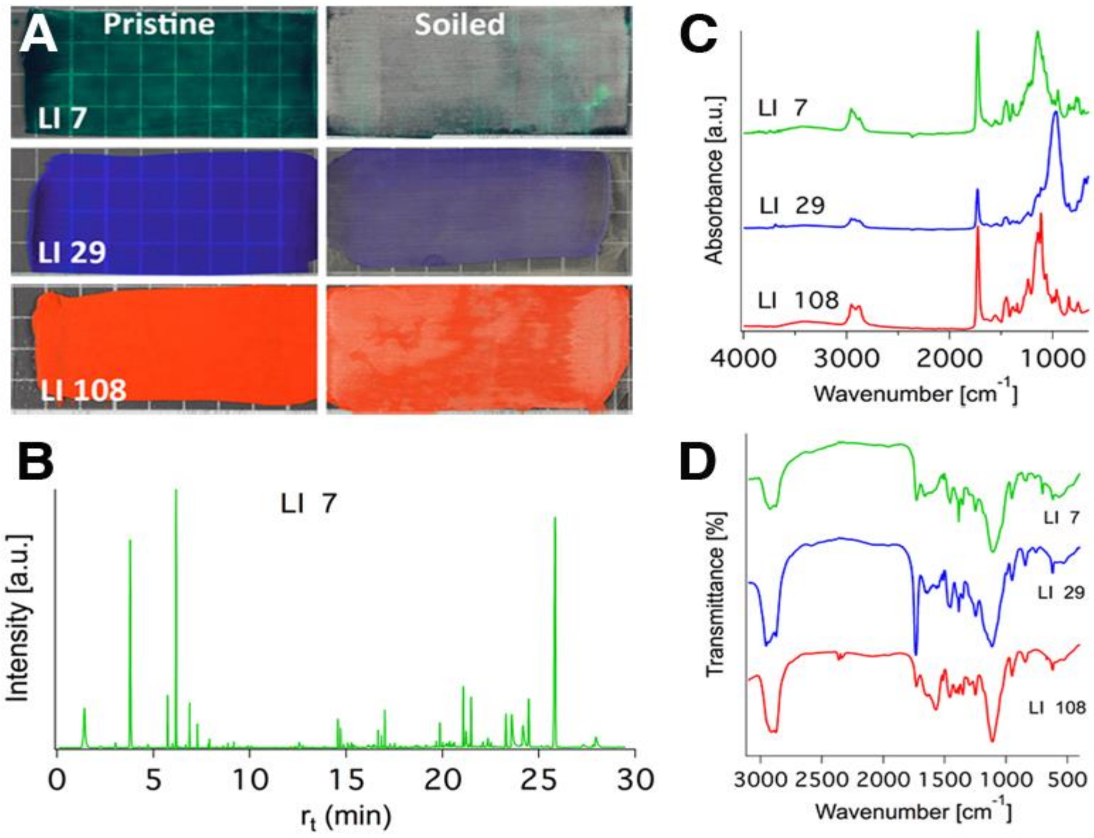

Figure 1 (A) Acrylic paint mock-ups before (pristine) and after the application of the artificial soil (soiled). (B) Py-GC-MS spectrum of the green acrylic paint. (C) ATR-FTIR analysis of pristine acrylic paint mock-ups. (D) FTIR transmission spectrum of water-soluble additives.

2.4. Cleaning systems

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

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

Table 1 Name and composition of the cleaning solutions. The amount of each component in the buffer and in the citric acid (chelator) solution can be found in the published literature [28].

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

As a reference method, cotton swabs, soaked in the same cleaning solution loaded in the cryogels, were also used in soil removal tests. Cotton swabs were gently rolled over the paint film, three times. Each application lasted 10 secs. After cleaning, a final rinse was performed with a cotton swab soaked in the rinse solution (pH 5, 6000 S/m) [28].

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

2.5. Infrared spectroscopy

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

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

The presence of residues from the gels was evaluated through 2D imaging-Fourier transform infrared (FTIR) using a Cary 620-670 FTIR microscope, equipped with an FPA 128x128 detector (Agilent Technologies). This set up allows the highest spatial resolution currently available to FTIR microscopes. The spectra were recorded directly on the surface of the samples (or the Au background) in reflectance mode, with open aperture and a spectral resolution of 4 cm^{-1}, acquiring 128 scans for each spectrum. A "single-tile" analysis results in a map of 700 x 700 μm^2 (128 x 128 pixels), and the spatial resolution of each imaging map is 5.5 μm (i.e. each pixel has dimensions of 5.5 x 5.5 μm^2).

2.6. Pyrolysis - gas chromatography - mass spectrometry

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

2.7. Scanning electron microscope

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

2.8. Atomic force microscope

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

3. Results and discussion

3.1. Characterization of acrylic paints

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

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

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

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

3.2. Cleaning tests using novel cryogels

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

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

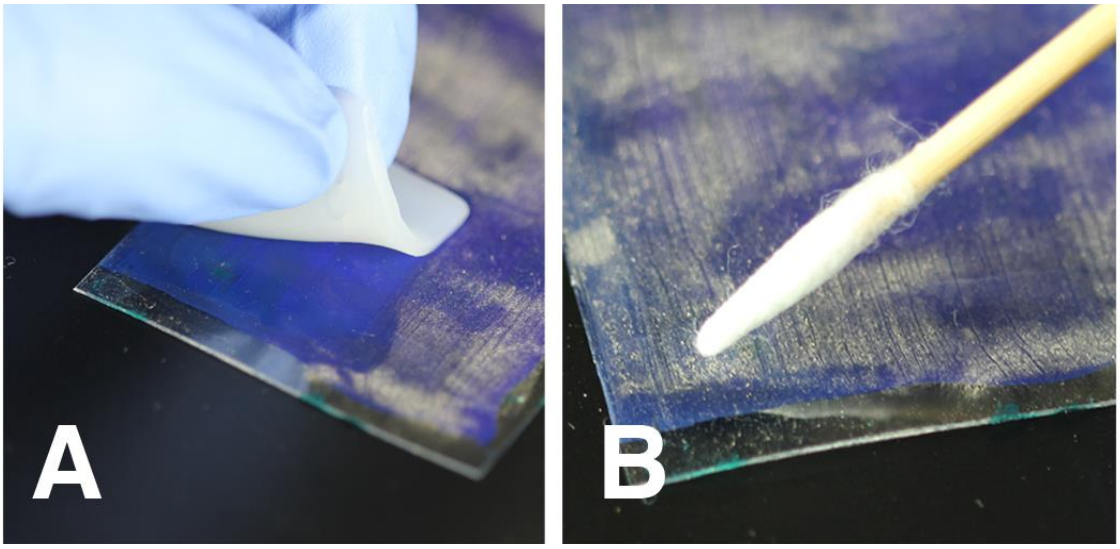

Figure 2 Cleaning tests on the blue acrylic paint covered with artificial soil: (A) PVA-based cryogel. (B) Cotton swab.

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

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

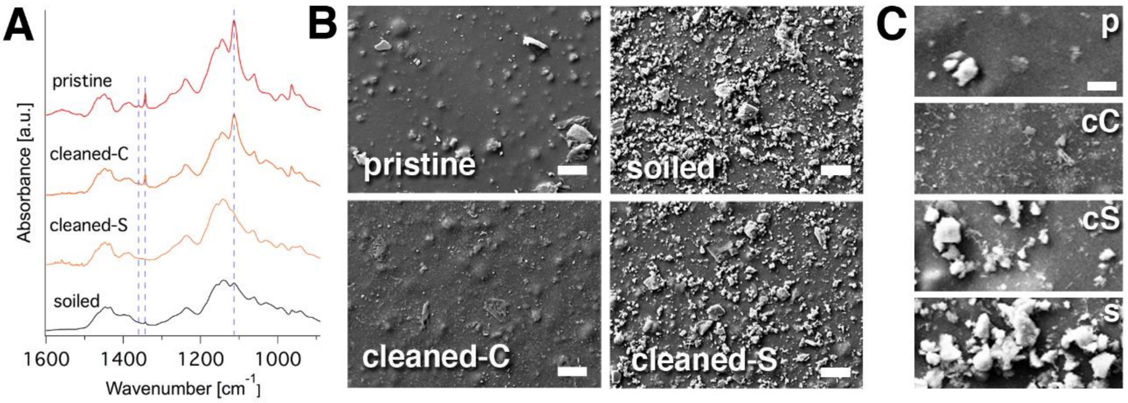

Figure 3 (A) ATR-FTIR spectra of the red acrylic paint, before and after the cleaning tests. Dashed lines indicate the absorptions bands of polyethoxylated surfactant at 1359 cm^{-1}, 1343 cm^{-1}, and 1114 cm^{-1}. (B) SEM images (magnification 1000x) taken on the green acrylic paint before and after soil removal tests. The scale bar is 30 µm. (C) SEM images (magnification 4000x) of the green acrylic paint before and after soil removal tests. The scale bar is 7.5 µm.

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

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

3.3 Gel residues evaluation

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

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

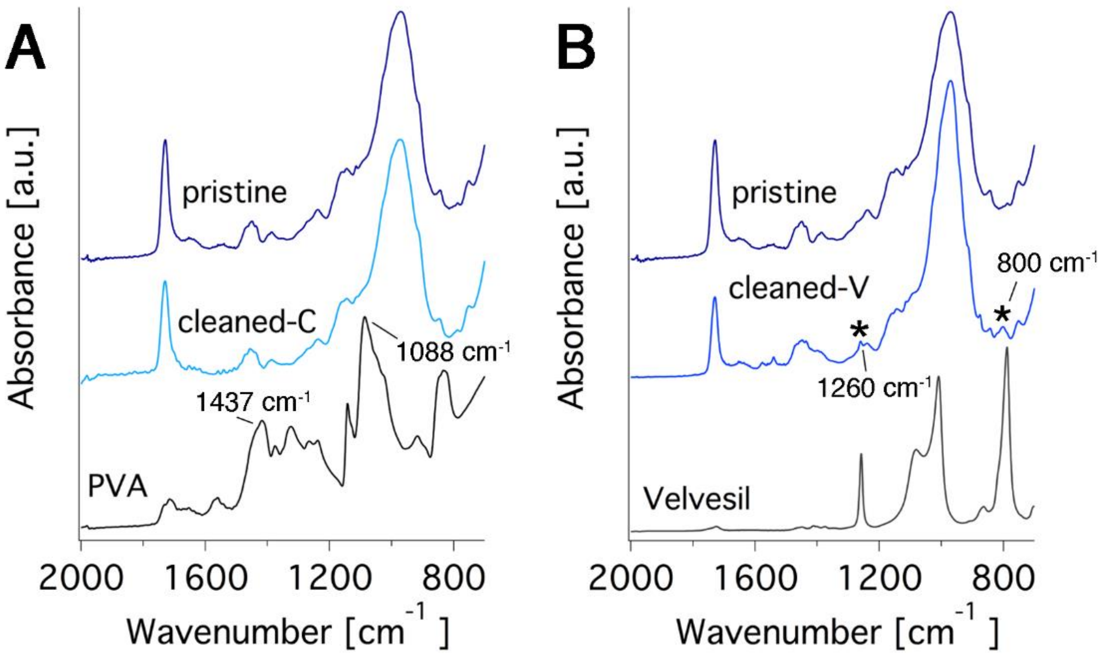

Figure 4 ATR-FTIR spectra of the blue acrylic paint. (A) A comparison between the pristine paint film, the sample cleaned with the cryogel (cleaned-C) and PVA, which is the main component of cryogel. (B) A comparison between the pristine paint film, the paint film surface cleaned with Velvesil Plus® (cleaned-V) and Velvesil Plus®. Stars indicate the two peaks due to Velvesil Plus® residues after cleaning operations.

In order to map Velvesil Plus® residues on a treated area, 2D FTIR Imaging was carried out in reflectance mode using an FPA detector. This set up was selected as it allows discriminating compounds with different chemical composition than the substrate down to a spatial resolution of few microns [45].

The mapping of the Si-CH$_3$ symmetric bending (about 1250-1260 cm^{-1}) showed the presence of significant residues due to Velvesil Plus® on the cleaned paint films, as can be seen in **Figure 5-A**. The two maps show the presence of a siloxane compound (i.e., likely, gel residues), distributed over the analyzed surface. Changes in the acrylic paint layer due to the cleaning with Velvesil Plus® are visible to the naked eye. In fact, as highlighted by the red square in Figure 5-B, the area treated with Velvesil Plus® and rinsed with cyclomethicone D5 exhibits a glossy finish altering the original visual aspect of paint film. It is worth noting that the conservation profession is still optimizing clearance for these silicone materials, and that the aforementioned KSG-350 z® (Shin Etsu Chemical, Japan) [26] has recently replaced Velvesil Plus® in the conservation practice, even though the latter is still available on the market.

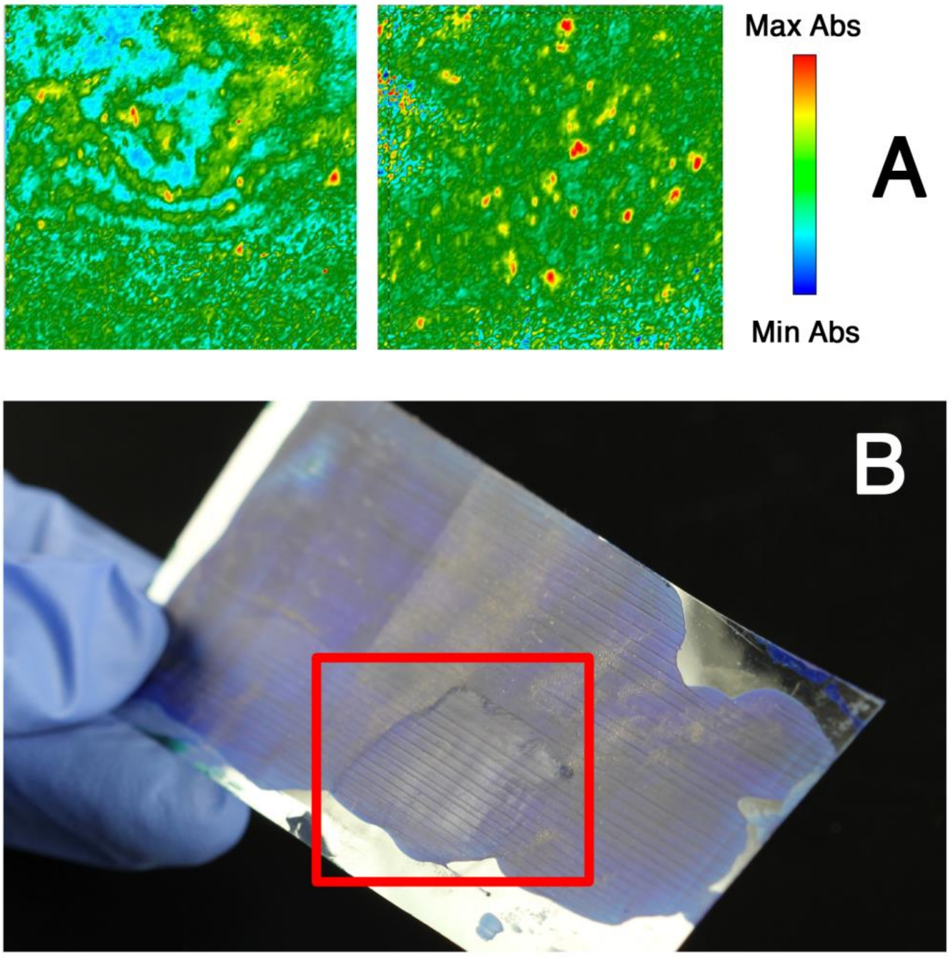

Figure 5 (A) 2D FTIR Imaging of the blue acrylic paint cleaned with Velvesil Plus®. Maps were obtained mapping the peak located at 1260-1250 cm^{-1}, corresponding to the symmetric bending of $Si\text{-}CH_3$ group. Each map measures about 700 x 700 μm^2. (B) The visual aspect of the paint surface after cleaning operation with Velvesil Plus® (including the final rinse with cyclomethicone D5). The picture was taken several weeks after cleaning tests.

The evaluation of possible gels' residues left over the treated surface after cleaning confirms one of the main drawbacks of standard physical gels, such as the Velvesil Plus®, i.e., the presence of residues. On the other hand, it shows that, even if PVA-based cryogels are physical gels, they behave as chemical gels, in the sense that they tend to not leave residues on the treated surfaces. This means that the energy of the bonds formed during the freezing/thawing cycles is high enough to overcome the adhesion forces that make the gel stick to solid surfaces.

4. Conclusions

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

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References

[1] B.H. Stuart, Analytical Techniques in Materials Conservation, John Wiley & Sons, Ltd, Chichester, UK, 2007.

[2] C. Lamb, Acrylics: New Material, New Problems, in: Conserv. Mod. Paint. Introd. Notes Pap. to Be Present., United Kingdom Institute for Conservation (UKIC) and Tate Gallery, London, UK, 1982: pp. 4–6.

[3] L. Pomerantz, D.C. Goist, R.L. Feller, Conservators Advise Artists, Art J. 37 (1977) 34.

[4] R.G. Lodge, A history of synthetic painting media with special reference to commercial materials, in: Am. Inst. Conserv. Hist. Artist. Work. Prepr. Pap. Present. Sixt. Annu. Meet. New Orleans, Louisiana, June 1-5, 1988, 1988: pp. 118–127.

[5] R.A. Perry, Problems of dirt accumulation and its removal from unvarnished paintings: a practical review., in: Dirt Pict. Separated Pap. given a Conf. Held Jointly by UKIC Tate Gall. January 1990, The United Kingdom Institute of Conservation, 1990: pp. 3–6.

[6] E. Jablonski, T. Learner, J. Hayes, M. Golden, Conservation concerns for acrylic emulsion paints, Stud. Conserv. 48 (2003) 3–12.

[7] A. Murray, C.C. de Berenfeld, S.Y.S.Y.S. Chang, E. Jablonski, T. Klein, M.C. Riggs, et al., The Condition and Cleaning of Acrylic Emulsion Paintings, MRS Proc. 712 (2002) II1.4.

[8] B.A. Ormsby, T. Learner, The effects of surface cleaning on acrylic emulsion paintings – a Preliminary Investigation, Surf. Clean. – Mater. Methods. (2006) 135–149.

[9] S. Zumbühl, F. Attanasio, N.C. Scherrer, W. Müller, N. Fenners, W. Caseri, Solvent action on dispersion paint systems and the influence on the morphology: changes and destruction of the latex microstructure, in: Mod. Paint. Uncovered Proc. from Mod. Paint. Uncovered Symp., 2007: pp. 257–268.

[10] B. Ormsby, T. Learner, G.M. Foster, J. Druzik, M. Schilling, Wet-cleaning acrylic emulsion paint films: An evaluation of physical, chemical and optical changes, in: Mod. Paint. Uncovered Symp., 2007: pp. 189–200.

[11] B. Ormsby, T. Learner, The effects of wet surface cleaning treatments on acrylic emulsion artists' paints – a review of recent scientific research, Stud. Conserv. 54 (2009) 29–41.

[12] D. Keynan, A. Hughes, Testing the Waters: New Technical Applications for the Cleaning of Acrylic Paint Films and Paper Supports, B. Pap. Gr. Annu. 32 (2013) 43–51.

[13] C. Stavroudis, T. Doherty, The Modular Cleaning Program in Practice: Application to Acrylic Paintings, in: M.F. Mecklenburg, A.E. Charola, R.J. Koestle (Eds.), New Insights into Clean. Paint. Proc. from Clean. 2010 Int. Conf. Univ. Politec. Val. Museum Conserv. Inst., Smithsonian Institution, Washington, D.C., 2013: pp. 139–145.

[14] E. Kampasakali, B. Ormsby, A. Cosentino, C. Miliani, T. Learner, A Preliminary Evaluation of the Surfaces of Acrylic Emulsion Paint Films and the Effects of Wet-Cleaning Treatment by Atomic Force Microscopy (AFM), Stud. Conserv. 56 (2011) 216–230.

[15] C.E. Dillon, A.F. Lagalante, R.C. Wolbers, Acrylic emulsion paint films: The effect of solution pH, conductivity, and ionic strength on film swelling and surfactant removal, Stud. Conserv. 59 (2014) 52–62.

[16] J.A.L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, Innovative Hydrogels Based on Semi-Interpenetrating p(HEMA)/PVP Networks for the Cleaning of Water-Sensitive Cultural Heritage Artifacts, Langmuir. 29 (2013) 2746–2755.

[17] J. Domingues, N. Bonelli, R. Giorgi, P. Baglioni, Chemical semi-IPN hydrogels for the removal of adhesives from canvas paintings, Appl. Phys. A. 114 (2013) 705–710.

[18] M. Baglioni, A. Bartoletti, L. Bozec, D. Chelazzi, R. Giorgi, M. Odlyha, et al., Nanomaterials for the cleaning and pH adjustment of vegetable-tanned leather, Appl. Phys. A. 122 (2016) 114.

[19] C. Mazzuca, G. Poggi, N. Bonelli, L. Micheli, P. Baglioni, A. Palleschi, Innovative chemical gels meet enzymes: A smart combination for cleaning paper artworks, J. Colloid Interface Sci. 502 (2017) 153–164.

[20] R. Mastrangelo, C. Montis, N. Bonelli, P. Tempesti, P. Baglioni, Surface cleaning of artworks: structure and dynamics of nanostructured fluids confined in polymeric hydrogel networks, Phys. Chem. Chem. Phys. 19 (2017) 23762–23772.

[21] N. Bonelli, G. Poggi, D. Chelazzi, R. Giorgi, P. Baglioni, Poly(vinyl alcohol)/poly(vinyl pyrrolidone) hydrogels for the cleaning of art, J. Colloid Interface Sci. 536 (2019) 339–348.

[22] B. Ormsby, M. Keefe, A. Phenix, E. von Aderkas, T. Learner, C. Tucker, Mineral Spirit-based micro emulsions: A novel cleaning system for painted surfaces, JAIC, Vol 55, 2016: pp. 12-32

[23] C. Stavroudis, More from CAPS3: Surfactants, silicone-based solvents and microemulsions, Newsl. (Western Assoc. Art Conserv. 34 (2012) 24–27.

[24] A.F. Lagalante, R. Wolbers, A.F. Lagalante, The Cleaning of Acrylic Paintings: New Particle-based water-in-oil Emulsifiers, in: Dall'Olio All'Acrilico, Dall'Impressionismo All'Arte Contemp., Il Prato, Padova, 2016: pp. 107–114.

[25] C. Stavroudis, Silicone-Based Solvents in Conservation. As free solvents and components of gel systems and microemulsions, in: Dall'Olio All'Acrilico, Dall'Impressionismo All'Arte Contemp., Il Prato, Padova, 2016: pp. 176–184.

[26] L. Angelova, B. Ormsby, J.H. Townsend, R. Wolbers, Gel in the conservation of Art, Archetype Books, 2017

[27] B. Ormsby, A. Soldano, M.H. Keefe, A. Phenix, T. Learner, An Empirical Evaluation of a Range of Cleaning Agents for Removing Dirt from Artists ' Acrylic Emulsion Paints Removing, in: AIC Paint. Spec. Gr. Postprints, 2013: pp. 77–87.

[28] C. Stavroudis, MCP receipes - Technical notes, (2013).

[29] A. Phenix, T. Learner, M.H. Keefe, B.A. Ormsby, Evaluation of Cleaning Agents for Artists' Acrylic Paints with the Aid of High-Throughput (HTP) Testing, in: Paint. Spec. Gr., Milwaukee, Wis, 2010.

[30] P. Schossler, I. Fortes, J.C.D. de F. Júnior, F. Carazza, L.A.C. Souza, Acrylic and Vinyl Resins Identification by Pyrolysis-Gas Chromatography/Mass Spectrometry: A Study of Cases in Modern Art Conservation, Anal. Lett. 46 (2013) 1869–1884.

[31] D. Scalarone, O. Chiantore, Separation techniques for the analysis of artists' acrylic emulsion paints, J. Sep. Sci. 27 (2004) 263–274.

[32] T. Learner, The analysis of synthetic paints by pyrolysis–gas chromatography–mass spectrometry (PyGCMS), Stud. Conserv. 46 (2001) 225–241.

[33] V. Pintus, S. Wei, M. Schreiner, UV ageing studies: evaluation of lightfastness declarations of commercial acrylic paints, Anal. Bioanal. Chem. 402 (2012) 1567–1584.

[34] M. Melchiorre Di Crescenzo, E. Zendri, C. Miliani, F. Rosi, A preliminary FTIR-based exploration of the surfactant phase-separation process in contemporary mural paintings, E-Preservation Sci. 10 (2013) 10–18.

[35] D.O. Hummel, Atlas of Plastics Additives, Springer Berlin Heidelberg, Berlin, Heidelberg, 2002.

[36] B.A. Ormsby, E. Kampasakali, C. Miliani, T. Learner, An FTIR-based exploration of the effects of wet cleaning treatments on artists' acrylic emulsion paint films, E Preserv. Sci. 6 (2009) 186–195.

[37] T.T. Duncan, B.H. Berrie, R.G. Weiss, A Comparison Between Gel and Swab Cleaning: Physical Changes to Delicate Surfaces, in: L. V. Angelova, B. Ormsby, J. Townsend, R. Wolbers (Eds.), Gels Conserv. Art, Archetype Publications, London, UK, 2017: pp. 250–256.

[38] A. Burnstock, R. White, A preliminary assessment of the aging/degradation of Ethomeen C-12 residues from solvent gel formulations and their potential for inducing changes in resinous paint media, in: Tradit. Innov. Adv. Conserv. Contrib. to Melb. Congr. 10–14 Oct. 2000, ICC, Melbourne (AUS), 2000: p. 38.

[39] D. Stulik, D. Miller, H. Khanjian, N. Khandekar, R. Wolbers, J. Carlson, et al., Solvent Gels for the Cleaning of Works of Art: The Residue Question, The Getty Conservation Institute - J. Paul Getty Trust, Los Angeles, USA, CA, USA, 2004.

[40] A. Casoli, Z. Di Diego, C. Isca, Cleaning painted surfaces: evaluation of leaching phenomenon induced by solvents applied for the removal of gel residues, Environ. Sci. Pollut. Res. 21 (2014) 13252–13263.

[41] E.F. dos Reis, F.S. Campos, A.P. Lage, R.C. Leite, L.G. Heneine, W.L. Vasconcelos, et al., Synthesis and characterization of poly (vinyl alcohol) hydrogels and hybrids for rMPB70 protein adsorption, Mater. Res. 9 (2006) 185–191.

[42] A.L. Smith, The Analytical Chemistry of Silicones, Wiley, New York, NY, 1991.

[43] B.C. Smith, Infrared spectral interpretation: a systematic approach, CRC Press, Boca Raton, 1999.

[44] B. Ormsby, J. Youn Chung, A. Burnstock, K. Jan van der Berg, J. Lee, An investigacion of options for surface cleaning unvarnished water sensitive oil paints based on recent developments for acrylic paints, ICOM-CC, 2017

[45] A. Cincinelli, C. Scopetani, D. Chelazzi, E. Lombardini, T. Martellini, A. Katsoyiannis, et al., Microplastic in the surface waters of the Ross Sea

(Antarctica): Occurrence, distribution and characterization by FTIR, Chemosphere. 175 (2017) 391–400.

Chapter 4.

EXTENSION STUDY OF THE ASSESSMENT OF AQUEOUS CLEANING ON NBA/MMA AND EA/MMA ACRYLIC PAINTS

Adapted version

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Abstract

Acrylic paints became popular among artists in the late 50's. Some of the main conservation issues of these paints are inherent to their composition characteristics, for instance, their high sensitivity to water and a wide range of polar solvents. This makes difficult to stablish an accurate and respectful cleaning treatment for this kind of artworks. As reported on previous studies, the application of pH and conductivity adjusted solutions using accurate methods, such as confined on chemical gels, improved this kind of procedures. The aim of this work is to extend a previous study where the effect of water based cleaning treatments was tested on Liquitex acrylic paint mock-ups, and deepen on evaluating the alterations both on the surface and in the bulk of the paint film. In this paper, six acrylic commercial paints of two widely used paint brands, Titan Arts – Acrílico extrafino (Spain) and Hyplar Acrylic Colors® (USA), were selected to compare the effect of the cleaning treatment on their surface and binder matrix. Samples were prepared using Mylar sheets and left to dry in a dark and dust-free environment for three years. Adjusted water solutions were applied both using cotton swab and cryogels for comparison. Paints were characterized using Fourier Transform Infrared spectroscopy (FT-IR), pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS), Thermogravimetric Analysis (TGA) and Atomic Force Microscope (AFM).

All the samples showed different reaction to cleaning according to their different composition. This study revealed that those paint films where most surface alterations are observed after cleaning, are not those that suffer greater changes in the binder matrix. Moreover, a set of samples was aged under accelerated conditions (solar radiation under controlled temperature and humidity). The accelerated ageing was carried out under isochronous sampling up to a maximum of 1426 h. This tests revealed certain degradation processes such as chain scission of the binder that coincide with those alterations observed in several mock-ups after application of the cleaning treatment.

Keywords: cleaning, cryogels, acrylic paints, Titan, Hyplar, Thermogravimetry

1. Introduction

Acrylic paints have been widely used by contemporary artists since they were first introduced in 1927 as acrylic organic solvent solutions [1]. At the beginning they were developed as house paints, until late 1940s when the first acrylic solution artist paints were marketed under the name of Magna [2]. Many artists such as Rothko, De Kooning or Kenneth Noland used these paints for their artworks. Acrylic emulsion paints were introduced in 1953 by Rohn and Haas facilitating the handling of the paint since they were water soluble. Thus, they quickly became the most popular medium among artists. Since then, numerous formulations have been incorporated into the market. To date, paint makers have constantly varied the paint formulations in order to improve their performance.

Acrylic emulsion paint is a mixture of dyes or pigments dispersed on an acrylic binder, together with a large amount of additives such as, emulsifiers, biocides, buffers and fillers [3], which dry through coalescence. The binder used in these paints is an acrylic copolymer made out of a hard acrylate such as methyl methacrylate (MMA) and a softer acrylate such as ethyl acrylate (EA) or n-butyl acrylate (nBA). Ethyl acrylate (EA) was employed as soft monomer in the earlier formulations, EA/MMA copolimer. However, since the end of the 1980s many of the resin formulations have changed to a poly (n-butyl acrylate/methyl methacrylate) copolymer, p(nBA/MMA) [4, 5]. According to other studies, nBA is more flexible than EA, thus reducing the need to add large amount of plasticizers to the paint formulation [5, 6]. In consequence, the resulting film formed by butyl acrylate copolymers tends to be slightly tougher and more hydrophobic than ethyl acrylate copolymers, which makes them more stable to outdoor conditions [3]. These paints contain an amount of stabilizing additives, each providing its function and contributing to the complexity of such a multi-component system. For instance, non-ionic PEO-based surfactants, which are the most abundant type detected on acrylic emulsion paints [4].

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

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

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

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

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

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

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

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

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

A wide range of analysis techniques has been applied to assess the efficacy and side effects of the different cleaning strategies, mainly to study the surface affections of the films [20]. For instance, ATR-FTIR is usually employed to verify the surfactant presence/absence on the paint surface [3, 8, 10, 17, 21-24], as well as to identify any organic residue of either the cleaning system [13]. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) are usually employed to detect morphological changes on the paint surface after cleaning [25-27]. Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) is used to characterize the organic components by identifying monomer units and thermal degradation products of the paint [9, 28-30]. Other methods, such as High Performance Liquid Chromatography/Mass spectrometry (HPLC/ MS) or Electrospray Ionisation Mass Spectrometry (ESI–MS) have also been used to identify water extractable materials and Unilateral Nuclear Magnetic Resonance (NMR) to monitor the rate of water penetration into acrylic paint films during cleaning [31]. Thermogravimetric techniques, on the other hand, have been used less frequently to assess the cleaning treatment. In the studies in which this technique has been used, the results served to identify the loss of weight of the volatile and soluble components [16].

2. Research aim

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

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

3. Materials and Methods

3.1. Materials

Glacial acetic acid (99.8-100.5%), sodium hydroxide (≥97.0%), ammonium hydroxide solution (33%) and citric acid (99.5%) were all supplied by Sigma Aldrich. Poly(vinyl alcohol) (PVA) (HD 99+% with M_w=146-186000, and HD 89% with M_w=89-124000) was used for the synthesis of the PVA-based cryogels. Acrylic paint mock-ups were prepared using Dark Ultramarine Blue (PB 29), Phthalocyanine Titan Dark Green (PG 7) and Cadmium Red Light (PR 108) paints from Titan and Ultramarine Blue (PB 29), Phthalo Green (PG 7) and Naphthol Red (PR 112) from Hyplar®.

Acrylic paint film mock-ups

Acrylic paints were applied on Mylar® sheets using a paint applicator (Baker Universal Applicator from Neurtek). The average thickness of films is 150 µm. Samples were then left to dry in a dark and dust-free environment for three years. Tests were carried out after one year and after three years of drying.

ID. Sample	**Paint Brand**	**Pigment**
TI 29	Titan Arts – Acrílico extrafino (Spain)	Ultramarine Blue (PB 29)
TI 108	Titan Arts – Acrílico extrafino (Spain)	Cadmium Red (PR 108)

TI 7	Titan Arts – Acrílico extrafino (Spain)	Phthalocyanine green (PG 7)
HY 29	Hyplar Acrylic Colors® (USA)	Ultramarine Blue (PB 29)
HY 112	Hyplar Acrylic Colors® (USA)	Naphthol Red (PR 112)
HY 7	Hyplar Acrylic Colors® (USA)	Phthalo Green (PG 7)

Table 1 Identification and description of paint mock-ups.

Accelerated ageing

A set of 19 phthalocyanine green mock-ups of both Titan and Hyplar brands were aged under accelerated conditions. The ageing procedure consisted in exposing the reference paint films (1 x 2 cm) to artificial solar radiation under controlled temperature, humidity and irradiance conditions, as reported in a previous work [20]. A Solarbox 1500e RH equipment (Neurtek Instruments, Spain) was used, with a Xenon Lamp, which provided radiation with wavelengths between 300 and 800 nm and a nominal irradiance of 600 W m^{-2}. The camera was equipped with an indoor 310 nm UV filter and set to a black panel temperature of 55 °C and 50% humidity. The accelerated ageing was carried out under isochronous sampling up to a maximum of 1426 h.

3.2. Cleaning tests

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

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

3.3. Analytical techniques

Infrared spectroscopy

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

Pyrolysis - gas chromatography - mass spectrometry

Pyrolysis - gas chromatography - mass spectrometry was carried out on dried pristine acrylic paints (10-20 g) using an integrated system composed of a micro-furnace pyrolyser (5250 pyrolyser, CDS Analytical, United States) and gas chromatograph equipped with a mass spectrometer (5975C GC/MSD System with Triple-Axis Detector, Agilent Technologies, USA) and a ZB-WAX (30 m x 0.25 mm x 0.25 m) capillary column. Pyrolysis was performed at 600°C [33-34]. The pyrolyser interface and injector were set at 300°C. The gas chromatography column temperature program used is the following: initial temperature 40°C, hold for 2 minutes, followed by an increase of 12°C/min up to 250°C, hold for 10 minutes. The helium gas (99,999%) flow was set at 1.7 mL·min^{-1} with a pressure of 13.7 psi. Mass spectra were recorded under electron impact ionization (EI) at 70 eV energy, in the range from 40–550 m/z, source temperature of 230°C and quadruple at 150°C. Analyzed micro-samples were weighed using a Sartorius SE2 10^{-7} g micro-balance (Sartorius Stedim Biotech, Germany).

Atomic force microscope

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

Thermogravimetric analysis (TGA)

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

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

4. Results and discussion

4.1. Characterization of acrylic paints

Acrylic paint binders were characterized by means of Py-GC-MS see Figure 1a and b. Results for Titan acrylic samples showed the presence of nBA-MMA polymer while for Hyplar paint mock-ups EA-MMA co-polymer was detected.

Most characteristic peaks found in Titan are those related to the monomers methyl methacrylate (MMA) at RT 3.79 (m/z 39, 41, 69, 100) and n-butyl acrylate at 6.18 (m/z 55, 56, 73). Moreover, dimers (nBA-MMA, m/z 112 at 14.69 r_t; nBA-nBA, m/z 127 at r_t 16.98), and trimers (nBA-nBA-MMA, m/z 195 at 21.07 r_t; nBA-nBA-MMA, m/z 195 at 21.48 r_t; nBA-MMA-nBA m/z 228 at 23.26 r_t and nBA-nBA-nBA m/z 181 at 24.46 r_t) derived from the pyrolysis products of both monomers were also detected [33].

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

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

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

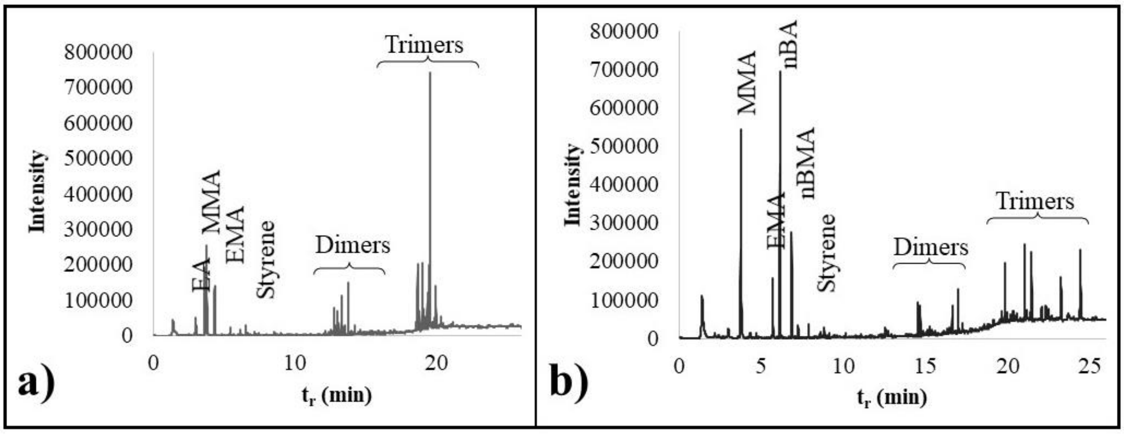

Figure 1 Py-GC identification of Hyplar phthalocyanine green paint (a) and Titan phthalocyanine green paint (b).

Py-GC-MS results are consistent with those obtained by ATR-FTIR. As shown in Figure 2, Titan samples show an intense absorption band at 1730 cm^{-1} (carbonyl stretching). The less intense peaks at 2982 cm^{-1} and 2952 cm^{-1} (CH stretching), and the signals at 1446 cm^{-1} and 1381 cm^{-1} (CH bending) are consistent with the presence of an acrylic binder [20]. However, nBA/MMA medium shows two peaks at 2960 and 2877 cm^{-1} and a shoulder at 2940 cm^{-1}.

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

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

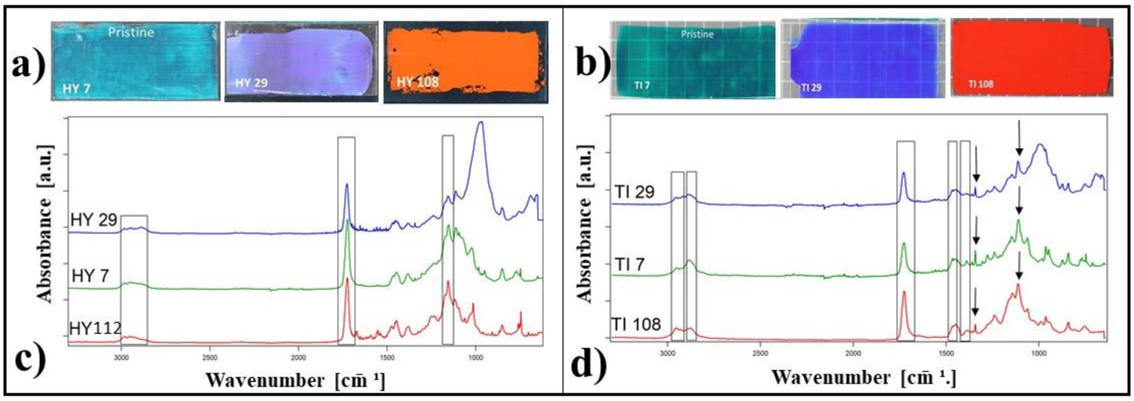

Figure 2 Pristine Hyplar (a) and pristine Titan (b) paint mock-ups: phthalocyanine green, Ultramarine blue and Naphthol and Cadmium red. ATR-FTIR of pristine acrylic paint mock-ups. Identification of co-polymer signals inside boxes and PEO-type surfactant signals marked with arrows in (c) Hyplar (d) and Titan acrylic paints

In the case of Titan paints, the intense absorption bands at 1110 cm^{-1} (O-C-O stretching), and less intense peaks at 2880 cm^{-1} (CH stretching), 1511 cm^{-1} (C=C ring stretching), and 1349 cm^{-1} (CH bending) revealed the presence of a nonionic alkylphenol ethoxylate surfactant (PEO type surfactant) [37].

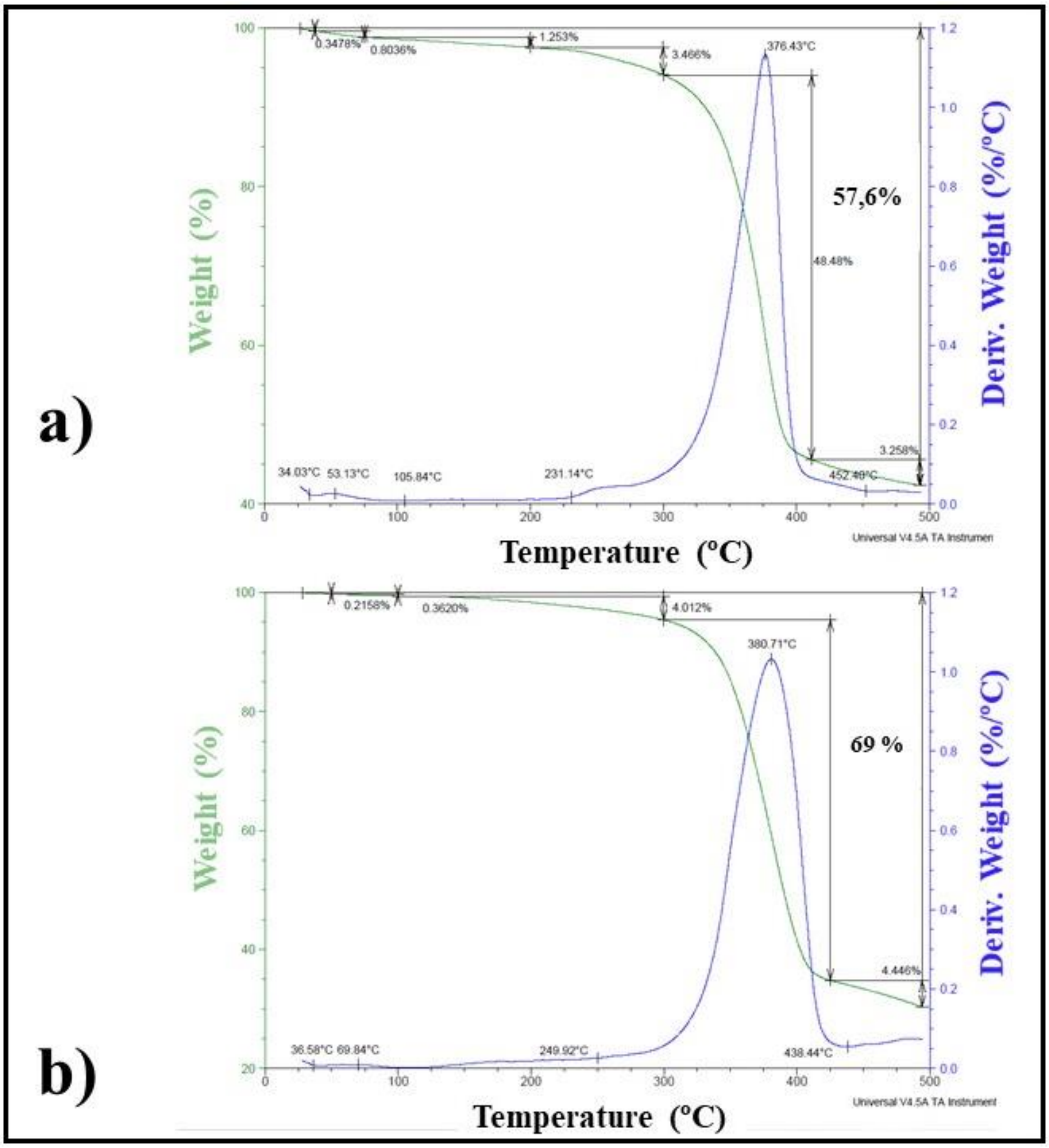

Figure 3 TGA-DTG of Titan inorganic blue (a) and organic green (b) pristine acrylic paint mock-ups.

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

	0-200 °C	200-300°C	300-450°C	Residue
TI 29	2,433	3,46	51,73	42.3
TI 29 W	1,79	5,24	50,12	42.2
TI 7	0,58	4,012	60,60	30.4
TI 7 W	1,19	2,87	72,53	22.8
TI 108	3,11	2,12	41,78	51.5
TI 108 W	3,45	2,62	43,30	52.3
HY 29	1,50	1,78	47,44	48.2
HY29 W	1,12	1,79	45,60	50.4
HY 7	5,21	2,13	62,64	30

HY 7 W	2,32	2,07	64,44	31.2
HY 112	0,94	9,44	63,57	18
HY112 W	0,42	8,68	56,01	26.5

Table 2 Weigh loss percentages in the different ranges of temperature of each acrylic paint mock-up before and after (W) swab cleaning.

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

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

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

ATR-FTIR was the technique of choice to follow up on the presence or absence of absorption bands corresponding to the various materials present in the paint layer before and after applying the cleaning treatment. The ATR-FTIR spectra shown in fig. 2 could be considered as representative of the whole surface since the small irregularities in the surfactant surface concentrations did not affect the qualitative evaluation of the results. As shown in figure 2, one year old Titan pristine untreated paint samples present a great amount of surfactant on the surfaces and as it can be observed on the swab cleaned samples, the bands ascribed to these additives: 2880 cm^{-1} (CH stretching), 1349 cm^{-1} (CH bending) and at 1110 cm^{-1} (O-C-O stretching), nearly disappear after the cleaning procedure, figure 4. On the contrary, cryogel effect on surfactant removal is not consistent in all the samples. As it can be observed on figure 4, the application of gel cleaning on both inorganic red and inorganic blue Titan samples almost completely remove surface surfactants while surfactant signals are still detected on Titan phthalocyanine organic green mock-ups. Further follow up FTIR analysis were performed on the same area of the cleaned surfaces one week after treatment, in order to observe surface behavior in the mid-short term after cleaning. Most of the surfaces remained unaltered one week after cleaning. Red and blue paints did not show any surface change one week after either gel or swab cleaning treatments. However, results of the green mock-up surfaces revealed the absence of surfactant signal one week after gel cleaning (figure 4d). Slight differences are observed by ATR-FTIR if comparing both methods. Although proven that gels incorporate less moisture than swab cleaning and do not subtract as much surfactant [13], it was observed that on those samples where additives remain on the surface after treatment, they disappear within the following days (figure 4d), which can be due to the resorption into the bulk of the film or their complete evaporation.

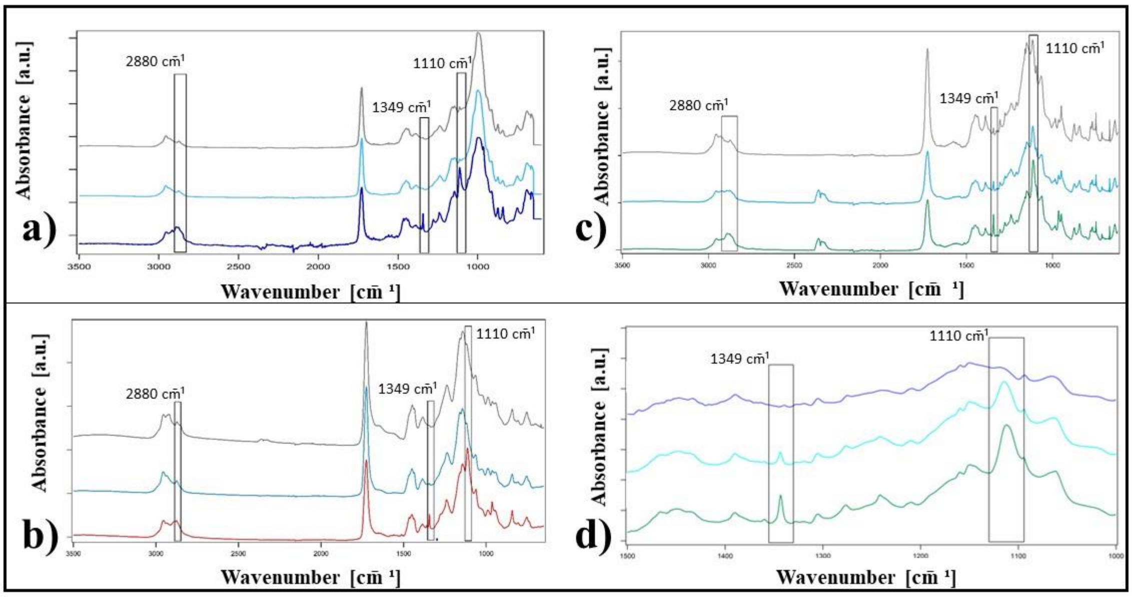

Figure 4 ATR-FTIR of Titan blue (a) Titan red (b) and Titan phthalocyanine green acrylic paint mock-up surfaces (c). Comparison between pristine (dark blue in (a), red in (b) and green line in (c) respectively), cryogel cleaning (light blue line), and swab cleaning (grey line) methods. (d) Surfactant detection on pristine Titan green sample (green line) after cleaning with cryogel (light blue line) and one week after treatment (dark blue line).

One year old Hyplar paints show less or none surfactant content on the film surface. This also demonstrates that paint´s chemistry depends on the initial formulation. Therefore, since it was not possible to check the effect of cleaning on surfactant removal, Hyplar mock-ups were naturally aged for a longer period and tested after three years, under the same conditions. As shown in Figure 5a, 3 years old Hyplar samples did show the presence of surfactants on the surface. In this case, both swab and cryogel cleaning resulted in instantaneous removal of surfactants, regardless of the colour. However, ATR-FTIR analysis of the treated area one week after cleaning, revealed the renewed presence of surfactant on the surface of Hyplar red and green mock-ups, unlike in blue colour. Therefore, we could consider that organic colour paints in either of the two studied brands undergo higher additive movements (migration and resorption) as a result of aqueous cleaning procedures. The movement of these additives can be ascribed to a higher amount of soluble materials, particle size and dispersant content that is needed to formulate organic pigment colours [16].

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

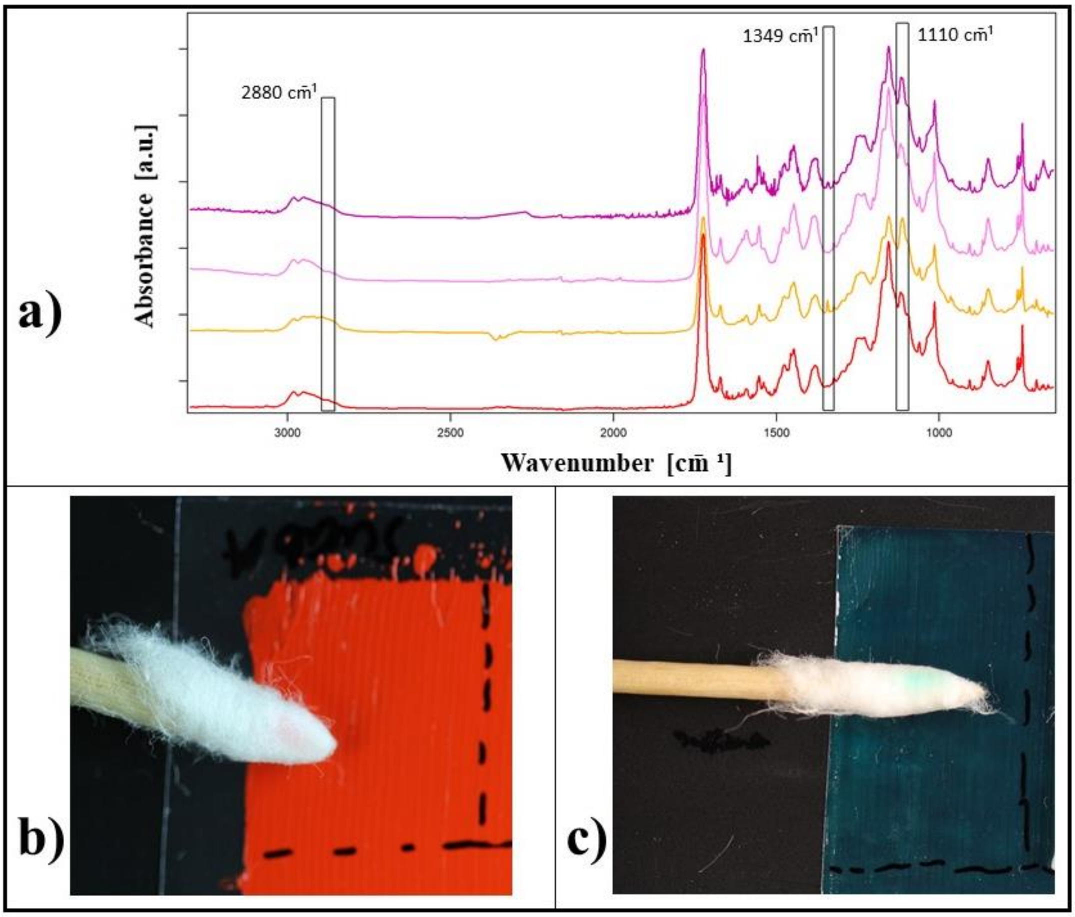

Figure 5 (a) ATR-FTIR identification of migration and disappearance of surfactant bands on the surface of Hyplar red acrylic paint after 1 year of natural aging (red line); after 3 years of natural aging (orange line); after swab cleaning on the 3 years old mock-up (light pink): 1 week after swab cleaning on the 3 years old mock-up (deep pink). (b) Red pigment traces on the cotton swab after treatment. (c) Green pigment traces on the cotton swab after treatment.

Finally, mock-ups of organic phthalocyanine green colour of both brands were aged under artificial accelerated conditions in order to observe changes on the surface composition. The selection was made based on previous results that revealed that this organic pigment was the most unstable. Therefore, two sets of 19 phthalocyanine green mock-ups of both brands were prepared and artificially aged in a Solarbox as described elsewhere [20]. Results demonstrated that surfactant migration on Titan paints is faster than on Hyplar paints (figure 6), which is consistent with the results observed after natural aging. Thus, while on Titan mock-ups the first surfactant signals are detected between the first 24 and 48 hours (equivalent to around 1 year of natural aging), on Hyplar paints, PEO signals are not detectable until past 360h of accelerated aging (equivalent to around 7 years of natural aging) [9]. Taking into account that samples were subjected to identical aging conditions, the faster migration of additives may be caused by other factors such the length of the surfactant chain or the polymer binder composition [7]. Along with this, TGA revealed that Titan mock-ups have more organic material than Hyplar, which may correspond to a greater amount of dispersants that might migrate faster to the surface during aging.

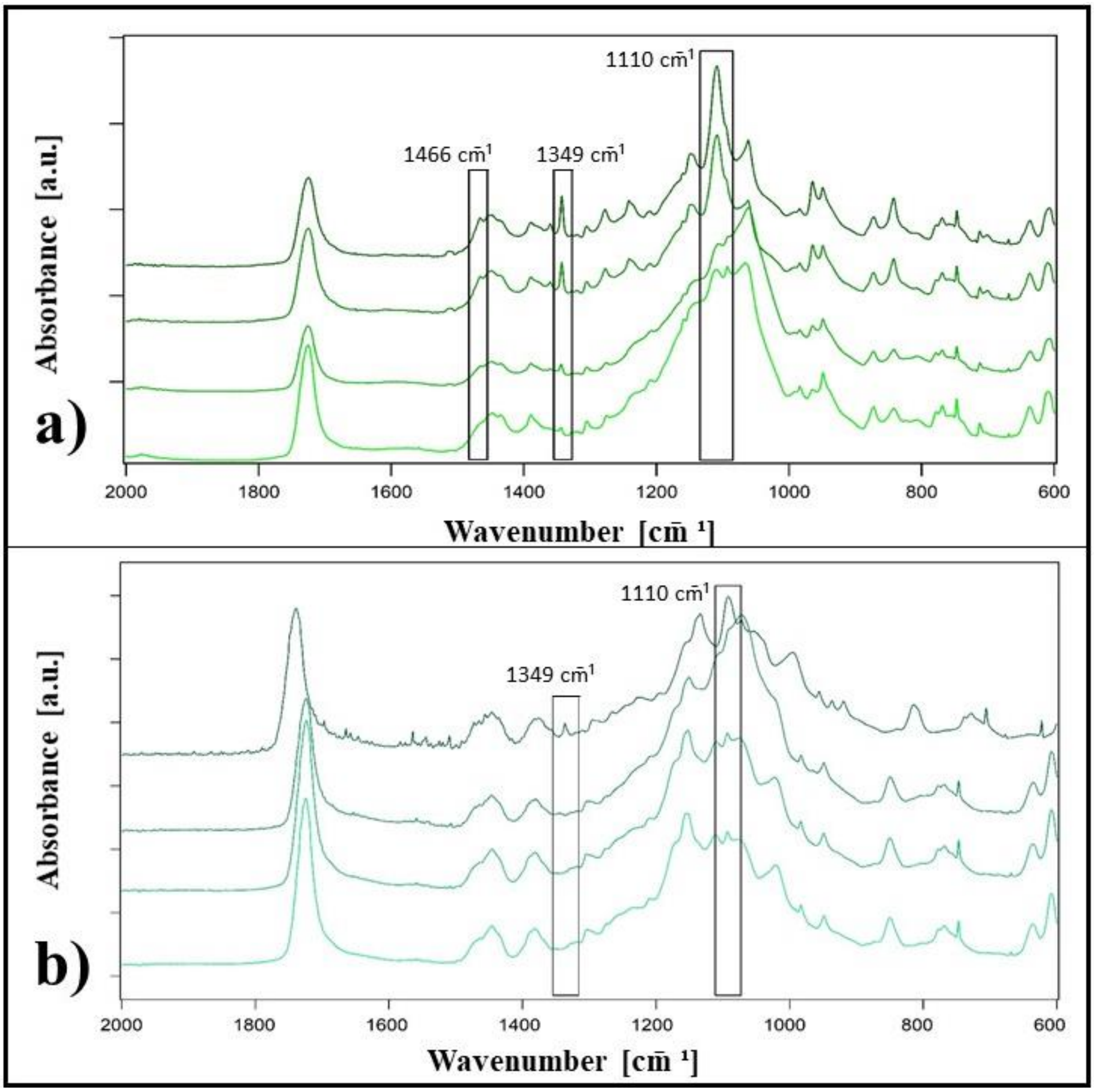

Figure 6 ATR-FTIR of artificially aged Titan (a) and Hyplar (b) phthalocyanine green acrylic paint mock-ups. From lighter green to darker green 24h, 192h, 360h and 456h aged samples. Identification of surfactant signals that appear progressively while aging.

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

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

DTG-TGA offered a tool to monitor the presence/absence of the water soluble components of the paint in the range of 0-200°C (figure 7) before and after cleaning. In the specific case of the organic green pigment samples, the DTG curve depicts a remarkable double slope that correspond to the presence of the thermally degraded pigment and binder. As shown on figure 8, while no double slope in the 300-450°C range can be observed for inorganic samples.

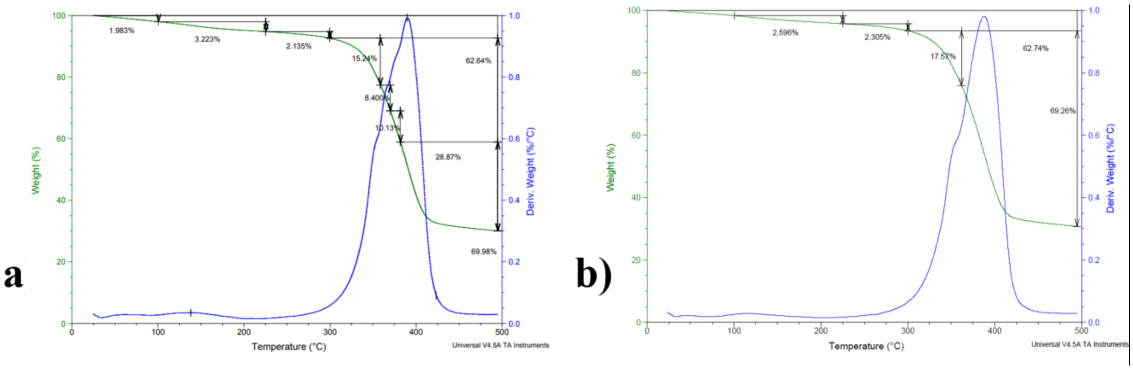

Figure 7 TGA-DTG curves of Hyplar green acrylic paints before (a) and after (b) swab cleaning.

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

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

Table 3 Maximum degradation temperature (Tmax) of the acrylic co-polymers before and after swab cleaning.

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

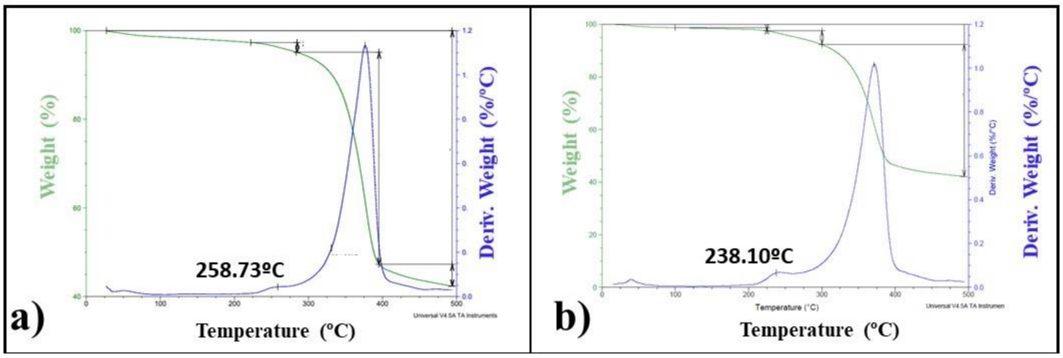

Figure 8 TGA-DTG curves of Titan blue acrylic paint mock-ups. Formation of a new peak at around 230-260ºC in pristine sample (a) and after swab cleaning (b).

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

4.4. The effect of aqueous cleaning on surface roughness.

Previous studies [13, 42] concluded that swab cleaning causes bigger changes to the morphology of the paint surface, in comparison to gel cleaning systems. Therefore, AFM was used to evaluate the roughness changes in both Titan and Hyplar pristine samples before and after swab and cryogel cleaning on one year old naturally aged samples. Images show remarkable morphological differences of the surface of the samples (figure 9). Regardless of the brand, pristine samples of same pigment color show similar appearance. All the results confirmed the extraction of components from the paint surface, formation of pinholes and roughness changes after application of both cleaning methods. The materials removed from the surface of each sample may be differ from surfactants to pigments: (figure 5). The root mean square roughness (Rq) value obtained as a calculation of the deviation of the roughness profile, represents the average roughness of the sample. Those values were obtained using the Nanoscope Analysis Software. The Rq of the Titan mock-ups increased in the three colors after swab rolling (ie. Rq of Titan blue, cleaned sample=229nm; Rq of Titan blue, pristine sample= 107nm), which can be interpreted as the removal of materials from the surface after treatment. The biggest changes are detected on red Titan surface and the smallest changes were detected on green samples. In general terms, slighter changes were observed on Hyplar brand samples (see table 4).

	TI_29	TI_7	TI_108	HY_29	HY_7	HY_112
Rq pristine (nm)	107	104	109	278	63.2	134

Rq gel (nm)	224	117	129	274	87.2	252
Rq Swab (nm)	229	146	407	273	103	192

Table 4 Profile roughness (Rq) of the unsoiled acrylic paint mock-ups before cleaning treatment (Rq pristine), after cleaning with the cryogel (Rq gel) and after swab cleaning treatment (Rq swab).

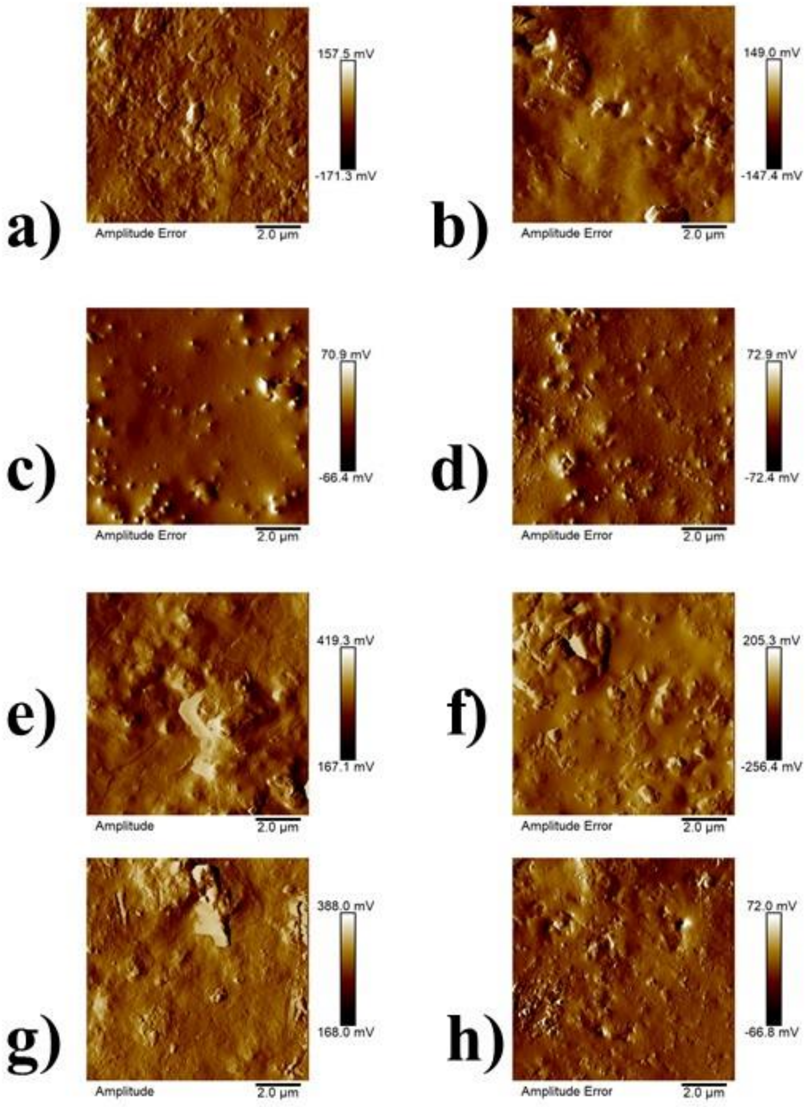

Figure 9 AFM amplitude images of Titan blue (TI_29) pristine and swab cleaned (a-b); Titan red (TI_108) pristine and swab cleaned (c – d); Hyplar blue (HY_29) pristine and swab cleaned (e-f); Hyplar red (HY_108) pristine and swab cleaned (g-h).

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

5. Conclusions

In this work the analysis by ATR-FTIR, Py-GC-MS and TGA-DTG of six commercial paints from two different acrylic commercial brands proved that the existence of differences regarding the copolymers used as binders resulted in a different behavior of the surfactants present within the films. Titan paints contain a poly n-butyl acrylate/methyl methacrylate copolymer while Hyplar paints are composed of ethyl acrylate/methyl methacrylate. This way, Titan samples show an early migration of surfactants to the surface (in less than one year) but this phenomenon is not observed on Hyplar samples until the third year of natural aging. Accelerated aged samples showed a progressive and unequal migration of surfactants but also depicted the earlier migration of additives in Titan samples.

On the other hand, when it comes to cleaning methods both brands in all tested colors showed similar sensitivity to swab cleaning in terms of surfactant removal.

Overall, the use of cryogels for cleaning proved to be more respectful than swab cleaning. Nevertheless, some surfactant removal was still observed on Hyplar samples and on the inorganic colors (blue and red) of the Titan paints. In general terms, the organic colour paints of both brands seem to undergo higher degree of additive migration to the surface and resorption into the bulk of the film, during and after application of the cleaning treatment.

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

Therefore, we can conclude that it is no possible to define a common cleaning system for all the acrylic brands and pigments. In general terms cryogels show more respectful cleaning results compared to cotton swab. However, Hyplar organic colours for instance have demonstrated a considerable sensitivity towards colour removal while Titan inorganic colours showed higher sensitivity to surfactant removal. These aspects should need further research in order to find a more suitable cleaning system for these cases.

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

References

[1] H.A.L. Standeven, House Paints, 1900-1960. History and use, Research in Conservation (2011) Getty Conservation Institute, Los Angeles.

[2] J. Crook and T. Learner, The impact of Modern Paints, (2000) Tate Gallery Publishing, Ltd, Millbank, London, UK.

[3] E. Jablonski, T. Learner, J. Hayes, M. Golden, Conservation concerns for acrylic emulsion paints, Stud. Conserv. (48) (2003) 3–12.

[4] B. Ormsby, T. Learner, The effects of wet surface cleaning treatments on acrylic emulsion artists' paints – a review of recent scientific research, Stud. Conserv. (54) (2009) 29–41.

[5] A. Solbes-Garcia, J.M. Miranda-Vidales, A. Nieto-Villena, L.S. Hernandez, L.Narváez, Evaluation of the oxalic and tartaric acids as an alternative to citric acid in aqueous cleaning systems for the conservation of contemporary acrylic paintings, Journal of Cultural Heritage, (25) (2017) 127-134.

[6] D.R. Karsa, Surfactants in Polymers, Coatings, Inks and Adhesives, (2003) Blackwell Pub, Florida, US.

[7] J.L. Keddie, A.F. Routh, Fundamentals of Latex film formation. Processes and properties. Springer laboratory, 2010.

[8] B. Ormsby, T. Learner, G.M. Foster, J. Druzik, M. Schilling, Wet-cleaning acrylic emulsion paint films: An evaluation of physical, chemical and optical changes, in: Mod. Paint. Uncovered Symp., 2007, pp. 189–200.

[9] L. Ortiz-Herrero, I. Cardaba S. Setien , L. Bartolomé , ML. Alonso , MI. Maguregui . OPLSmultivariate regression of FTIR-ATR spectra of acrylic paints for age estimation in contemporary artworks. Talanta (2019) Dec 1;205:120114.

[10] B. Ormsby, P. Smithen, F. Hoogland, T. Learner, C. Miliani, A scientific investigation into the surface cleaning of acrylic emulsion paintings, ICOM Committee for Conservation, 15th Triennial Conference Preprints Vol. II , New Delhi, 22–26 September, 2008, pp. 857–865.

[11] R. Perry, Problems of dirt accumulation and its removal from unvarnished paintings: a practical review., in: Dirt Pict. Separated Pap. given a Conf. Held

Jointly by UKIC Tate Gall. January, 1990, pp. 3–6.

[12] J. Lee, I. Bonaduce, F. Modugno, J. La Nasa, B. Ormsby, K.J. Van den Berg, Scientific investigation into the water sensitivity of twentieth century oil paints, in Michrochem. J., 138 (2018) 282-295.

[13] I. Cardaba, G. Poggi, M. Baglioni, D. Chelazzi, I. Maguregui, R.Giorgi, Assessment of aqueous cleaning of acrylic paints using innovative cryogels, Microchem. J., 152 (2020) 104311.

[14] D. Keynan, A. Hughes, Testing the Waters: New Technical Applications for the Cleaning of Acrylic Paint Films and Paper Supports, B. Pap. Gr. Annu. 32 (2013).

[15] S. Zumbühl, F. Attanasio, N.C. Scherrer, W. Müller, N. Fenners, W. Caseri, Solvent action on dispersion paint systems and the influence on the morphology: changes and destruction of the latex microstructure, in: Mod. Paint. Uncovered Proc. from Mod. Paint. Uncovered Symp., 2007, pp. 257–268.

[16] T. Learner, O. Chiantore, D. Scalarone, Ageing studies of acrylic emulsion paint, ICOM Committee for Conservation, 13th Triennial Meeting Preprints Vol. II, Rio de Janeiro 20-27 September, 2002, pp. 911-919.

[17] C.E. Dillon, A.F. Lagalante, R.C. Wolbers, Acrylic emulsion paint films: The effect of solution pH, conductivity, and ionic strength on film swelling and surfactant removal, Stud. Conserv. 59 (2014) 52–62.

[18] J.A.L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, Innovative Hydrogels Based on Semi-Interpenetrating p(HEMA)/PVP Networks for the Cleaning of Water-Sensitive Cultural Heritage Artifacts, Langmuir. 29 (2013) 2746–2755.

[19] C. Mazzuca, G. Poggi, N. Bonelli, L. Micheli, P. Baglioni, A. Palleschi, Innovative chemical gels meet enzymes: A smart combination for cleaning paper artworks, J. Colloid Interface Sci. 502 (2017) 153–164.

[20] D. Scalarone, O. Chiantore, Separation techniques for the analysis of artists' acrylic emulsion paints, J. Sep. Sci. 27 (2004) 263–274.

[21] B. Ormsby, R. Barker, R. Hellen, P. Smithen, Cleaning acrylic emulsion paintings: case study treatments, evaluation and reflections, in: M.D.C.

Mundici (Ed.), What's Changing: Theories and Practices in the Restoration of Contemporary Art Symposium, Castello di Rivoli Museo D'Arte, 10–11 February 2012, Contemporanea, Turin, Thames & Hudson, 2012, pp. 227–242.

[22] E. Kampasakali, B. Ormsby, A. Phenix, M. Schilling, T. Learner, A preliminary study into the swelling behaviour of artists' acrylic emulsion paint films, ICOM Committee for Conservation, 16th Triennial Conference Preprints, Portugal, September 2011, pp. 1–8.

[23] R. Ploeger, H. Shurvell, E. Hagan, A. Murray, Infrared analysis of materials leached by water from acrylic paint films, in: M. Picollo (Ed.), The Sixth Infrared and Raman Users Group Conference (IRUG6), Il Prato, Florence, 2005, pp. 46– 51.

[24] R. Wolbers, A. Norbutus, A. Lagalante, Cleaning of acrylic emulsion paints: preliminary extractive studies with two commercial paint systems, in: M.F. Mecklenburg, A. Charola, R. Koestler (Eds.), New Insights into the Cleaning of Paintings, 2010, Smithsonian Contributions to Museum Conservation, Number 3, Smithsosian Institution Scholarly Press, Washington DC, 2013, pp. 147–157.

[25] O. Chiantore, D. Scalarone, The Macro- and Microassessment of Physical and Aging Properties in Modern Paints, in: Mod. Paint. Uncovered Proc. from Mod. Paint. Uncovered Symp., 2007, pp. 96-103.

[26] E. Kampasakali, B. Ormsby, A. Cosentino, C. Miliani, T. Learner, An evaluation of the surfaces of acrylic emulsion paint films and the effects of wet–cleaning treatment by Atomic Force Microscopy (AFM), Stud. Conserv. 56 (2011) pp. 216–223.

[27] D. Scalarone, M. Lazzari, V. Castelvetro, O. Chiantore, Surface monitoring of surfactant phase separation and stability in waterborne acrylic coatings, Chem. Mater. 38 19 (2007) 6107–6113.

[28] L. Ortiz-Herrero, A.C. de Almeida Assis, L. Bartolomé, M.L. Alonso, M.I. Maguregui, R.M. Alonso, J.S. Seixas de Melo, OPLS multivariate regression of FTIR-ATR spectra of acrylic paints for age estimation in contemporary artworks, Chemom. Intell. Lab. Syst., (2020) 207: 104187.

[29] T. Learner, The analysis of synthetic paints by pyrolysis–gas

chromatography–mass spectrometry (PyGCMS), Stud. Conserv. 46 (2001) 225–241.

[30] P. Schossler, I. Fortes, J. Cura D'Ars de Figueiredo, F. Carazza, L. Cruz Souza, Acrylic and vinyl resins identification by pyrolysis-gas chromatography/mass spectrometry: A study of cases in moderna art conservation, Analytical Letters, 46 (2013) 1869–1884.

[31] T. Fardia, V. Pintus, E. Kampasakalia, E. Pavlidoue, K. G. Papaspyropoulos, M. Schreinerb, G. Kyriacoua, A novel methodological approach for the assessment of surface cleaning of acrylic emulsion paints, Michrochem. J. 141 (2018) 25-39.

[32] B. Ormsby, A. Soldano, M.H. Keefe, A. Phenix, T. Learner, An empirical evaluation of a range of cleaning agents for removing dirt from artists' acrylic emulsion paints, AIC Paint. Spec. Gr. Postprints, (2013) pp. 77-87.

[33] T. Fardi, V. Pintus, E. Kampasakali, E. Pavlidou, M. Schreiner, G. Kyriacou, Analytical characterisation of artist's paint systems based on emulsion polymers and synthetic organic pigments, J. Anal. Appl. Pyrolysis 135 (2018) 231-241.

[34] M.F. Silva, Analytical study of accelerated light ageing and cleaning effects on acrylic and PVAc dispersion paints used in Modern and Contemporary Art, Universitat Politècnica de València, PhD Thesis (2011).

[35] H.M. Ng, M.S. Norshahirah, O. Fatin Saiha, K. Ramesh, S. Ramesh, S. Bashir, Thermogravimetric Analysis of Polymers, Encyclopedia of Polymer Science and Technology (2018).

[36] Learner, T. Analysis of modern paints. Getty Publications (2004).

[37] M. Melchiorre Di Crescenzo, E. Zendri, C. Miliani, F. Rosi, A preliminary FTIR-based exploration of the surfactant phase-separation process in contemporary mural paintings, E-Preservation Sci. 10 (2013) 10–18.

[38] D.O. Hummel, Atlas of Plastics Additives, (2002) Springer Berlin Heidelberg, Berlin, Heidelberg.

[39] S. Vahur, U. Knuutinen, I. Leito, ATR-FT-IR spectroscopy in the region of 500–230cm−1 for identification of inorganic red pigments, Spectrochim. Acta

Part A Mol. Biomol. Spectrosc. 73 (2009) 764–771.

[40] S. Parvate, P. Mahanwar, Insights into the preparation of water-based acrylic interior decorative paint: tuning binder's properties by self-crosslinking of allyl acetoacetate - hexamethylenediamine, in Progress in Organic Coatings(126) (2019), pp: 42-149.

[41] C.H. Hare, Thermal degradation, Part 2: pigments, Journal of Protective Coatings and Linings, 16, 10 (1999).

[42] T.T. Duncan, B.H. Berrie, R.G. Weiss, A Comparison Between Gel and Swab Cleaning: Physical Changes to Delicate Surfaces, in: L. V. Angelova, B. Ormsby, J. Townsend, R. Wolbers (Eds.), Gels Conserv. Art (2017) Archetype Publications, London, UK, pp. 250–256.

Chapter 5

EASY-TO-MAKE POLYMER HYDROGELS BY UV-CURING FOR THE CLEANING OF ACRYLIC EMULSION PAINT FILMS

Adapted version

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Abstract

The cleaning of acrylic emulsion paint surfaces poses a great challenge in the conservation field, due to their high water sensitivity. In this article, we present easy-to-make polymer hydrogels, made by UV-photopolymerization, that show excellent cleaning properties. The formulation of hydrogels obtained by UV-curing and their performance as dry cleaners for acrylic paints was investigated. First, different hydrogel formulations based on functional acrylic monomers were used to formulate a series of UV cross-linked hydrogels by fast UV photopolymerization. Their effectiveness on surface dirt removal was investigated by SEM microscopy and colorimetry. The hydrogels showed excellent cleaning properties and controlled water release, and they still performed satisfactorily after several cleaning uses. The obtained UV-hydrogels were compared to the well-known agar gels, showing benefits in terms of reducing excess water. This article shows that easy-to-make UV-cured hydrogels are an efficient tool for the cleaning of surface dirt from water-sensitive paintings, overcoming the limits of traditional cleaning methods.

Keywords: *acrylic paint; UV-cured hydrogels; art conservation; cleaning*

1. Research Aim

The aim of this work is to make the first approach to improving the cleaning methodology of water-sensitive paint surfaces by using fast, easy-to-make, and tunable UV-cured hydrogels. The main advantage of the proposed method is that UV-curing is afast and available method [1–4] with high success in the coating industry and 3D printing,as well as other daily applications in health and esthetics. Besides the chemical compounds, it only needs a UV-lamp for obtaining the needed material in a rapid manner. Thus, avoiding complex laboratory processes while optimizing the preparation times is what makes these gels more affordable for the restorer than other types of hydrogels or cleaning materials.

In this work, we assessed the cleaning performance of several acrylic hydrogels. To do this, we investigated several formulations of UV-cured hydrogels based on commercially available functional (meth)acrylates, in order to find the most effective formulation for removing surface dirt while not harming the paint surface. The second part of the work compares the cleaning capability of UV hydrogels with the well-known agar gel. Agar is a commonly used and easy-to-make system in the conservation of art which has shown several drawbacks in terms of water retention capability [5]. This studyshows the improvement in terms of water containment when using the UV-cured hydrogels presented here.

2. Introduction

The cleaning of water-sensitive paintings such as acrylic emulsion paint films is a very common practice in the conservation of contemporary art. The gradual accumulationof surface grime on paintings is a very common concern everywhere that art is present [6]. Even in a presumably benign museum environment, the slow accumulation of surfacegrime leads to the discernible visual alteration of a painted surface after approximately 50years [6,7]. Therefore, we can assume that most of the artworks made out of acrylic paint,which was first introduced in 1953 by Rohm and Haas [8], are now prone to needing surface cleaning. In fact, many contemporary artists employed acrylic paints as their main media to create artworks [9]. Moreover, the vast production of contemporary painters has filled museum collections with these kinds of works [10]. However, this apparently simple conservative intervention is a delicate and challenging operation, due to, on the one hand, the complexity of the paint system itself [6], and on the other hand, its high water sensitivity [11–16].

Acrylic emulsion paints are made from water, acrylic monomers, stabilizers, thickeners, coalescing agents, pigments, and a wide range of additives that improve the paint's properties [6,17]. The resulting film can become tacky at room temperature due to a low glass transition temperature (T*g*), which triggers the adhesion of airborne dust [11,17]. Moreover, static charges and hydrophilic additives accumulated in the surface, such as surfactants, can attract and embed environmental soil [11,18,19]. Research carriedout by a number of conservation scientists [13,14,16–27], identified the factors that influence the sensitivity of acrylic paint films to organic solvents and water-based cleaningsystems [6,11]: additive migration, swelling of the paint film, and re-transport of solubilized matter through the porous matrix of the artifacts during the cleaning procedure [12–15] are, among other factors, only a few of the obstacles ahead.

According to some authors, the swelling of the paint corresponds to the sensitivity of the thickeners that are part of the composition [6]; others stated that water sensitivity is related to the quantity of non-ionic surfactants that are commonly present in acrylic paintsurfaces [18,22].

Several authors agree that the modification of the pH and the conductivity in a cleaning solution can help to control water absorption and material extraction [6,18,28– 34]. In an alkaline or neutral environment, acrylic film hydrates and swells, softening and causing disruption [31]. Therefore, to minimize the swelling, the pH of the cleaning system must be kept as low as possible [6]. Furthermore, the ionic strength needs to be controlled. Both the cleaning solution and the paint layer have to be isotonic, in order to avoid the movement of ions between layers [6]. All this leads to large problems in finding accurate and safe cleaning systems, and the subsequent need to investigate new cleaning methods [20,32].

The controlled release of water needs to be considered as a tool to improve effectivity, especially when non-confined solvents and solutions are employed [15,16]. Therefore, theuse of confined cleaning fluids within a gel matrix that releases them in a controlled wayonto the surface of the work of art has been proposed [15,16]. In recent years, several methods have been tested to improve the control of cleaning fluids. Some researchers proposed thickeners, such as cellulose derivatives and polyacrylic-based formulations [33], to enhance the control of solvent diffusion by increasing the viscosity of the liquid [15,16,33,34]. However, the residue in thickened systems is still a challenge that has not been resolved [17,35,36]. Rigid gels, which can be classified as physical or chemical, according to their bonding nature [15,37], were proposed as residue-free confining systems. Polysaccharides such as gellan gum and agar are the most popular gelling agents employed to obtain the rigid physical gels used by conservators/restorers [15,38], due to their fast and easy preparation and handling. However, they retain high amounts of water, making control over the liquid release problematic [39–41].

As an alternative, xPVOH-borax gels [42,43], freeze-thaw PVA gels [44], and pHEMA/PVP [5,39] chemical hydrogels have emerged, proving to be more efficient, safe, retentive and tunable for the cleaning of water-sensitive artifacts. However, the manufacture of these chemical gels usually requires complex chemicalprocesses, with the exception of the borax gels, and are therefore less integrated (extended) into the daily work of the restorer.

This paper aims to be the first approach to introducing UV-cured hydrogels using commercially available acrylic monomers, in order to achieve a system with good cleaning properties and with the ease of being able to prepare them in your own workspace.

3. Materials and Methods

3.1. Materials

2-(Hydroxyethyl)methacrylate (HEMA) (assay 97%-) vinylpyrrolidone (VP), [2- (methacryloyloxy)ethyl]trimethylammonium chloride (METAC) 75 wt % in H_2O, 2- acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (99%), poly(ethylene glycol) dimethylmethacrylate (PEGDMA, MW 550 g mol^{-1}), 2-hydroxy-4-(2-hydroxyethoxy)-2- methylpropiophenone (IRGAcure 2956), glacial acetic acid (99.99%), and ammonium hydroxide solution (28% NH_3 in H_2O), were all supplied by Sigma Aldrich and used as received for the synthesis of the UV-cured hydrogels. Agar-agar was provided by C.T.S. España. S.L. Acrylic paint mock-ups were prepared using brown PBr7 and titanium white PW6 paints from Liquitex® (Cincinnati, OH, USA)

3.2. Preparation of Hydrogels by UV-Photopolymerization

Chemically cross-linked UV-cured hydrogels were synthesized by photo-polymerization according to the reaction shown in **Figure 1**. In a typical reaction, for 4 g of hydrogel solution, 1.79 g of HEMA, 0.2 g of VP, 0.01 g of PEGDMA and 0.04 g of the photoinitiator IRGAcure 2956 were dissolved in 2 g of pH-adjusted water. All the components were stirred together except the photoinitiator, which was added just beforethe UV exposure. Different hydrogels were designed by varying the proportions of monomer/cross-linker ratio, photoinitiator percentages, and the pH of the adjusted water. Preliminary tests were performed to find the most adequate copolymer compositions and monomer/crosslinker ratio. The compositions of the hydrogels selected for the cleaning trials are presented in **Table 1**. Components were chosen for their affinity with water to create hydrogels. Different monomers were tested in order to check the cleaning capacityof their different functional groups. HEMA and VP were chosen to obtain a water- insoluble network, as they comprise two reactive groups capable of cross-linking the hydrogel acrylate backbone [5]. METAC and AMPS were used as monomers in order to improve cleaning efficiency while maintaining the good mechanical

properties of the structure (stickiness and flexibility). PEGDMA was added as a crosslinker in order to ensure mechanical stability without stiffening the hydrogel [3]. Two water buffers of pH5.0 and 6.5 were prepared for comparison. The highest and lowest pH values were selected according to the safety range proposed by Stavroudis in the modular cleaning program (MCP) recipes for the cleaning of acrylic paints [6,45]. Both buffers were adjustedin conductivity to 6.0 mS/cm^2, as advised elsewhere [17,45].
The solution was irradiated with UV light for 15 min for polymerization. A UV chamber from Boekel Scientific was used for hydrogel crosslinking, model 234100. Crystal vials were used as molds, obtaining 2.5-cm diameter and 1-cm thick gels.

3.3. Acrylic Paint Mock-Ups

Acrylic paint was applied on Mylar sheets as described elsewhere [17]. Two commercial paints (Liquitex white PW6 and brown PBr7) were selected to evaluate the cleaning efficiency of the method. Both colors were chosen in order to detect the variableresults that may be obtained according to the different nature of the pigments. White samples were employed to test the cleaning efficiency, and brown paint was used to test the sensitivity toward the cleaning method. Some samples were kept as reference and others were artificially soiled according to published protocols [24], using a mixture of carbon black, iron oxide, silica, kaolin, gelatin powder, soluble starch, cement, olive oil, mineral oil and petroleum spirit, in the stated proportions [24]. Cleaning tests were conducted after three years [24] of natural aging. The excess loose soil was removed witha brush and the gel cleaning tests were performed on the embedded soiling layer. All mock-ups were stored in dark conditions and a dust-free environment.

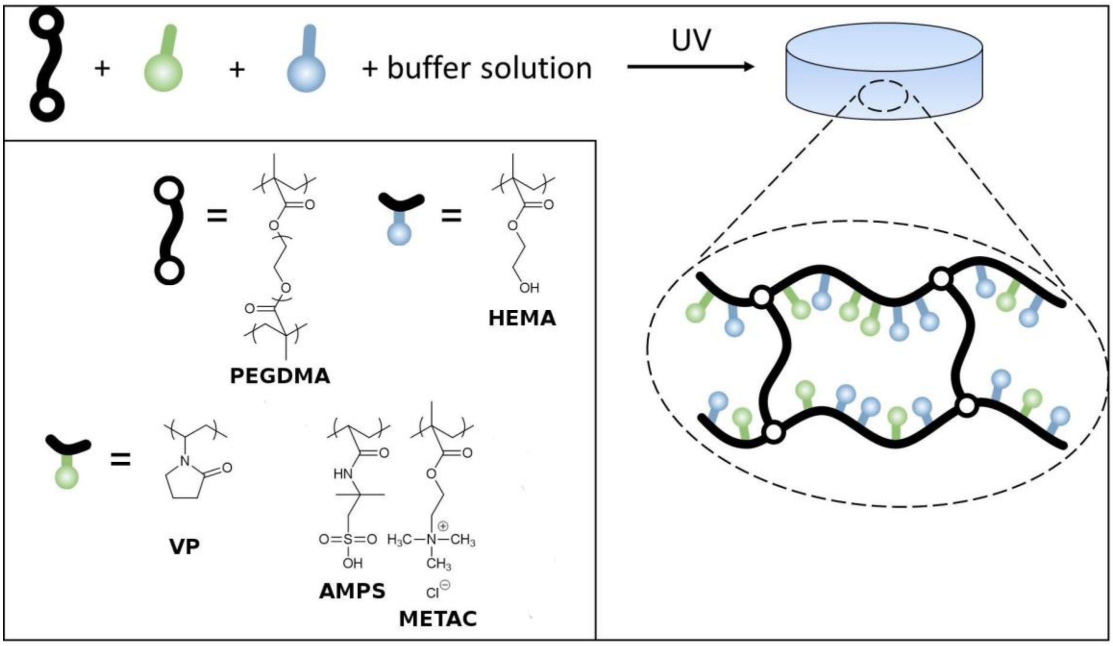

Figure 1 UV-cured hydrogels for the cleaning of water-sensitive paintings: reaction scheme and chemical structure of the monomers used and representation of a UV-cured hydrogel

Name	Monomer 1 (wt %)	Monomer 2 (wt %)	Crosslinker (wt %)	Aqueous Solution (wt %)
HEMA_5	HEMA (49.75)	-	PEGDMA (0.25)	pH 5.0 buffer (50)
HEMA_VP5	HEMA (39.8)	VP (10)	PEGDMA (0.25)	pH 5.0 buffer (50)
HEMA_METAC 5	HEMA (39.8)	METAC (10)	PEGDMA (0.25)	pH 5.0 buffer (50)
HEMA_AMPS5	HEMA (39.8)	AMPS (10)	PEGDMA (0.25)	pH 5.0 buffer (50)
HEMA_6.5	HEMA (49.75)	-	PEGDMA (0.25)	pH 6.5 buffer (50)
HEMA_VP6.5	HEMA (39.8)	VP (10)	PEGDMA (0.25)	pH 6.5 buffer (50)
HEMA_METAC6.5	HEMA (39.8)	METAC (10)	PEGDMA (0.25)	pH 6.5 buffer (50)
HEMA_AMPS6.5	HEMA (39.8)	AMPS (10)	PEGDMA (0.25)	pH 6.5 buffer (50)

Table 1 Weight percent composition of the UV-cured hydrogels; 2% weight based on monomer (wbm) of IRGACURE 2956 was added to each solution

3.4. FTIR

A Brueker ALPHA FTIR spectrometer was used to record IR spectra of the synthesized hydrogel. The spectra were collected using 32 scans with a resolution of 2 cm^{-1} in the ATR mode. An average spectrum was obtained out of several measurements taken from the surface of the hydrogels, in order to probe the complete curing of the hydrogels.

3.5. Colorimetry

Color measurements were carried out using a Konica-Minolta spectro-colorimeter, model CM700d. It was equipped with an integrating sphere, d/8° measurement geometry,and worked in the 400–700 nm spectral range with a 10 nm acquisition step. The light source and detector were, respectively, a pulsed xenon lamp with a UV cut filter and a silicon photodiode array. The instrument was provided with its own white reference (100% reflective) and a zero-calibration box (0% reference). Color measurements were acquired using D65 illuminant, a 10° supplementary standard observer, and excluded thespecular component of light. The data reported were based on an average of three measurements and were calculated for the CIE L*a*b* 1976 color space. For each measurement, the spectro-colorimeter was positioned in exactly the same spot (∅ 8 mm) for each sample. Color differences, Δ(L*a*b*) and ΔE [46], were calculated on average values.

3.6. Scanning Electron Microscope

Scanning electron microscope (SEM) pictures were acquired using a IGMA (Carl Zeiss Microscopy GmbH, München, Germany) scanning electron microscope with an acceleration potential of 5 kV. Acrylic paint film mock-ups were gold-metalized using an Agar Scientific auto sputter coater.

4. Results and Discussion

4.1. Characterization of UV-Cured Hydrogels

Eight different hydrogels were synthesized by UV-photopolymerization according to the reaction scheme shown in **Figure 1**. By this method, a ready-to-use hydrogel is directly obtained in less than 30 min. As shown in **Table 1**, each hydrogel was named according to the constituent monomers, followed by the pH value of the aqueous part. The UV-curing degree of the hydrogels was characterized by using FTIR-ATR, as shown in **Figure 2-A**, which depicts a typical FTIR-ATR spectrum of a hydrogel. The spectrum shows the distinctive stretch of the ester carbonyl group C=O at 1729 cm^{-1} and the distinctive CO ether stretches at 1096 cm^{-1} associated with the acrylic polymer network. Other bands, corresponding to the CH stretch at 2866 cm^{-1}, CH2 bending stretch at 1450 cm^{-1}, and CH3 bending stretch at 1350 cm^{-1}, were also observed. Interestingly, quantitative monomer polymerization was demonstrated by the disappearance of the characteristic C=C stretch band of the acrylic groups in the fingerprint region at 1640 and 660 cm^{-1}. All in all, the hydrogel formation through the effect of the radical photopolymerization process induced by the UV-curing is confirmed. Next, scanning electron microscopy (SEM) images were taken in order to characterize the surface morphological features of the UV-cured hydrogels. **Figure 2-B** shows one typical image showing a homogeneous smooth surface of a representative HEMA-VP pH 5 hydrogel. All the hydrogels showed similar SEM images, and none of the samples showed relevant morphological features that could affect their cleaning performance.

Gravimetric measurements determined the water retention/release capability of the hydrogel. After gently drying the hydrogel with blotting paper, a fully swollen hydrogelwas weighed and placed in a Petri dish over absorbent paper and covered with a mylard sheet to avoid water evaporation. After 30 min, water release was determined by the weight difference of the hydrogel before and after its application (**Table 2**). The measurements were repeated three times.

It was also necessary to assess the optical characteristics of the hydrogels according to the needs of the art conservators. Therefore, the selected hydrogels were those with the most adequate physical properties (transparency, stickiness, malleability, flexibility) for performing the cleaning. Transparent hydrogels were preferred, since they allow better control of soil removal from the work of art. HEMA_5 and HEMA_6.5 were too opaque, while HEMA_METAC5 and HEMA_METAC6.5 were more rigid and less sticky. On the contrary, both HEMA_VP and HEMA_AMPS gels are more malleable.

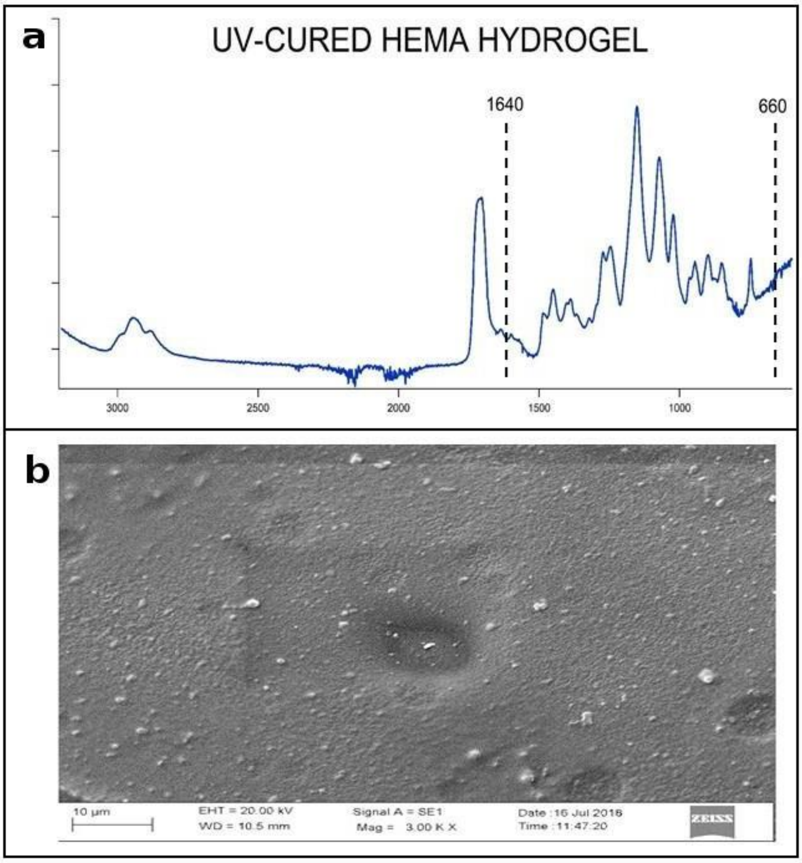

Figure 2 (A) FTIR-ATR spectra of HEMA_5. (B) SEM image of HEMA_5 gel surface.

Name	**gr/cm^2**
HEMA_METAC	0.03
HEMA_AMPS	0.02
HEMA_VP	0.026

Table 2 Gravimetric results of water release from UV-cured hydrogels.

The mechanical properties of the hydrogels were analyzed by tensile tests and dynamic mechanical analysis (DMA) tests. In **Figure 3-A and B**, the results of controlled tensionversus elongation of the hydrogels prepared in buffers 5 and 6.5 can be observed. At pH 5, the hydrogels based on poly(HEMA) homopolymer show maximum elongation at a break of around 50%. The hydrogels based on the HEMA, including other comonomers such as VP, METAC and AMPS, show higher elongation at break values between 200% and 400% but are shorter. A similar trend is observed for the hydrogels prepared with a buffer of a pH of 6.5. In addition, DMA tests were carried out to study the behavior of these hydrogels against a frequency sweep (**Figure 3-C and D**). The storage modulus (E) of thehydrogels synthesized with both buffers showed values between 1E10^{9} and 1E10^{10} Pa at 1Hz of frequency, high values that allow hydrogels to be considered as rigid materials. These results, together with the tensile tests, are indicative that these hydrogels are soft, elastic and ductile materials with sufficient rigidity to be used with little need for care.

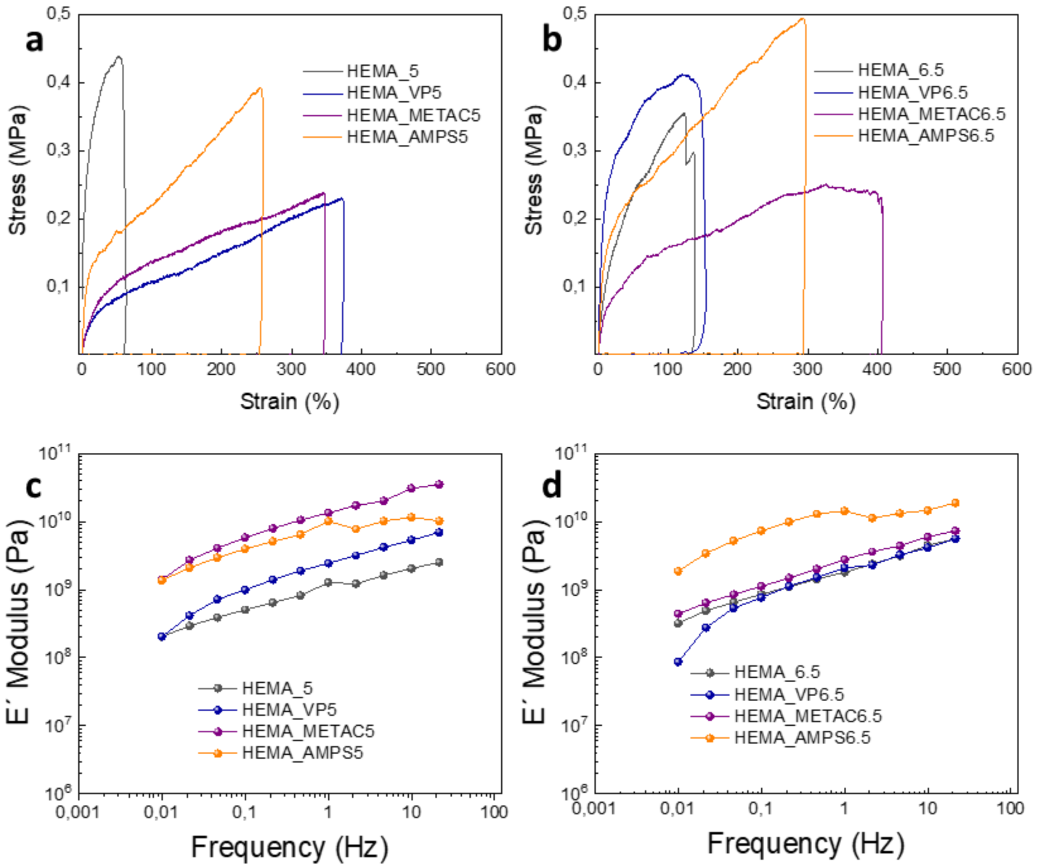

Figure 3 Tensile test (A, B) and dynamic mechanical analysis (DMA) (C, D), employing the hydrogelsprepared with buffer pH 5 and buffer pH 6.5.

4.2. Application and Maintenance of the Hydrogels

UV-cured hydrogels can be applied both dry (directly after synthesis) or loaded (after 24-hour immersion in a water-based cleaning solution). If the gel is used water-loaded, itis recommended to blot the gel with absorbent paper before application in order to remove the excess liquid.

The swelling capability of the hydrogels and their water uptake depends on their chemical composition. After 24-hour immersion in water, HEMA hydrogels showed 0% water uptake, HEMA-VP at 11%, HEMA-METAC at 43% and HEMA-AMPS up to 52%, respectively.

Gels can be manipulated using tweezers and the conservator's own hands, always with clean gloves. For the application, place the gel on the surface that needs to be cleaned and apply a little pressure to enhance the adhesion between the gel and the surface. A plastic film can be placed over the gel to reduce the evaporation of water during the cleaning process.

Gels should be stored, whether dry or immersed in water, in closed containers. Theycan be kept in dark conditions at room temperature for several months after the synthesis.It is advisable to check gels after a long storage time, in order to verify that no alteration has occurred.

4.3. Cleaning Efficiency of UV-Cured Hydrogels

All the hydrogel formulations described in **Table 1** were tested in order to assess the cleaning performance when applying the hydrogels on artificially soiled mock-ups. Cleaning tests were carried out by direct application of the UV-cured hydrogels onto the soiled paint layers for 20 s. Application time can be adjusted according to the specific needs of the surface. Good mechanical properties allow easy handling and it is worth noting that they can be directly applied to the surface of the painting. UV-cured hydrogelswere used as prepared, without the need for any additional loading of buffered aqueous solutions, thus reducing the water content.

SEM images were taken before and after cleaning of the soiled surfaces for comparison with the cleaned areas. The most representative images of the resulting surfaces after cleaning are shown in **Figure 4-A**. Cleaning with HEMA_VP5, HEMA_VP6.5, HEMA_AMPS5 and HEMA_AMPS6.5 gels showed the best results regarding efficient soil removal, not wetting the surface and inducing no color change of the surface. As shown in **Figure 4-E**, hydrogels with the best cleaning capability were also those that showed the best optical performance. According to UNE EN 15886:2011, the ΔE* value should be below 2 (red line in **Figure 5**) for the color variation to not be perceptible to the human eye.

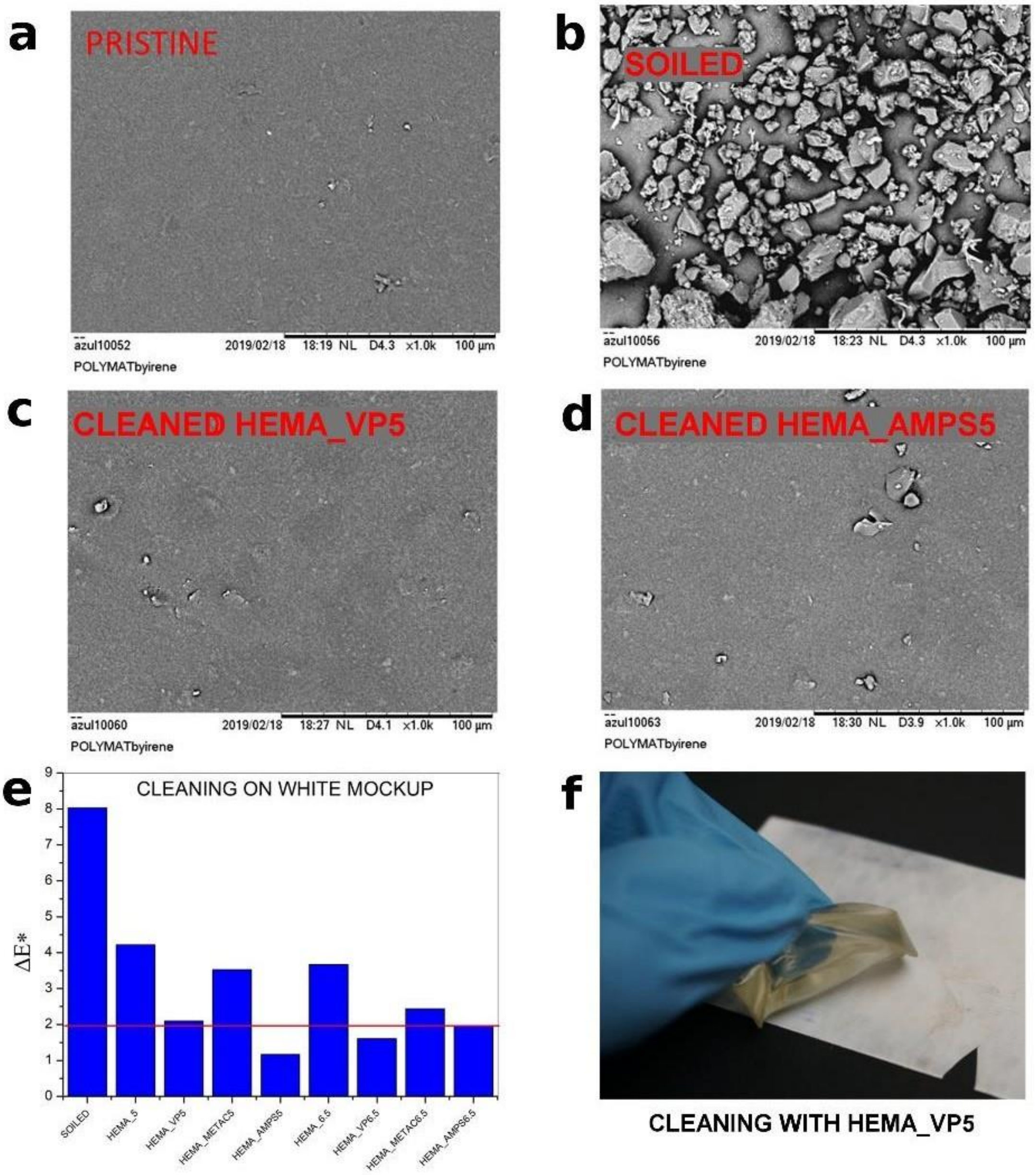

Figure 4 (A–D) SEM images before and after cleaning of white Liquitex mock-ups using HEMA_VP5.0 and HEMA_AMPS5.0 gels. (E) Colorimetry results before and after cleaning using the studied gel formulations. The red line represents ΔE* limit

for visual color-change perception. (F) Cleaning with HEMA_VP5.0 on white mock-up.

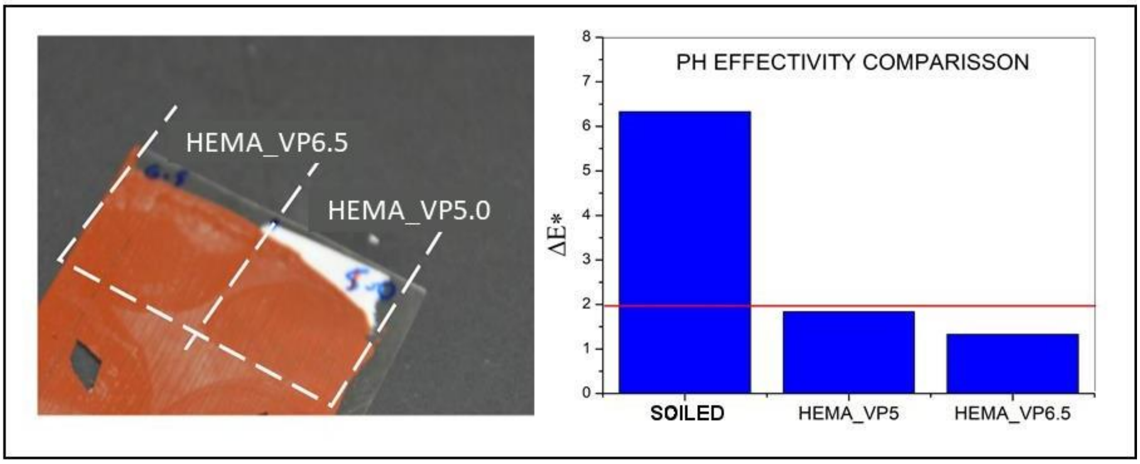

Figure 5 Cleaning test with HEMA_VP6.5 and HEMA_VP5.0 (left). Colorimetry results for soiled and cleaned surfaceswith HEMA_VP5.0 and HEMA_VP 6.5 gels.

4.4. Testing the Cleaning Efficiency According to pH

To check the effect of the pH on the cleaning efficiency [6], hydrogel formulations were cured by using two different pH-adjusted water solutions, with pHs at the upper and lower security range for acrylic emulsion paints (pH 5 and pH 6.5) [6,18]). Accordingto previous works, gels with higher pH were expected to perform a deeper albeit more aggressive cleaning [27,29]. However, as shown in **Figure 5**, no significant differences were observed. The cleaning results for HEMA_VP gels are shown in **Figure 5**, which are consistent for all the formulations. Macroscopic results showed a similar cleaning efficiency for both pH values, supported by colorimetry data. Thus, pH 5.0 hydrogels were chosen since they achieved good cleaning results while maintaining the system in lower (safer) values of pH.

4.5. Agar Gels vs. UV-Cured Hydrogels

The cleaning performance of UV-cured hydrogels was compared with a reference agar hydrogel loaded with a pH 5.0 buffered aqueous solution.

The agar hydrogel was prepared in a 3% aqueous buffer solution, as described elsewhere [47]. Agar gel is very popular among conservators since it is easy to prepare out of laboratory conditions, which is more attractive for users. However, the higher water absorption and the syneresis property [48] of agar gels led to a less controllable release of liquid that remains on the surface after removing the gel (see **Figure 5**) [40]. This carries several drawbacks for water-sensitive paints [49]. In contrast, UV-cured hydrogels have proven to be highly retentive,allowing the controlled action of the aqueous solutions even on highly sensitive substrates. The water release capacity of both UV-cured hydrogels and agar gels was measured gravimetrically, for comparison. Fully swollen gels were placed on a Petri dishover absorbent paper and covered with a mylar sheet to avoid water evaporation. After 30 min, water release was determined by weighing the filter paper before and after the application. The measurements were repeated three times.

The water release rate of the UV-cured hydrogel and of the agar gel is reported in **Table 3**. The excess wetting of the surface when using agar is evidenced by the water remaining on the surface together with the gravimetric results.

As shown in **Figure 6**, UV-cured hydrogels were able to achieve effective cleaning without wetting the surface. Colorimetry results showed that soiling removal when usingUV-cured gels was even more efficient after surface water evaporation.

gr/cm^2	
HEMA_VP	0.006
AGAR	0.036

Table 3 Gravimetric results of water release of UV-cured hydrogels and agar-agar gels.

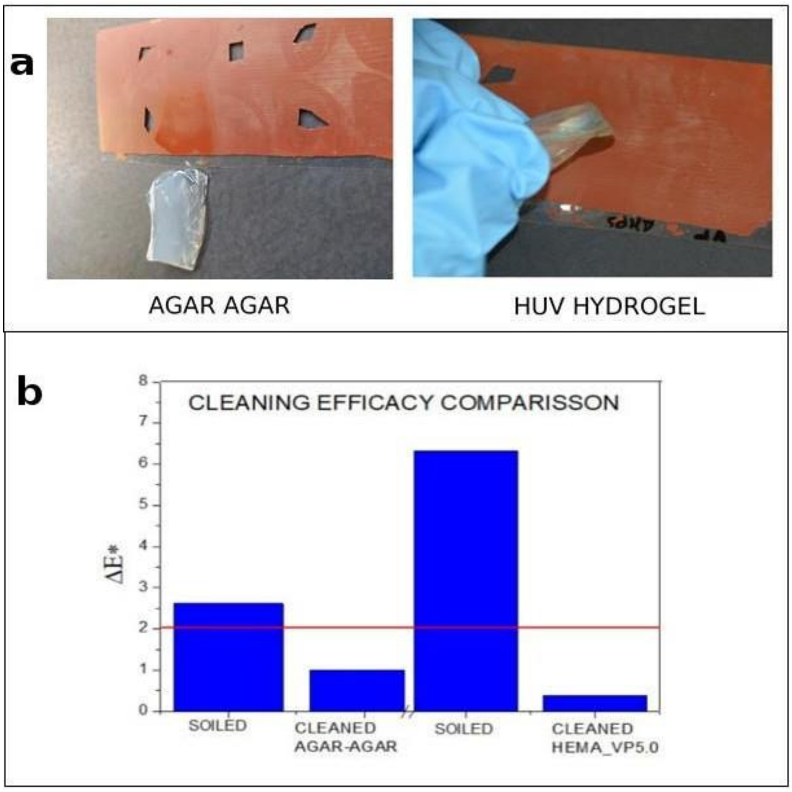

Figure 6 (A) Cleaning with ph 5.0 buffer confined in agar agar (left), cleaning with HEMA_VP5.0 (right). (B) Comparison of colorimetry results before and after cleaning with pH 5.0 agar-agar andUV-cured gels.

4.6. Gel Working Life/Number of Uses

The number of effective applications using the same hydrogel has been explored so as to determine its working life. We selected the HEMA_VP5 hydrogel for this test, sinceit showed the best cleaning performance. The same side of the hydrogel was applied several times on the artificially soiled paint mock-up. As shown in **Figure 7**, as the numberof uses increases, the dirt removal is less effective. However, even after six applications without a washing step between applications, the result remains acceptable, as can be observed on the colorimetry plot. **Figure 7-B** shows how the hydrogel maintains its effectiveness after the sixth use, since ΔE* remains below two. This shows that the hydrogel is capable of removing dirt several times without needing rinsing. Obviously, the number of uses could vary depending on the type and amount of dirt present on the surface.

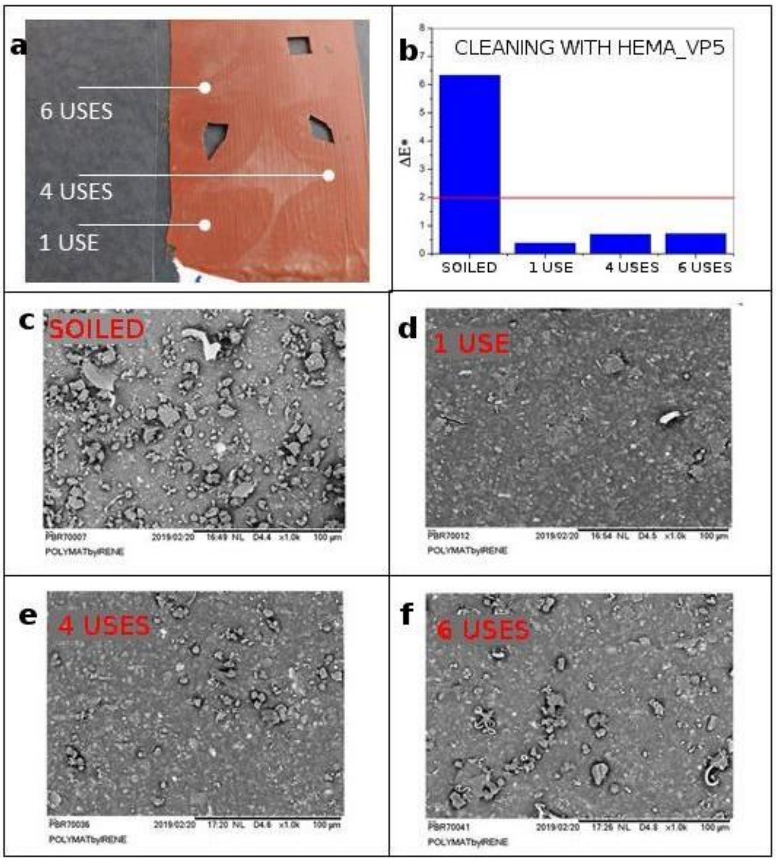

Figure 7 (A) Cleaning results after 1, 4 and 6 uses of the same HEMA_VP5.0 gel. (B) Colorimetry results of the cleaning after several uses. (C–F) SEM images of the surface before and after cleaning with gels that have been repeatedly used.

5. Discussion and Conclusions

In this article, we report a new family of easy-to-make UV-cured hydrogels for dry cleaning on water-sensitive paints. The hydrogels show good performance as efficient and safe cleaning tools for water-sensitive paint surfaces. The main advantage of the hydrogels presented here is that they are easy to make and they only need a UV lamp to prepare them. They could therefore trigger the incorporation of chemical gels in the daily practice of the art conservator–restorer. A wide range of formulations was tested, from which acrylic hydrogels based on HEMA-VP and HEMA-AMPS monomers were selected since they proved to be more adequate for the requirements posed by the conservation field. Their performance is similar to that of other chemical gels proposed before, with the advantage of not needing a complex laboratory process to create them.

Interestingly, UV hydrogels did not present wet residue problems after cleaning, and the pH of choice did not seem to affect the cleaning performance. In addition, water release is under control due to the good retaining properties of the hydrogel, which showed a reduction of moistening compared to other commonly used easy-to-make gels. Moreover, no extra aqueous solution needs to be loaded in order to achieve good cleaning efficiency. In conclusion, these hydrogels are very easy to make, are tunable, and they provide conservators with an optimal and comfortable cleaning system, thus contributing to the wide use of chemical hydrogels among conservators.

References

1. L. Meabe, T.V. Huynh, D. Mantione, L. Porarelli, C. Li, L. A. O'Dell, H. Sardon, M Armand, M. Forsyth, D. Mecerreyes, UV-cross linked poly(ethylene oxide carbonate) as free standing solid polymer electrolyte for lithium batteries, Electrochim. Acta. 302 (2019) 414–421.
2. C. Proctor, C. Y. Chan, L. Porcarelli, E. Udabe, A. Sanchez, I. del Agua, D. Mecerreyes, G. Malliaras, Ionic Hydrogel for accelerated dopamine delivery via retrodialysis, Chem. Mater. 31, 17 (2019) 7080–7084.
3. I. Del Agua, L. Porcarelli, V.F. Curto, A. Sanchez, E. Ismailova, G. Malliaras, D. Mecerreyes, A Na conducting hydrogel for protection of organic electrochemical transitors, J. Mater. Chem. B. 6 (2018) 2901–2906.
4. A. Gallastegui, L. Porcarelli, R.E. Palacios, M.L. Gómez, D. Mecerreyes, Catechol-Containing acrylic poly (ionic Liquid) hy- drogels and bioinspired filters for water decontamination, Appl. Polym. Mater. 1 (2019) 1887–1895.
5. N. Bonelli, G. Poggi, D. Chelazzi, R. Giorgi, P. Baglioni, P. Poly (vinyl alcohol)/poly (vinyl pyrrolidone) Hydorgels for the Clean- ing of Art, J. Colloid Interface Sci. 536 (2019) 339–348.
6. C. Stavroudis, T. Doherty, The Modular Cleaning Porgram in Practice: Application to Acrylic Paintings. Smithson. Contrib. Mus. Conserv. 3, (2013) 139–145.
7. J.R. Druzik, G.R. Cass, A new look at soiling of contemporary painting by soot in art museums, in: Presentation Abstracts and Additional Notes, Proceedings of the Third Indoor Air Quality Meeting, Oxford Brookes University, Oxford, UK, 10–12 July 2000, Ryhl- Svendsen, M., Ed, IAQ Working Group, Oxford Brookes University, Oxford, UK, 2000.
8. J. Crook, T. Learner, The Impact of Modern Paints; Tate Gallery Publishing Ltd.: London, UK, 2000.
9. F.N. Jones, W. Mao, P.D. Ziemer, F. Xiao, J. Hayes, M. Golden, Artist paints—An overview and preliminary studies of dura- bility. Prog. Org. Coat. 52 (2005) 9–20.
10. I. Cardaba, M.I. Maguregui, Estudio de limpiezas aplicadas a pinturas de emulsión acrílica sobre soporte poroso y no poroso, in: Emerge 2014, Valencia, Spain, 22–24 September 2014, Proceedings, 2014: pp. 117–124.
11. E. Jablonski, T. Learner, J. Hayes, M. Golden, Conservation concerns for acrylic emulsion paints, Stud. Conserv, 48 (2003) 3–12.

12. S. Zumbühl, F. Attanasio, N.C. Scherrer, W. Müller, N. Fenners, W. Caseri, Solvent action on dispersion paint systems and the influence on the morphology: Changes and destruction of the latex microstructure, in: T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007: pp. 257–268.
13. B. Ormsby, T. Learner, G.M. Foster, J. Druzik, M. Schilling, Wet-cleaning acrylic emulsion paint films: An evaluation of physical, chemical and optical change, in: T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: proceedings from the modern paints uncovered symposium. Getty Conservation Institute, 2007: pp. 189–200.
14. B. Ormsby, T. Learner, The effects of wet surface cleaning treatments on acrylic emulsion artists' paints—A review of recent scientific research, Stud. Conserv, 54 (2009) 29–41.
15. P. Baglioni, D. Chelazzi, R. Giorgi, Nanotechnologies in the Conservation of Cultural Heritage, Springer, Dordrecht, The Netherlands, 2015.
16. T. Fardi, V. Pintus, E. Kampasakali, E. Pavlidou, K. Papaspyropoulos, M. Schereiner, G. Kyriacou, A novel methodological approach for the assessment of surface cleaning of acrylic emulsion paints, Microchem. J. 141 (2018) 25–39.
17. I. Cardaba, G. Poggi, M. Baglioni, D. Chelazzi, M.I. Maguregui, R. Giorgi, Assessment of aqueous cleaning of acrylic paints using innovative cryogels, Microchem. J. 152 (2020) 104311.
18. A. Solbes-García, J.M. Miranda-Vidales, A. Nieto-Villena, L. Salvador Hernandez, L. Narváez, Evaluation of the oxalic and tartaric acids as an alternative to citric acid in aqueous cleaning systems for the conservation of contemporary acrylic paintings. J. Cult. Herit. 25 (2017) 127–134.
19. I. Ziraldo, K. Watts, A. Luk, A. Lagalante, R.C. Wolbers, The influence of temperature and humidity on swelling and surfactant migration in acrylic emulsion paint films, Stud. Conserv. 61 (2016) 209–221.
20. B.A. Ormsby, T. Learner, The effects of surface cleaning on acrylic emulsion paintings—A Preliminary Investigation. Tate Pap. 6 (2006) 135–149.
21. B. Ormsby, E. Kampasakali, C. Miliani, T. Learner, An FTIR-based exploration of the effects of wet cleaning treatments on artists' acrylic emulsion paint films, e-Preserv. Sci. 6 (2009) 186–195.
22. T. Learner, P. Smithen, J. Krueger, M. Schilling, Modern Paints Uncovered;

Getty Conservation Institute: Los Angeles, CA, USA, 2007.

23. B. Ormsby, P. Smithen, F. Hoogland, T. Learner, C. Miliani, A scientific evaluation of surface cleaning acrylic emulsion paintings, in: Proceedings of the 15th Triennial Conference, New Delhi, India, 22–26 September 2008, Bridgland, J., Eds., ICOM Committee for Conservation: Paris, France, 2008: pp. 865–873.
24. B. Ormsby, A. Soldano, M.H. Keefe, A. Phenix, T. Learner, An empirical evaluation of a range of cleaning agents for removing dirt from artists' acrylic emulsion paints removing, AIC Paint. Spec. Gr. Postprints. 23 (2010) 77–87.
25. E.A. Willneff, B.A. Ormsby, J.S. Stevens, C. Jaye, D.A. Fischer, S.L.M. Schroeder, Conservation of artists' acrylic emulsion paints: XPS, NEXAFS and ATR-FTIR studies of wet cleaning methods, Surf. Interface Anal. 46 (2014) 776–780.
26. M.T. Doménech-Cargbó, M.F. Silva, E. Aura-Castro, A. Doménech-Carbó, L. Fuster-López, J.V. Gimeno-Adelantado, Multitechnique approach to evaluate cleaning treatments for acrylic and polyvinyl acetate paints, in: New Insights into the Cleaning of Paintings, Proceedings of the 2010 Cleaning International Conference, Universidad Politecnica de Valencia and Museum Conservation Institute, Washington, DC, USA, 2013, Smithsonian Institution: Washington, DC, USA, 2013: pp. 125–134.
27. E. Kampasakali, B. Ormsby, A. Cosentino, C. Miliani, T. Learner, A preliminary evaluation of the surfaces of acrylic emulsion paint films and the effects of wet cleaning treatment by atomic force microscopy (AFM), Stud. Conserv. 56 (2011) 216–230.
28. R. Wolbers, A. Norbutus, A. Lagalante, Cleaning of Acrylic Emulsion Paints: Preliminary Extractive Studies with Two Commercial Paint Systems, Smithson. Contrib. Mus. Conserv. 3 (2012) 147–157.
29. C.E. Dillon, A. Lagante, R.C. Wolbers, Acrylic emulsion paint films: The effect of solution pH, conductivity, and ionic strength on film swelling and surfactant removal, Stud. Conserv. 59 (2014) 52–62.
30. L.M. Tiedemann, A.J. Kunov-Kruse, Surface cleaning acrylic emulsion paints: Evaluating conductivity adjusted aqueous solutions, in: CESMAR7—Colour and Conservation, Milan, Italy, 13–14 November 2015, proceedings, 2015; pp. 169–175.
31. T. Learner, Analysis of Modern Paints, The Getty Conservation Institute: Los Angeles, CA, USA, 2004.

32. C. Murray, C. de Berenfeld, S. Chang, E. Jablonski, T. Klein, M.C. Riggs, The Condition and Cleaning of Acrylic Emulsion Paintings, Mater. Res. Soc. Proc. 712 (2002) 83–90.
33. C. Stavroudis, Gels: Evolution in practice, in: Gels in Conservation of Cultural Heritage, London, UK, 6–18 October 2017, proceedings, 2017: pp. 209–217.
34. D, Kronkright, Review of Solvent gels for the cleaning of works of art: The residue question and Cleaning painted surfaces: Aqueous methods, J. Am. Inst. Conserv. 48 (2009) 83–96.
35. J. Domingues, N. Bonelli, R. Giorgi, E. Fratini, Innovative method for the cleaning of water sensitive artifacts: Synthesis and application of highly retentive chemical hydrogels, Int. J. Conserv. Sci. 4 (2013) 715–722.
36. N. Bonelli, D. Chelazzi, M. Baglioni, R. Giorgi, P. Baglioni, Confined Aqueous Media for the Cleaning of Cultural Heritage: Innovative Gels and Amphiphile-Based Nanofluids, in: Nanoscience and Cultural Heritage; Springer: Berlin, Germany, 2016: pp. 238–311.
37. L.V. Angelova, E. Carretti, B.H. Berrie, R.G. Weiss, Poly (vinyl alcohol)-borax "gels": A flexible cleaning option, in: Gels in the Conservation of Art, Archetype Publication: London, UK, 2017: pp. 231–236.
38. A. Sansonetti, M. Bertasa, C.. Canevali, A. Rabbolini, M. Anzani, D. Scalarone, A review in using agar gels for cleaning art surfaces, J. Cult. Herit. 44 (2020) 285–296.
39. J. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, Innovative Hydrogels Based on Semi-Interpenetrating p(HEMA)/PVP Networks for the Cleaning of Water-Sensitive Cultural Heritage Artifacts, Am. Chem. Soc. 29 (2013) 2746–2755.
40. L. V. Angelova, B. Ormsby, E. Richardson, Diffusion of water from a range of conservation treatment gels into paint films studied by unilateral NMR. Part I: Acrylic emulsion paint, Microchem. J. 124 (2016) 311–320.
41. L.V. Angelova, B. Ormsby, J. Townsend, R. Wolbers, Gels in the Conservation of Art; Archetype: London, UK, 2017.
42. E. Carretti, S. Grassi, M. Cossalter, I. Natali, G. Caminati, R.G. Weiss, P. Baglioni, L. Dei, Poly(vinyl alcohol)–borate hy- dro/cosolvent gels: Viscoelastic properties, solubilizing power, and application to art conservation, Langmuir. 25 (2009) 8656– 8662.
43. L.V. Angelova, B.H. Berrie, A. Ghetaldi, R. Weiss, Partially hydrolysed poly(vinyl acetate)borax-based gel-like materials for conservation of art:

Characterization and application, Stud. Conserv. 60 (2015) 227–244.

44. R. Mastrangelo, C. Montis, N. Bonelli, P. Tempesti, P. Baglioni, Surface clening of artworks: Structure and dynamics of nanostructured fluids confined in polymeric hydrogel networks, Phys. Chem. Chem. Phys. 19 (2017) 23762–23772.
45. C. Stravoudis, MCP Receips, Technical Notes, in: Cleaning of Acrylic Painted Surfaces, Washington, DC, USA, 30 April–3 May 2013, proceedings, 2013.
46. Asociación Española de Normalización y Certificación. UNE EN 15886:2011, Conservación del Patrimonio Cultural. Métodos de Ensayo. Medición del Color de Superficies; AENOR: Madrid, Spain, 2011.
47. P. Cremonesi, A. Casoli, Thermo-reversible rigid agar hydrogels: Their properties and action in cleaning, in: Gels in the Conservation of Art; Archetype Publication: London, UK, 2017: pp.19–28.
48. S. Boral, A. Saxena, H. B. Bohidar, Syneresis in Agar hydrogels, Int. J. Biol. Macromol. 46 (2010) 232–236.
49. A. Mateescu, S. Freese, P. Frank, U. Jonas, C. Theodorakopoulos, Novel surface-attached gels from photocrosslinkable poly- acrylamides for the cleaning of works of art, in: Gels in Conservation of Art; Archetype Publication: London, UK, 2017: pp. 237– 244.

Chapter 6.

GENERAL DISCUSSION AND PROSPECTS

1. General discussion

Several investigations [1-34] focus on searching for safer and more effective methods to perform the surface cleaning of water-sensitive paintings such as acrylics and all of them conclude on the difficulty of carrying out treatments in an effective, controlled, safe and easy way for the restorers and the paintings themselves. This research has focused on evaluating the cleaning methods currently in use in the field of conservation and restoration of contemporary artworks, as well as assessing recently incorporated methods. Thus, these cleaning methods have been assessed by applying them onto different acrylic paint brands and colours, and their effects have been carefully followed up by using a wide variety of analytical techniques.

In order to carry out this study, aqueous cleaning was selected as the reference cleaning method throughout the practical work, since it is so far the most effective system for dirt removal from acrylic surfaces [3]. Likewise, different application methods were also studied and compared, analysing their pros and cons, in order to achieve more adequate and controlled treatments. In this way, the evaluation focused on optimizing the aqueous cleaning methods by testing different application systems.

The first step in the practical study was to deepen the characterization of different acrylic brands and colours, in order to cover as many variants as possible and obtain representative results from the application of the tested cleaning treatments. Furthermore, the characterization intends to favour the understanding of the different acrylic paint formulations and colours by drawing conclusions on their behaviour to each applied cleaning method. In this regard Chapter 3 focuses on studying a single brand of acrylics, Liquitex, which is widely studied due to its success among international artists. Chapter 4 extends the study to Titan and Hyplar acrylics. The former because it is a common brand among Spanish artists and the latter because despite not being on the market any longer, it was widely used by international artists of a previous generation, and its composition corresponds to the first acrylic emulsion type formulations. Focused on identifying the paint's composition, Chapter 3 and 4 deal with the results of Py-GC-MS and ATR-FTIR analyses for the characterization of the studied mock-ups, revealing the composition of the binder, pigments and other additives such as dispersants, thus providing the necessary knowledge about the acrylic films prior to the application of the cleaning procedures. In this sense, EA/MMA binder was identified in Hyplar acrylic paints and nBA/MMA binder in Titan and Liquitex acrylic paints. Organic phtalocyanine green pigment was identified in all three brands, as well as the inorganic ultramarine blue colour. Inorganic cadmium red was identified in Liquitex and Titan acrylic paint mockups, while an organic naphtol red pigment was detected on Hyplar samples. FTIR spectra revealed the presence of non-ionic alkylphenol ethoxylate surfactants in the three brands and different colours. Moreover, in Liquitex inorganic colour mockups the presence of sodium polyacrylate was identified, which acts as pigment dispersant. This analytical information allows us to interpret the subsequent cleaning results, being able to ascribe certain phenomena to the characteristics of the composition of the paints.

Chapter 4 also deepens in the characterization of the paint films by means of thermogravimetric analysis, revealing substantial differences ascribed to composition issues, such as the different percentage of inorganic and organic materials between brands and colours. The main result pointed out that the Titan brand green colour and the Hyplar brand red colour, show a greater amount of organic components (pigments, additives, binder) than the rest of organic paint mockups. As expected, the amount of organic compounds detected on inorganic pigmented paints is lower. However, differences have also been discovered within them and in general terms, the Titan brand paints comprise a greater amount of organic additives than the other brands.

Different ageing tendencies have also been observed between brands, linked to the different composition of the paints. Titan paint shows an earlier tendency for surfactant migration to the surface compared to Hyplar acrylics. This has been verified in both naturally aged samples and those subjected to accelerated ageing. This indicates that Titan brand paints may have a greater and earlier tendency to trap dirt on their surface and are potentially more susceptible to aqueous cleaning treatment and surfactant extraction.

Once the acrylic paints were characterised, the second step focused on assessing the effect of the cleaning methods on the physical and chemical behaviour of the studied acrylic surfaces.

The results obtained from the assessment of the different cleaning methods are the core of this Thesis. Cleaning tests on various paint samples have shown that the method of application is crucial to achieve an efficient treatment, completely discarding siliconized systems due to residue problems. In this regard even the most sophisticated and fine-tuned methods such as rigid hydrogels are not capable of actually cleaning the acrylic surface in a completely harmless way.

Therefore, chapter 3 focuses on analysing the effect of the application methods on the cleaning results. Several cleaning solutions were applied on the pictorial layers by using cotton swabs, confined in a PVA cryogel and emulsified with Velvesil Plus.

Cotton swab cleaning has been used as the reference method because it is the most widely documented method in the field of cleaning, both because of its ease of use and because cotton swab cleaning is the most accessible method for restorers. Convenience of use and affordability are paramount for restorers when choosing an application method, therefore they are essential aspects to take into account when carrying out the practical assessment. Despite its widespread use, both Chapters 3 and 4 demonstrate that swab cleaning is the most aggressive method for the pictorial film due to its mechanical action together with the impossibility of controlling water release. On the other hand, PVA cryogels, commercially called Nanorestore gels®, have been studied as an alternative to the use of swabs and physical gels, less able to control water release. Moreover, unlike physical gels, cryogels are safe of leaving gel residues after application on the pictorial surface and in this case the rinse is only necessary to remove possible residues from the cleaning agents contained in the solution confined in the gel. The results reported in chapters 3 show that this method is sufficiently effective for removing dirt while controlling the release of the aqueous cleaning solutions. Nevertheless, as described on chapter 4, some brands and colours, such as Titan blue and Hyplar red samples, are still susceptible to the humidity degree provided by these gels, proven by the chain scission of the polymer that could be detected by means of TGA analysis. These cases would need further attention and new improved methods for better moisture release control. On the other hand, non-polar emulsifying particles (Velvesil Plus) were also tested for comparison, since they are a relatively new and widely used method for the treatment of water-sensitive works in the restoration field. This method proved to be inadequate given the amount of residue left on the surface after its application. Therefore, in Chapter 4 only PVA cryogels and cotton swabbing were further tested.

The effect of these treatments were evaluated in the short and mid-terms. In this regard, one of the main effects studied within this work was the extraction of surfactants from the paint films. While swab cleaning seems to induce partial or total removal of surfactants from the surfaces in all cases, cryogels do not alter the original composition of the Liquitex paint layers. This was not the case for Hyplar paints, where cryogels removed nearly the whole surfactant content from the surface after application. Moreover, gel cleaning also caused instant changes in the amount of surfactants on the surface of the inorganic blue and red Titan mock-ups. This was not the case for the organic colour samples, where surfactants were still detectable after cleaning with cryogel. However, the analysis of these later surfaces one week after the treatment showed the absence of surfactants, suggesting that also in these cases, the treatment may affect the behaviour of the paint components in the mid-term. Therefore, although gel cleaning provides better moisture control than swab-rolling, cryogels can cause either the complete removal of surfactant type additives or trigger the resorption of the remaining additives into the bulk of some films within the following days after applying the cleaning treatment.

Overall, the surface of Hyplar mockups proved to be very sensitive to moisture. Additives showed a later migration tendency but both swab and cryogel cleaning removed surfactants from the surfaces regardless of the colour. In this case, however, ATR-FTIR analysis of the samples one week after the treatment showed the reappearance of additives on the surface of the organic paint mockups.

In general, in all the studied brands, the organic colours showed higher additive migration and desorption as a result of aqueous cleaning treatments, regardless of the method used. However, in general terms, it was demonstrated that despite not being innocuous, the effect of the cleaning treatment on the migration of additives can be better controlled by means of cryogel than by using cotton swabs. Thus, the effect of cleaning treatments depend, to a great degree, on the brand and colours on which they are applied.

Chapter 3 and 4 also assess the pigment removal effect in relation to the application of different cleaning methods. In all the cases, the mechanical action of the swab-rolling causes the extraction of colour to a greater or lesser extent. As expected, analysis confirmed that, in general terms, Hyplar acrylic paint brand colours as well as the organic colours of any other brand are more sensitive to colour removal.

Microscopy analysis techniques, SEM and AFM, revealed roughness changes caused by the different cleaning methods. Swab-rolling is the most damaging method in terms of roughness changes due to the mechanical action itself. The change in surface roughness caused by the application of either of the two methods, gel or swab, is in general, greater in the paint samples belonging to the Titan brand. As far as pigment origin is concerned, the greatest changes in roughness are observed on the inorganic colours. These results are consistent with the surface surfactant extraction already described for Titan inorganic paints.

Thermogravimetric analysis helps assessing the alterations caused by the cleaning procedures inside the bulk of the paint film. After swab cleaning, the polymer chain degrades causing the scission of PAA monomers, triggering the decrease of the temperatures of the maximum degradation rate of the co-polymers. This alteration is detected mainly in Titan acrylic paint mockups, leading to think that Titan binder is less stable than Hyplar binder. This result is consistent with our previous study where we demonstrated by means of an accelerated ageing that the binder of Titan acrylic mockups degrades faster than the Hyplar one. However, if we compare these results with the surface analysis results, we can conclude that the samples that undergo the greatest changes in the bulk of the film, are not always those that show the greatest alterations at surface level. Therefore, the monitoring of the treated surfaces may be insufficient since it does not always give reliable results in terms of side-effects.

Cleaning effectiveness was also evaluated by means of SEM and AFM microscopy. AFM results showed that a complete cleaning could be achieved with cotton swabs, but a more energetic mechanical action was needed, which would eventually lead to severe damages on the delicate paint film surface. Alteration of the surface morphology was induced even in the mildest conditions, where only a gentle rolling over the surface would be carried out, trying to avoid scratches or any mechanical stress on the paint layer. SEM images in chapter 3 depict how cotton swabs can partially remove soil particles, while with cryogel cleaning, the surface almost recovers its original aspect. These results are consistent with those obtained by means of AFM.

Residues left after applying the cleaning treatment were mainly evaluated by FTIR-ATR analysis, which confirmed that no gel residues were left on the surface after cryogel application. On the contrary, much silicone residue was detected after cleaning with Velvesil Plus. 2D -FTIR mapping results confirmed the presence of siloxane compounds all over the analysed surfaces after cleaning treatment with Velvesil Plus. On the other hand, none of the gel methods tested on chapters 3, 4 and 5 posed residue problems. PVA cryogels left no residue on the surface after cleaning thanks to their intra-network cohesion forces, which are strong enough to grant no polymer deposition on the treated surface after the application. Nevertheless, although PVA cryogel method does not show residue problems, and has proven to provide a good aqueous retention capacity, it has also shown that in certain cases this retention is not sufficient to perform a safe cleaning, such as in Hyplar organic and Titan inorganic colour mockups.

Finally, Chapter 5 focuses on the study of the application of non-preformed rigid gels, such as agar-agar, and develops a new type of easy to make hydrogel adapted to the needs of the field: respectful for the paint film, controllable, tuneable, and easy to make. The development of this new gel prototype, synthesised by means of ultraviolet radiation, is the major outcome of this thesis since it has opened the way to a new type of easy to make gels, fast and tuneable according to the specific needs of each surface and with a better control of water release. The development of this gel was designed according to the needs and conclusions obtained from testing other methods. The aim of this proposal was to introduce an easy to prepare method, tuneable and affordable for restores. Mechanical properties of the copolymers conforming the gel were studied by means of DMA analysis that revealed both the sufficient rigidity of the product and the good elongation capability of around 200-400%. Gravimetric results revealed that water release with UV-cured hydrogels was much better controlled than with either Agar or cryogel application.

Agar, a commonly used and easy-to-make gel system has shown several drawbacks in terms of water retention capability, showing a water release of twice the number of gr/cm^2 than UV-cured hydrogels. Moreover, according to the results of these initial studies, UV cured hydrogels also show an efficient and safe cleaning performance, being HEMA-VP and HEMA_AMPS the cleaning methods that revealed the most successful performance. The useful lifetime was limited to six applications, while maintaining the efficacy in removing dirt. The possibility of tuning all the components of the hydrogel, starting from the monomers to the additives, provides an easy way to tailor its characteristics, expanding the possibilities for the restorers, who will be able to adapt the method to each concrete case, refining to the maximum the properties of the gel.

2. Prospects

- The effect of the cleaning treatments can change significantly depending on several variables, such as the condition of the paint films, their age and most of all their composition, which depends on the brand or even the origin of the pigment itself. Therefore, it is safe to say that it is no possible to establish an optimal common cleaning system for all the acrylic brands and colours and although cryogels show more efficient cleaning results compared to cotton swab, a slight sensitivity was observed in certain acrylic paint surfaces, such as those of Titan inorganic colours, which showed higher sensitivity in terms of surfactant removal. These aspects need further research in order to find a more accurate treatment strategy for those complex cases.

- With regard to the alterations of the polymer binder, detected by means of thermogravimetric analysis, it would be interesting to deepen the study of the origin of the spectral peak appearing at around 240 - 260°C, which was detected after applying aqueous based cleaning treatments on some mock-ups, regardless of the brand and colour. In this sense, TGA analysis reaffirms the fact that the side-effects of applying water based cleaning treatments on acrylic paint films should be integrally assessed (bulk and surface), since those colours that show biggest chemical surface changes (Titan acrylic mock-ups) do not coincide with those that suffer the most noticeable bulk binder alterations (TI_29 and HY_112). In any case, the results for the moment do not point at any brand or colour dependent clear degradation pattern, so it would be interesting to extend the study in that sense.

- Furthermore, it would be necessary to continue studying in greater depth the effect of non-polar silicone based solvent systems on acrylic paint layers. To date, they are widely accepted as an almost harmless cleaning systems, particularly regarding the use of silicone based solvents such as cyclomethicone, often employed as a barrier between the paint surface and the cleaning solutions, is becoming more and more widespread among conservators and restores as a common practice when tackling the cleaning of water sensitive paint surfaces. However, recent research has shown that these types of solvent systems may also have several drawbacks on certain contemporary paint formulations. Therefore, further research on their effect on acrylic paints would be recommendable.

- Likewise, the most interesting research development prospect would be to continue researching on the application of the UV-cured hydrogels in the field of cleaning of art. To study in depth the effects of the method and to broaden the synthesis variables by including new monomers to formulate the gels, in order to make them suitable for the variety of situations that contemporary paint surfaces exhibit.

References

[1] T. Learner, P. Smithen, J. Krueger, M.R. Schilling, eds., Modern Paints Uncovered: Proceedings from the Modern Paints Uncovered Symposium. Los Angeles: Getty Conservation Institute, 2007.

[2] E. Jablonski, T. Learner, J. Hayes, M. Golden, Conservation concerns for acrylic emulsion paints, Stud. Conserv. 48 (2003) 3–12.

[3] B. Ormsby, T. Learner, The effects of wet surface cleaning treatments on acrylic emulsion artists' paints – a review of recent scientific research, Stud. Conserv. 54 (2009) 29–41.

[4] N. Agarwal, R.J. Farris, Water absorption by acrylic-based latex blend films and its effect on their properties, Journal of Applied Polymer Science. 72: 11 (1999) 1407-1419

[5] R. Ploeger, A. Murray, S. Hesp, D. Scalarone, An investigation of the chemical changes of artists' acrylic paint films when exposed to water, in: Materials issues in art and archaeology VII: symposium held November 30-December 3, 2004, Boston, Massachusetts, U.S.A., 2004: 49-56.

[6] B. Ormsby, O. Lundsbakken, L. Monaco, A. Bartoletti, J. Lee, Revisiting cleaned acrylic emulsion painting surfaces 10 years on: observations and implications: Transcending Boundaries: Integrated Approaches to Conservation, ICOM-CC 19th Triennial Conference Preprints, Beijing, 17–21 May 2021, Paris, International Council of Museums, 2021.

[7] L. Pagnin, R. Wiesinger, A.N. Koyun, M. Schreiner, The Effect of Pollutant Gases on Surfactant Migration in Acrylic Emulsion Films: A Comparative Study and Preliminary Evaluation of Surface Cleaning, Polymers. 13 (2021) 1941.

[8] T. Fardi, V. Pintus, E. Kampasakali, E. Pavlidou, K. Papaspyropoulos, M. Schreiner, G. Kyriacou, A novel methodological approach for the assessment of surface cleaning of acrylic emulsion paints, Microchem J. 141 (2018) 25-39

[9] C. Stavroudis, T. Doherty, R. Wolbers, A new Approach to Cleaning I: Using Mixtures of Concentrated Stock Solutions and a Database to Arrive at an Optimal Aqueous Cleaning System, WAAC Newsletter. 27: 2 (2005) 17-28

[10] C.E. Dillon, A.F. Lagalante, R.C. Wolbers, Acrylic emulsion paint films: The effect of solution pH, conductivity, and ionic strength on film swelling and surfactant removal, Stud. Conserv. 59 (2014) 52–62.

[11] L. M. Tiedemann, A. J. Kunov-Kruse, Surface cleaning acrylic emulsion paints: evaluating conductivity adjusted aqueous solutions, CESMAR7 Colour and Conservation, Proceedings. (2015) 169-175

[12] A. Solbes-Garcia, J. Miranda-Vidales, A. Nieto-Villena, L. Salvador Hernandez, L. Narvaez, Evaluation of the oxalic and tartaric acids as an alternative to citric acid in aqueous cleaning systems for the conservation of contemporary acrylic paintings, JCult Heritage. 25 (2017) 127-134

[13] B. Ormsby, T. Learner, G.M. Foster, J. Druzik, M. Schilling, Wet-cleaning acrylic emulsion paint films: An evaluation of physical, chemical and optical changes, in: Mod. Paint. Uncovered Symp., 2007: pp. 189–200.

[14] B.A. Ormsby, E. Kampasakali, C. Miliani, T. Learner, An FTIR-based exploration of the effects of wet cleaning treatments on artists' acrylic emulsion paint films, E Preserv. Sci. 6 (2009) 186–195.

[15] B. Ormsby, T. Learner, M. Schilling, J. Druzik, Herant Khanjian, D. Carson, G. Foster, M. Sloan, The effects of surface cleaning on Acrylic Emulsion Paintings: A preliminary Investigation, Tate Papers. 6 (2006) www.tate.org.uk/research/tate-papers/06/effects-of-surface-cleaning-on-acrylic-emulsion-painting-preliminary-investigation (accessed April 21, 2023)

[16] B. Ormsby, A. Soldano, M.H. Keefe, A. Phenix, T. Learner, An Empirical Evaluation of a Range of Cleaning Agents for Removing Dirt from

Artists ' Acrylic Emulsion Paints Removing, in: AIC Paint. Spec. Gr. Postprints, 2013: pp. 77–87

[17] D. Scalarone, M. Lazzari, V. Castelvetro, O. Chiantore, Surface monitoring of surfactant phase separation and stability in waterborne acrylic coatings, Chem. Mater. 19 (2007) 6107–6113.

[18] E. Kampasakali, B. Ormsby, A. Cosentino, C. Miliani, T. Learner, A Preliminary Evaluation of the Surfaces of Acrylic Emulsion Paint Films and the Effects of Wet-Cleaning Treatment by Atomic Force Microscopy (AFM), Stud. Conserv. 56 (2011) 216–230.

[19] S. Zumbühl, F. Attanasio, N.C. Scherrer, W. Müller, N. Fenners, W. Caseri, Solvent action on dispersion paint systems and the influence on the morphology: changes and destruction of the latex microstructure, in: Mod. Paint. Uncovered Proc. from Mod. Paint. Uncovered Symp., 2007: pp. 257–268.

[20] T.T. Duncan, B.H. Berrie, R.G. Weiss, A Comparison Between Gel and Swab Cleaning: Physical Changes to Delicate Surfaces, in: L. V. Angelova, B. Ormsby, J. Townsend, R. Wolbers (Eds.), Gels Conserv. Art, Archetype Publications, London, UK, 2017: pp. 250–256.

[21] A. Bartoletti, R. Barker, D. Chelazzi, Reviving WHAAM! A comparative evaluation of cleaning systems for the conservation treatment of Roy Lichtenstein's iconic painting, Herit Sci. 8:9 (2020).

[22] M. De Sousa Ramos Félix Silva, Analytical study of accelerated light ageing and cleaning effects on acrylic and PVAc dispersion paints used in Modern and Contemporary Art, Doctoral dissertation, Universitat Politècnica de València, 2011.

[23] A. Solbes García, Evaluación de sistemas de limpieza acuosa, basados en ácidos orgánicos, para pinturas acrílicas, Doctoral dissertation, Universidad Autónoma de San Luis Potosí, 2017.

[24] C. Riedo, G. Rollo, D. Scalarone, O. Chiantore, Improved PVA gels for the cleaning of painted surfaces, in: L. Angelova, B. Ormsby, J. Townsend,

R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017: pp. 283

[25] T. Doherty, C. Stavroudis, Desarrollando sistemas de limpieza para pinturas sensibles al agua mediante ajuste del pH y de la conductividad, in: Conservación de arte contemporáneo: 13ª jornadas, febrero 2012, Centro de Arte Reina Sofía, Departamento de Conservación-Restauración, Madrid, 2012: pp. 39-48

[26]L. Angelova, E. Carreti, B.H. Berrie, R. G. Weiss, Poly (vinyl alcohol)-borax "gels": a flexible cleaning option, in: L. Angelova, B. Ormsby, J. Townsend, R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017: pp. 23

[27] M. Bertasa, O. Chiantore, T. Poli, C. Riedo, V. Di Tullio, C. Canevali, A. Sansonetti, D. Scalarone, A study of commercial agar gels as cleaning materials, in: L. Angelova, B. Ormsby, J. Townsend, R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017: 11

[28] A. Sansonetti, M. Bertasa, C. Canevali, A. Rabbolini, M. Anzani, D. Scalarone, D. A review in using agar gels for cleaning art surfaces, J Cult Heritage. 44 (2020) 285-296

[29] O. Dimond, M. Barkovic, M. Cross, B. Ormsby, The role of agar gel in treating water stains on acrylic paintings: Case study of Composition, 1963 by Justin Knowles, Journal of the American Institute for Conservation. 58 (2019) 144-157

[30] P. Cremonesi, A. Casoli, Thermo-reversible rigid agar hydrogels: their properties and action in cleaning, in: L. Angelova, B. Ormsby, J. Townsend, R. Wolbers (eds.) Gels in the Conservation of Art, London: Archetype Publications Ltd, 2017: 19

[31] P. Baglioni, D. Berti, M. Bonini, E. Carreti, L. Dei, E. Fratini, R. Gigorgi, Micelle, microemulsions and gels for the conservation of cultural heritage, Advcolloid Interface Sci. 205 (2014) 361-371

[32] C. Riedo, G. Rollo, O. Chiantore, D Scalarone, Detection and Identification of Possible Gel Residues on the Surface of Paintings after Cleaning Treatments, Heritage. 4 (2021) 304–315.

[33] N. Khandekar, A survey of the conservation literature relating to the development of aqueous gel cleaning on painted and varnished surfaces, Reviews in conservation, IIC, London, 1 (2000) 10-20

[34] J.S. Tsang, S. Babo, Soot Removal from Acrylic Emulsion Paint Test Panels: A Study of Dry and Non-Contact Cleaning, in: Preprints, ICOM-CC 16th Triennial Conference, Lisbon, Portugal, 19-23 September 2011, 2011: 1–9

Chapter 7.

CONCLUSIONS

The most important conclusions of this thesis are summarised below.

1. The paintings with higher amount of organic components, in addition to the pigment itself, are those that show a higher tendency for additive migration as a result of an aqueous cleaning treatment, regardless of the application method. Thus, the effect of cleaning treatments depends to a high degree on the binder composition and colours on which they are applied, being Titan green and Hyplar red the most susceptible paint mockups in terms of surfactant. This indicates that not always the paints made out of EA/MMA copolymer are those that suffer bigger changes. Given that susceptibility to cleaning methods depends to a large extent on the chemical composition of the paintings (which varies according to the brands and colours), knowing their compositions by performing chemical analysis becomes a key factor in the correct conservation and intervention of this type of painting.

2. Hyplar acrylic paint brand shows a slower additive migration process when compared with the rest of the tested brands. However, those additives were easily extracted from the surface after applying any water based cleaning treatment. This brand, also shows a higher sensitivity to pigment extraction. Thus, although these paints are more stable with regard to surfactant migration, they are very sensitive to cleaning treatments. This indicates that, the application of preventive measures that retard the migration of surfactants and prevent the deposition of dirt on the surface is especially necessary with these paints in order to guarantee their correct preservation.

3. Titan acrylic Paint brand shows a faster migration of additives to the surface, which may be related to the fact of being the brand with the highest organic material content in its composition. It was demonstrated that the application of the various cleaning methods cause the movement of additives both in the short and medium term. Titan paints are also those that show the biggest roughness changes on the surface after the cleaning processes. Moreover, the maximum degradation temperature of the co-polymer decreases significantly after cleaning, leading to think that its binder is less stable and that the thermal stability of the paint film decreases after cleaning.

4. The most meaningful chain scission of the polymer binder was detected on both Titan blue and Hyplar red paints, after cleaning. However, they are not those that show the biggest morphological changes on the surface. Therefore, it is safe to say that the samples that undergo the greatest changes in the bulk of the film, are not necessarily those that show the greatest alterations on the surface. Therefore, this data shows that monitoring the surfaces does not always give reliable results in terms of assessing the side-effects of the cleaning processes.

5. Silicone based methods proved to be harmful in terms of residue. Siloxane compounds were detected all over the analysed surfaces after cleaning treatment with Velvesil Plus, even after gently rinsing. The unctuous texture of this system complicates its removal spreading it beyond the treated area. Moreover, the low evaporation rate of the clearance solvent (Cyclomethicone), makes this procedure more time-consuming.

6. Cleaning by using cryogels proved to be less harmful when cleaning Liquitex acrylic paint films. However, cryogel application on Titan and Hyplar proved to affect them negatively, triggering the movement of additives on the surface. However, in general terms, it was demonstrated that the effect of the cleaning with cryogels is less harmful than swab and Velvesil cleaning.

7. UV-cured hydrogels proved to be easy to make, and fast and tuneable according to the specific needs of each surface, offering a better control of water release. These gels can be adapted to the needs of the field, being respectful for the paint film, controllable, tuneable and affordable for restores. Thus, water is released in a more controllable way than when using other widespread easy to prepare methods such as Agar gels. Moreover they can be considered an alternative to the use of cryogels in the most sensitive surfaces, such as Titan green (PG7) and Hyplar red (PR112) mockups.

8. Moreover, according to the results of this first tests, UV cured hydrogels also show an efficient and safe cleaning performance, being HEMA-VP and HEMA_AMPS the cleaning methods that revealed the most successful performance.

9. UV-hydrogels offer the possibility of tuning all the components of the hydrogel in a tailored way, starting from the monomers to the incorporation of additives to adjust its characteristics, expanding the possibilities for the restorers who will be able to adapt the method to each concrete case in an easy way, refining to the maximum the properties of the gel.

Anex.

SCIENTIFIC PUBLICATIONS

List of scientific publications included in this Thesis:

I. Cárdaba and A. Solbes, Gelled cleaning systems for acrylic emulsion paints: a scientific literature review, Ge-Conservación, 20(1) (2021) 337-351 DOI: https://doi.org/10.37558/gec.v20i1.1075

I. Cardaba, M. I. Maguregui, Extension study of the assessment of aqueous cleaning on nBA/MMA and EA/MMA acrylic paints Journal of Cultural Heritage, 67 (2024) 290-301 DOI: https://doi.org/10.1016/j.culher.2024.03.008

I. Cárdaba, L. Porcarelli, A. Gallastegui, D. Mecerreyes and M.I. Maguregui, Easy-to-make polymer hydrogels by uv-curing for the cleaning of acrylic emulsion paint films, Polymers, 13 (2021) (13):2108 DOI: 10.3390/polym13132108

I. Cárdaba, G. Poggi, M. Baglioni, D. Chelazzi, I. Maguregui, R. Giorgi, Assessment of aqueous cleaning of acrylic paints using innovative cryogels, Michrochemical Journal, 152 (2021) 104311 DOI: https://doi.org/10.1016/j.microc.2019.104311


Ge-conservación
Conservação | Conservation

Sistemas de limpieza gelificados para pinturas acrílicas en emulsión: una revisión de la literatura científica

Irene Cárdaba López, Álvaro Solbes García

Resumen: Las pinturas acrílicas en emulsión acuosa se han utilizado en el arte de forma masiva desde los años 60. Sus propiedades ópticas y versatilidad posibilitaron su rápida incorporación al ámbito artístico, convirtiéndola en una de las técnicas más reconocibles a nivel internacional. Desde entonces, muchos artistas se han servido de estos productos sintéticos y sus derivados para realizar sus obras, conformando un gran acervo en fondos y colecciones que hoy en día presenta problemas de conservación. Lo más grave de esta situación es que los problemas identificados están intrínsecamente relacionados con su composición y propiedades de envejecimiento. En general, las películas acrílicas son muy sensibles a los solventes orgánicos y el agua, por lo que los métodos de limpieza tradicional no son adecuados para su intervención. Esta publicación pone en contexto parte relevante de la literatura científica referente a los nuevos métodos de limpieza basados en sistemas acuosos y gelificados.

Palabras clave: pinturas acrílicas, limpieza acuosa, geles rígidos, arte contemporáneo, conservación

Gelled cleaning systems for acrylic emulsion paints: a scientific literature review

Abstract: Acrylic emulsion paints have been widely used in art since the '60s. Their good optical properties and versatility triggered their rapid incorporation into the artistic field. Thus, becoming one of the most internationally recognizable techniques. Since then, many artists have employed these synthetic products and their derivatives to do their works, forming extensive collections that nowadays show considerable conservation problems. The main concern regarding the degradation of this kind of artwork is the intrinsic relationship with their composition and ageing properties. In general, acrylic films are very sensitive to organic solvents and water, so traditional cleaning methods are unsuitable for their intervention. This paper puts a relevant part of the scientific literature concerning new cleaning methods based on aqueous and gelled systems.

Keywords: acrylic paints, water based cleaning, rigid gels, contemporary art, conservation

Introducción

Desde su creación a mediados de los años 50, las pinturas acrílicas en emulsión acuosa han sido ampliamente utilizadas en el ámbito artístico como alternativa a la pintura al óleo. Sin embargo, los especialistas en conservación y restauración observaron que, tras cortos períodos de exposición al ambiente, las obras acumulaban suciedad superficial por diversos motivos asociados a su composición (Jablonski *et al.* 2003). Este fenómeno de envejecimiento acelerado ha supuesto un grave problema para la conservación, pues la aplicación de cualquier método de limpieza se ve condicionado por la delicada morfología de la película acrílica y su alta sensibilidad a los solventes orgánicos o el agua. En este sentido, la literatura ha reportado ampliamente (Ormsby y Learner 2009) que los problemas más relevantes están

Introduction

Since their creation in the mid-1950s, acrylic emulsion paints have been widely used in the artistic field as an alternative to oil paint. However, after a short period of exposure to the environment, conservation specialists observed that the artworks accumulated surface dirt for different reasons associated with their composition (Jablonski *et al.* 2003). This phenomenon of accelerated ageing has been a severe problem for conservation since the application of any cleaning method is conditioned by the acrylic film's delicate morphology and its high sensitivity to organic solvents or water. In this sense, the literature has widely reported (Ormsby and Learner 2009) that the most relevant problems are associated with the presence of certain hydrophilic additives such

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Assessment of aqueous cleaning of acrylic paints using innovative cryogels

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ABSTRACT

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

1. Introduction

Waterborne acrylic paints have been frequently used in modern and contemporary art. They usually feature high molecular weight acrylic polymers that are based on the esters of acrylic acid and methacrylic acid, and a broad range of additives including surfactants, stabilizers, wetting agents and viscosity modifiers, added to enhance stability, longevity, flow and film formation properties [1]. Different colors are obtained by the addition of either organic dyes or inorganic pigments. The usually low glass transition temperature of the acrylic resin, which results in films that are soft at room temperature [2–4] and the migration to the surface of hydrophilic additives, i.e. surfactants, upon drying [5] make acrylic paint films prone to attract airborne dust. Therefore, acrylic paintings need to be cleaned, even though this operation is particularly challenging [6]. The community has been searching for the safest and most effective procedure since 2003 [7,8]. The main problem of acrylic paints is their sensitivity to water and to organic solvents over a broad range of polarities. In fact, they show a swelling capacity of up to ten times higher than oil films [9]. It was observed that in 3 months old samples the interaction with solvents causes the partial disruption of films' microstructure, which, in turn, induces considerable optical changes and a decrease in the mechanical strength [9]. The cleaning of acrylic paintings can also lead to the solubilization of migrated additives on the surface and extraction of additives from the bulk of the film, and their migration to the surface, resulting in changes in the physico–chemical and mechanical properties of the film [10,11]. Even if aliphatic and low-molecular weight aromatic hydrocarbons induce the lowest swelling [9] and are less prone to interact with the hydrophilic components of the acrylic paint layer [11], the use of water for the removal of airborne dust, which is mainly hydrophilic, grants better cleaning performances.

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

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Original article

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

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A B S T R A C T

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

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

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

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

Introduction

Acrylic paints have been widely used by contemporary artists since they were first introduced in 1927 as acrylic organic solvent solutions [1]. At the beginning they were developed as house paints, until late 1940s when the first acrylic solution artist paints were marketed under the name of Magna [2]. Many artists such as Rothko, De Kooning or Kenneth Noland used these paints for their artworks. Acrylic emulsion paints were introduced in 1953 by Rohn and Haas facilitating the handling of the paint since they were water soluble. Thus, they quickly became the most popular medium among artists. Since then, numerous formulations have been incorporated into the market. To date, paint makers have constantly varied the paint formulations in order to improve their performance.

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

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polymers

MDPI

Article

Easy-to-Make Polymer Hydrogels by UV-Curing for the Cleaning of Acrylic Emulsion Paint Films

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Abstract: The cleaning of acrylic emulsion paint surfaces poses a great challenge in the conservation field, due to their high water sensitivity. In this article, we present easy-to-make polymer hydrogels, made by UV-photopolymerization, that show excellent cleaning properties. The formulation of hydrogels obtained by UV-curing and their performance as dry cleaners for acrylic paints was investigated. First, different hydrogel formulations based on functional acrylic monomers were used to formulate a series of UV cross-linked hydrogels by fast UV photopolymerization. Their effectiveness on surface dirt removal was investigated by SEM microscopy and colorimetry. The hydrogels showed excellent cleaning properties and controlled water release, and they still performed satisfactorily after several cleaning uses. The obtained UV-hydrogels were compared to the well-known agar gels, showing benefits in terms of reducing excess water. This article shows that easy-to-make UV-cured hydrogels are an efficient tool for the cleaning of surface dirt from water-sensitive paintings, overcoming the limits of traditional cleaning methods.

Keywords: acrylic paint; UV-cured hydrogels; art conservation; cleaning

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1. Research Aim

The aim of this work is to make the first approach to improving the cleaning methodology of water-sensitive paint surfaces by using fast, easy-to-make, and tunable UV-cured hydrogels. The main advantage of the proposed method is that UV-curing is a fast and available method [1–4] with high success in the coating industry and 3D printing, as well as other daily applications in health and esthetics. Besides the chemical compounds, it only needs a UV-lamp for obtaining the needed material in a rapid manner. Thus, avoiding complex laboratory processes while optimizing the preparation times is what makes these gels more affordable for the restorer than other types of hydrogels or cleaning materials.

In this work, we assessed the cleaning performance of several acrylic hydrogels. To do this, we investigated several formulations of UV-cured hydrogels based on commercially available functional (meth)acrylates, in order to find the most effective formulation for removing surface dirt while not harming the paint surface. The second part of the work compares the cleaning capability of UV hydrogels with the well-known agar gel. Agar is a commonly used and easy-to-make system in the conservation of art which has shown several drawbacks in terms of water retention capability [5]. This study shows the improvement in terms of water containment when using the UV-cured hydrogels presented here.

2. Introduction

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