



UNIVERSITÀ
DEGLI STUDI
FIRENZE

Da un secolo, oltre.



HR EXCELLENCE IN RESEARCH

PhD in Chemical Sciences –
Conservation of Cultural Heritage
CYCLE XXXVIII

COORDINATOR Prof. ANNA MARIA PAPINI

**Sustainable Conservation of Contemporary Murals:
Development and Evaluation of a Chitosan–Nanosilica
Protective Coating for Outdoor Artworks.**

Academic Discipline (SSD): CHEM-01/B

Doctoral Candidate

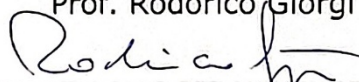
Dr. Chiara Cianci



(signature)

Supervisor

Prof. Rodorico Giorgi



(signature)

Co-Supervisor

Prof. Giovanna Poggi



(signature)

Coordinator

Prof. Anna Maria Papini



(signature)

The consultation of the thesis is free. Unless a specific authorization is obtained from the author, the thesis can be, however, downloaded and printed only for strictly personal purposes related to study, research and teaching, with the explicit exclusion of any use that has – even indirectly – a commercial nature.

Ai miei Nonni

ABSTRACT

Street Art and contemporary muralism have become recognised forms of cultural heritage, yet their conservation remains a major challenge. The industrial materials used in their creation, especially spray paints applied on inorganic supports, such as bricks, concrete and mortar, are highly sensitive to environmental factors such as solar radiation, humidity, and pollution. Their intrinsic instability, combined with the lack of specific preservation strategies, results in rapid deterioration and loss of artistic and social value.

This doctoral research investigates sustainable approaches to the protection of contemporary murals through the development of a chitosan–nanosilica hybrid coating. The formulation combines the film-forming, biocompatible, and reversible nature of chitosan with the mechanical strength and stability of nanosilica, creating a transparent and durable system suitable for outdoor applications. The hybrid coating was synthesised using a sustainable procedure and characterised through spectroscopic, microscopic, and physico-chemical analyses. Results confirmed stable organic–inorganic interactions, high homogeneity, and resistance to accelerated ageing.

Application tests on concrete spray-painted mock-ups demonstrated the coating's compatibility, transparency, and breathability, as well as its ability to reduce colour change and surface degradation. A preliminary Life Cycle Assessment highlighted its favourable environmental profile compared with conventional synthetic protectives.

Complementary analytical and field studies on alkyd spray paints and on a real-case study, the mural painting “Anna Maria” in Sesto Fiorentino (Italy), further contributed to understand the degradation processes affecting modern paints. The outcomes of this research provide both methodological and practical insights for

the sustainable conservation of Street Art, promoting a responsible balance between material protection, environmental awareness, and cultural significance.

List of contents

i. Background	1
ii. Aim of the study	4
iii. Scope and limitations	5
iv. Research question and structure of the thesis	6
PART A	8
1. State of the Art: Street art and contemporary muralism.....	13
1.1. General introduction	13
1.2. Street Art as emerging Cultural Heritage.....	17
1.3. Conservation Challenges in Street Art and Contemporary Muralism.....	20
1.4. Deontological Code for the Conservation of Material Cultural Heritage	26
1.5. Bridging the Conservation Gap: Towards Hybrid Formulations	29
2. Chitosan and Nanosilica.....	32
2.1. Chitosan	32
2.1.1. General properties	32
2.1.2. Antimicrobial Activity	35
2.1.3. Sustainability.....	40
2.1.4. Applications of Chitosan.....	42
2.1.5. Chitosan in Cultural Heritage Conservation	45
2.1.6. Molecular Mechanisms of Chitosan exploited in Cultural Heritage Conservation	48
2.1.7. Formulation and Application Techniques of Chitosan in Cultural Heritage Conservation.....	51
2.1.8. Case Studies on the Application of Chitosan in Cultural Heritage Conservation	54
2.1.9. Limitations and Open Questions in the Use of Chitosan for Cultural Heritage Conservation.....	57
2.1.10. Future Directions for the Use of Chitosan in Cultural Heritage Conservation	59

2.2.	Nanosilica.....	61
2.2.1.	General properties	61
2.2.2.	Surface Properties	62
2.2.3.	Chemical Stability	62
2.2.4.	Other Relevant Properties	63
2.2.5.	Nanosilica applications in coatings and composites	63
2.2.6.	Applications of nanosilica in cultural heritage	66
3.	Chitosan–Nanosilica hybrids	69
3.1.	Rationale for combining the two materials.	69
3.2.	Overview of advantages for Street Art preservation: mechanical strength, adhesion, stability, sustainability.....	71
3.3.	From State of the Art to Research Objectives: Towards a Sustainable Hybrid Coating for Street Art.....	74
PART B		76
4.	Hybrid Formulation and characterization	78
4.1.	Materials and methods	79
4.1.1.	Chemicals.....	79
4.1.2.	Coatings preparation	82
4.1.3.	Accelerated artificial aging tests	82
4.1.4.	ATR-FTIR	84
4.1.5.	Field emission scanning electron microscopy (FE-SEM).....	85
4.1.1.	Size distribution and zeta potential	85
4.2.	Results and discussion	85
4.2.1.	Coating preparation.....	85
4.2.2.	Exploring the interactions of chitosan and nanosilica	86
4.2.3.	Accelerated artificial aging effect	92
4.3.	Conclusions.....	96
5.	Application test of the hybrid formulation on concrete	98
5.1.	Introduction.....	98

5.2.	Materials and methods	99
5.2.1.	Mock-ups preparation	99
5.2.2.	Accelerated artificial aging tests	102
5.2.3.	Colour measurements.....	105
5.2.4.	Gloss measurements.....	106
5.2.5.	Film properties	106
5.3.	Results and discussion	107
5.3.1.	Film properties evaluation	107
5.4.	Conclusions.....	117
6.	Life Cycle Assessment of the Chitosan–Nanosilica Hybrid Coating ..	119
6.1.	Introduction.....	119
6.2.	Goal and Scope of the Study.....	120
6.3.	Methodology	120
6.4.	Life Cycle Inventory (LCI).....	121
6.5.	Results.....	122
6.6.	Discussion	124
6.7.	Conclusions and Future Perspectives.....	125
PART C		127
7.	Chemical characterization of spray paints	130
7.1.	Introduction.....	130
7.2.	Materials and Methods.....	133
7.2.1.	Original spray paints	133
7.2.2.	ATR–FTIR spectroscopy – Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy	135
7.2.3.	Micro-Raman spectroscopy	135
7.2.4.	SEM-EDX analysis	137
7.2.5.	Fiber Optic Reflectance Spectroscopy - FORS.....	137
7.2.6.	TGA – Thermogravimetric Analysis.....	138
7.3.	Results and discussion	139

7.3.1.	Binder.....	140
7.3.2.	Pigments and organic dyes.....	142
7.3.3.	White alkyd spray paint	150
7.3.4.	Black alkyd spray paint.....	153
7.3.5.	Yellow alkyd spray paint.....	154
7.3.6.	Orange alkyd spray paint	156
7.3.7.	Red alkyd spray paint.....	159
7.3.8.	Pink alkyd spray paint.....	162
7.3.9.	Light and Dark Violet alkyd spray paints	165
7.3.10.	Light Blue alkyd spray paint.....	168
7.3.11.	Dark Blue alkyd spray paint.....	171
7.3.12.	Green alkyd spray paint	174
7.3.13.	Light Brown alkyd spray paint	177
7.3.14.	Dark Brown alkyd spray paint	180
7.3.15.	Quantification of the inorganic fraction.....	185
7.4.	Conclusions.....	188
8.	Monitoring and Validation through a Case Study: Degradation of the “Anna Maria” Mural	190
8.1.	Introduction.....	190
8.2.	Materials and methods	191
8.2.1.	Photographic Documentation.....	191
8.2.2.	Colour measurements.....	192
8.2.3.	Gloss measurements.....	195
8.2.4.	Thermographic analysis	195
8.3.	Results and discussion	196
8.3.1.	Colour changes.....	196
8.3.2.	Cracks and efflorescences – possible degradation mechanisms ..	202
8.3.3.	Inorganic substrate - S.....	204
8.3.4.	Efflorescences	207

8.3.5.	Thermographic measurements	211
8.4.	Conclusions.....	215
9.	Study on the degradation of the alkyd sprays	217
9.1.	Introduction.....	217
9.2.	Materials and methods	218
9.2.1.	Spray paints.....	218
9.2.2.	Accelerated artificial aging tests.....	218
9.2.3.	Aged original spray paints ATR–FTIR spectroscopy – Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy.....	218
9.3.	Results and discussion	219
9.3.1.	Molecular changes	219
9.3.1.1.	White (W)	219
9.3.1.2.	Black	222
9.3.1.3.	Yellow (Y).....	224
9.3.1.4.	Orange (O)	226
9.3.1.5.	Red (R).....	230
9.3.1.6.	Pink (P)	232
9.3.1.7.	Light Violet (LV).....	234
9.3.1.8.	Dark Violet (DV)	236
9.3.1.9.	Light Blue (LB).....	238
9.3.1.10.	Dark Blue (DB).....	241
9.3.1.11.	Green (G)	243
9.3.1.12.	Light Brown (LBr).....	245
9.3.1.13.	Dark Brown (DBr)	247
9.4.	Conclusions.....	250
10.	Hybrid application on ETICS mock-ups.....	251
10.1.	Introduction.....	251
10.2.	Materials and methods	253
10.2.1.	Mock-ups preparation	253

10.2.2.	Chs-NS Hybrid coating application	254
10.2.3.	Colorimetric measurements	254
10.2.4.	Gloss measurements.....	255
10.2.5.	Accelerated artificial aging tests	255
10.3.	Results and discussion	256
10.3.1.	Natural vs artificial accelerated aging.....	256
10.3.2.	Evaluation of the hybrid coating on ETICS mock-ups	260
10.4.	Conclusions.....	263
11.	Collaboration with the artist and dissemination at school	266
11.1.	Collaboration with Skim	266
11.2.	Reflections on the Importance of Collaboration between Artists and Heritage Scientists.....	268
11.3.	Collaboration with “Anna Maria Enriques Agnoletti” High School	271
	Research outputs and future perspectives	274
	Symbols and abbreviations	278
	List of Figures	280
	List of Tables.....	284
	Acknowledgements.....	286
	Publications related to the PhD project.....	289
	Side Activities during the PhD period.....	289
	References.....	289
	Appendix – Scientific Publication Arising from this Doctoral Research	321

i. Background

Over the past few decades, Street Art and contemporary muralism have profoundly transformed urban environments, redefining the visual identity of cities and prompting new reflections on the nature of cultural heritage. Once regarded as acts of vandalism, these artistic expressions have gradually gained recognition as legitimate forms of contemporary art and as meaningful testimonies of social, political, and community values. Their accessibility, immediacy, and ability to convey collective narratives have made them an integral component of the public cultural landscape.

At the same time, the materials used in the creation of contemporary murals – industrial spray paints, synthetic binders, usually applied to inorganic-based supports – were never intended for long-term artistic purposes. Therefore, these artworks are inherently vulnerable to environmental stressors such as solar radiation, humidity and thermal fluctuations, and pollution. The rapid deterioration of these materials, combined with the absence of specifically designed conservation methodologies, has raised critical questions about how to preserve this emerging and ephemeral heritage without compromising its aesthetic and social essence. While the degradation mechanisms of modern paint films have been extensively investigated and are relatively well understood, significant knowledge gaps persist regarding the interactions at the interface between paint layers, preparation layers, and underlying substrates, particularly in the context of contemporary murals exposed to outdoor environments. In preventive conservation theory, the spectrum of environmental risks affecting cultural heritage objects and structures is commonly framed through the concept of the “ten agents of deterioration”, developed by the Canadian Conservation Institute. These agents include physical forces, incorrect temperature and relative humidity, light and ultraviolet radiation, pollutants, water, pests, custodial neglect

and other factors that can cause or accelerate deterioration of materials over time. Systematic consideration of these agents supports risk assessment and preventive strategies aimed at minimizing or avoiding damage prior to intervention.

In the context of outdoor mural conservation, several of these agents – such as solar radiation, humidity fluctuations, atmospheric pollutants, and water exposure – are directly relevant to both the degradation of paint films and the interaction between surface layers and preparation layers.

To contextualize these risks for the present case study, regional environmental data indicate notable climatic and air-quality conditions in the area of Sesto Fiorentino. According to annual environmental reports published by the *Agenzia regionale per la protezione ambientale della Toscana* (ARPAT), the Tuscan region exhibits measurable levels of key atmospheric parameters, including seasonal variations in air quality and pollutant concentrations, that are consistent with typical urban and peri-urban stressors for outdoor cultural heritage (e.g., particulate matter, ozone, nitrogen oxides), and form part of the local exposure profile affecting the mural under study .

While publicly accessible annual climatological datasets specific to Sesto Fiorentino are limited, regional summaries and meteorological archives provide a basis for understanding long-term patterns of temperature, humidity, and precipitation, which are key factors in assessing environmental stress on outdoor painted surfaces.

In this context, scientific research has recently increasingly turned its attention to the study of modern materials and the development of sustainable protective systems capable of addressing both the technical and ethical challenges of conserving Street Art. The exploration of natural and hybrid materials, in particular, has opened promising pathways towards environmentally responsible conservation strategies that align with contemporary principles of sustainability

and cultural inclusiveness. Before introducing the materials and approaches investigated in this research, it is necessary to clarify the terminology adopted with respect to conservation treatments. In conservation practice, cleaning refers to the removal of unwanted materials, consolidation aims to restore mechanical cohesion to degraded substrates, while protective treatments are intended to reduce the interaction between the artwork and external environmental agents without significantly altering the original material.

In contrast, within polymer and materials science, the term *coating* is commonly used to describe a thin functional layer applied to a surface to impart specific properties. In this thesis, the term *protective coating* is therefore used consistently to bridge these two perspectives, referring to a polymer-based surface treatment specifically designed for conservation purposes. This terminology follows established conservation definitions and practice, while maintaining coherence with materials science nomenclature [1].

ii. Aim of the study

Within contemporary conservation practice, increasing emphasis is placed on planned maintenance strategies (*conservazione programmata*), which aim to shift conservation from sporadic, interventive actions toward long-term management based on regular monitoring, preventive measures, and low-impact maintenance. Such approaches seek to minimize material loss, reduce the frequency of invasive interventions, and improve the sustainability of conservation practices over time. In the context of Street Art and contemporary murals, planned maintenance is particularly relevant due to continuous outdoor exposure and the inherently vulnerable nature of modern paint materials. Framing material development and diagnostic investigation within a planned maintenance perspective allows conservation strategies to be evaluated not only in terms of immediate performance, but also in relation to durability, retreatability, and long-term preservation goals, in line with internationally recognized conservation guidance. The general objective of this doctoral research is to develop and critically evaluate a sustainable protective coating specifically designed for the conservation of Street Art and contemporary mural paintings, combining material innovation with diagnostic investigation and field validation within the framework of preventive conservation.

To achieve this overarching aim, the study focuses on the formulation of a chitosan–nanosilica hybrid coating capable of providing transparent, breathable, and potentially reversible protection, while meeting key conservation requirements such as chemical compatibility, stability, and environmental sustainability.

In addition to material development, the research pursues a set of specific objectives, namely:

- to deepen the understanding of the materials constituting contemporary murals through the analytical characterisation of thirteen commercially available spray paints, representative of those commonly used in urban muralism;
- to investigate the degradation behaviour of these materials through laboratory studies and different accelerated ageing tests, aimed at elucidating colour change, chemical modification, and photo-oxidative processes;
- to evaluate the interaction between the hybrid coating and painted substrates through application on laboratory mock-ups, using a multi-analytical approach;
- to validate laboratory findings through the monitoring of a real contemporary mural artwork, integrating non-invasive analytical techniques and long-term field observations.

By combining material science, analytical chemistry, and conservation-oriented evaluation, the research aims to contribute to the development of evidence-based and ethically sound strategies for the sustainable preservation of an art form that has gained increasing relevance within both the socio-artistic sphere and heritage science.

iii. Scope and limitations

The scope of this thesis encompasses the formulation, characterisation, and performance evaluation of the chitosan–nanosilica hybrid coating, as well as the analytical study of spray paints and mural degradation phenomena. The research integrates laboratory-based experimentation with a Contemporary Muralism real-case observations, bridging fundamental materials science with applied conservation practice.

The experimental work is, however, limited by certain factors inherent to doctoral research. The accelerated ageing tests were performed under controlled laboratory conditions and therefore represent only an approximation of real environmental exposure. The application of the hybrid coating was restricted to

mock-ups and selected case studies rather than large-scale murals. Moreover, the environmental assessment, carried out through a screening Life Cycle Analysis, provides a first indicative evaluation of sustainability rather than a complete industrial-scale assessment.

Despite these limitations, the study attempted to establish a solid methodological foundation for further research and offer practical insights into the development of eco-compatible conservation materials.

iv. Research question and structure of the thesis

The main research question guiding this study can be expressed as follows:

How can hybrid materials be designed and applied to ensure the long-term preservation of Street Art, balancing technical performance, material compatibility, and environmental sustainability?

In this thesis, the concept of sustainability is primarily addressed in environmental terms, referring to the sourcing of raw materials, manufacturing processes, and end-of-life considerations, as well as to the reduction of environmental impact through durability and reduced need for repeated interventions. The proposed hybrid system is therefore discussed as “eco-compatible” with respect to conservation substrates and environmental exposure, and as “green” in relation to material selection and production strategies.

To address this research question, the thesis is organised into three main sections. The first outlines the theoretical and contextual framework, tracing the evolution of Street Art as a form of cultural heritage and discussing its conservation challenges, together with the potential offered by biopolymer-based nanomaterial systems such as chitosan and nanosilica. The second section presents the experimental work, encompassing the formulation and characterisation of the hybrid coating, its preliminary application on concrete

mock-ups, and its environmental assessment through life-cycle analysis. The third section expands the investigation to the materials and degradation phenomena of contemporary murals, including the chemical characterisation of spray paints, the monitoring of a real mural case study, and collaborative initiatives involving artists and educational institutions.

Collectively, these sections aim to provide a thorough and multidisciplinary contribution to the sustainable conservation of contemporary murals, linking scientific research with practical applications while fostering broader cultural awareness and public engagement.

PART A

Street Art and Contemporary Muralism have rapidly expanded across the urban landscape over the last decades, transforming city environments into “dynamic cultural palimpsests”. Once perceived primarily as acts of vandalism, these artistic practices are nowadays increasingly recognized as socially and culturally significant forms of heritage. Their democratizing nature, close connection with communities, and capacity to convey political, ethical, and aesthetic messages have elevated their cultural value, while at the same time posing unique conservation challenges. Unlike traditional wall paintings, contemporary murals are created with industrially manufactured spray paints – mainly acrylic and alkyd-based – often directly applied on inorganic substrates such as concrete, brick walls, and plaster. These materials, originally designed for commercial purposes rather than long-term artistic durability, are particularly vulnerable to environmental stressors. Solar radiation, thermal fluctuations, humidity, pollutants, and biological colonization accelerate degradation processes, leading to various deterioration phenomena, such as colour fading, chalking, detachment, and the consequent loss of legibility in relatively short timescales.

Solar radiation, thermal fluctuations, humidity, pollutants, and biological colonization accelerate degradation processes, leading to various deterioration phenomena, such as colour fading, chalking, detachment, and the consequent loss of legibility in relatively short timescales, which are consistent with deterioration patterns commonly documented for built heritage and painted architectural surfaces in international conservation glossaries [2].

From a legal and institutional perspective, it is important to distinguish between cultural heritage assets and artworks, as the planning, authorization, and funding of conservation interventions are strongly influenced by their juridical status. In the Italian context, cultural heritage is formally defined and protected under national legislation (Legislative Decree No. 42/2004, *Codice dei beni culturali e*

del paesaggio) and refers to properties officially recognized for their historical, artistic, or cultural significance. Conservation actions on such assets are subject to specific regulatory frameworks, authorization procedures, and public funding mechanisms.

In contrast, many contemporary murals and Street Art interventions fall outside formal heritage listings and are more appropriately classified as artworks, whose cultural value is collectively recognized by communities, artists, and institutions, but whose legal protection is often partial, absent, or evolving. This distinction has direct implications for conservation practice, as the absence of formal heritage status may limit access to public funding, define the responsibilities of stakeholders, and influence decision-making processes regarding conservation, maintenance, or removal. Acknowledging this duality is essential to properly frame conservation strategies for contemporary muralism, which must often operate at the intersection between heritage protection, artistic intent, and community engagement.

Conservation practice for urban murals is still in its early stages, and no universally accepted protocols or products specifically formulated for Street Art exist to date. Current approaches often rely on materials inherited from other conservation fields, such as acrylic or silane-based coatings, which present significant limitations when applied to outdoor murals. These include poor optical stability, risk of yellowing or cracking, incompatibility with modern synthetic binders, and compromised water vapour permeability of the support. Furthermore, the fundamental conservation principles of compatibility, reversibility, and sustainability are often not fully met. The absence of tailored strategies underscores the urgency of developing protective systems designed specifically for this emerging form of heritage.

Source	Typical Origin	Industrial Relevance	Sustainability Aspects	Key References
Crustaceans	Shrimp, crab, lobster shells (seafood processing waste)	Primary commercial source of chitin and chitosan worldwide	Valorization of fishery by-products; supports circular economy models; seasonal and geographically dependent supply	[3,5–7]
Insects	Beetles, flies, larvae (e.g., <i>Hermetia illucens</i>)	Emerging alternative source; increasing interest in industrial scaling	Controlled farming systems; lower mineral content; potential for more standardized extraction	[3,4]
Fungi	<i>Aspergillus</i> , <i>Mucor</i> , <i>Rhizopus</i> spp.	Biotechnological production under controlled fermentation	Independent from seasonal marine waste; lower heavy metal contamination; potentially more uniform polymer characteristics	[3,4]

Table 1 Main natural sources of chitin and relevance for chitosan production.

Within this context, biopolymers and nanomaterials offer promising opportunities. Chitosan, derived from the deacetylation of chitin, is an abundant, renewable, and environmentally friendly polymer, widely studied for its film-forming capacity, optical transparency, biodegradability, and antimicrobial activity. Chitin, the precursor of chitosan, is the second most abundant natural polysaccharide after cellulose and occurs in the exoskeletons of crustaceans (e.g., shrimp and crab shells), insects, and in the cell walls of fungi [3,4].

Industrial chitosan production is currently based primarily on the valorisation of crustacean-processing waste, aligning with circular economy principles and contributing to the sustainable use of marine by-products, as shown in Table 1 [5–7].

Its potential for cultural heritage applications has been highlighted in coatings, consolidants, and protective films. Nevertheless, pure chitosan suffers from limitations, such as mechanical weakness, sensitivity to moisture, and variable stability. In parallel, nanosilica has long been investigated for conservation purposes, especially in stone consolidation and protective treatments, due to its excellent mechanical reinforcement, stability, hydrophobicity, and chemical resistance.

The integration of chitosan with nanosilica into organic–inorganic hybrid systems would combine the strengths of both components. Nanosilica improves the structural and mechanical properties of chitosan films, enhances water resistance, reduces swelling, and provides long-term stability under environmental stressors. Chitosan, in turn, contributes sustainability, film-forming ability, and surface compatibility. Together, they generate hybrid coatings that are transparent, durable, and potentially reversible, while maintaining the breathability of underlying supports. Such materials would respond to the conservation criteria required for Street Art, namely transparency,

compatibility with both synthetic binders and inorganic substrates, stability under outdoor conditions, water vapour permeability, and environmental sustainability. In this section, the socio-cultural importance and fragility of Street Art are discussed alongside the current lack of conservation protocols, followed by a review of the potential of chitosan, nanosilica, and their hybrids. This framework clarifies the rationale for developing a new protective formulation and provides the conceptual basis for the experimental investigations presented in the following part of the dissertation, dedicated to the formulation, characterisation, and application testing of a chitosan–nanosilica hybrid coating for the conservation of contemporary murals.

1. State of the Art: Street art and contemporary muralism

1.1. General introduction

Street Art and Contemporary Muralism represent a dynamic and constantly evolving artistic field that has become deeply embedded in the urban landscape. Street Art can be broadly defined as a contemporary form of artistic expression rooted in the urban environment, often born as an act of opposition to dominant cultural systems and historically associated with illegal practices [8–10]. Yet this definition remains dynamic and context-dependent, as the phenomenon is subject to continuous social negotiation. Its manifestations are wide-ranging, extending from small-scale stickers to monumental murals covering entire façades, and employing diverse techniques such as graffiti, stencils, posters, and urban installations [10,11].

The term “Street Art” is at times generically applied also to commissioned works in outdoor spaces, which are more properly categorized as Urban Art. Unlike illicit graffiti, Urban Art is usually a shared expression involving artists, citizens, and municipalities, and plays a central role in shaping the social and visual identity of contemporary cities [10,12,13]. When such works are realized with

public funding or through institutional commissions, they may also be considered part of Public Art. Within this broad spectrum, Contemporary Muralism stands out as one of the most widespread forms [10,13]. These large-scale paintings, typically executed on building façades, are often commissioned by local authorities or created as part of street art festivals. Particularly in Italy, mural painting has found fertile ground since the 1920s and 1930s, and in recent decades it has been revitalized as “New Muralism”[10].

Graffiti, closely linked to the etymology of the Italian verb *graffiare* (“to scratch”), refers more specifically to inscriptions or drawings carved, written, or painted on public surfaces. In its modern form it is most often associated with spray paint, where the simplest expression is the tag: a stylized personal signature or cryptic logo [11,14–16].

The practice of painting or inscribing walls is not a modern invention but rather a constant in human history, with origins that date back to prehistoric cave paintings. In Roman times, for instance, Pompeii preserves abundant examples of wall writings of both private and vandalistic nature [11]. Modern Street Art, however, has its roots in the graffiti writing movements that emerged in the 1960s and 1970s in U.S. cities such as Philadelphia, Chicago, and New York [8,17]. These practices first developed in marginalized neighborhoods, where young people began marking walls with their “tags,” initially using markers and later spray cans, which rapidly became the dominant medium. This modern archetype, often referred to as Independent Public Art, is regarded as the direct forerunner of today’s Street Art [11,15,16].

Another important precursor was international muralism in the post-war period, particularly the Mexican muralist movement led by Rivera, Orozco, and Siqueiros, which strongly influenced subsequent urban painting [11,15,18]. From the 1980s onwards, Street Art evolved into an increasingly multifaceted phenomenon. While originally perceived as vandalism, it progressively came to

engage with broader social and political issues, paving the way for the emergence of *Contemporary Muralism*, in which artists produce sanctioned large-scale works that have become integral parts of the urban fabric [9,18].

In the last decade, the perception and cultural status of Street Art have undergone a profound transformation, leading in some cases to its institutional recognition and even “musealization” [8,18]. Already in 1979, graffiti works were exhibited in Rome at the *Galleria La Medusa*, and in 1984 the exhibition *Arte di frontiera: New York Graffiti*, curated by Francesca Alinovi in Bologna, further disseminated this form of expression in Italy [10,11]. Today, large-scale murals are frequently realized within institutional projects, often as part of cultural festivals or urban regeneration initiatives [8,19–22]. Increasingly, such works are also viewed as elements of cultural heritage and as beloved community icons. Some murals, such as those by Keith Haring in Pisa and Melbourne, have achieved protected status as cultural landmarks, while the controversial practice of detaching and commercializing works of Street Art illustrates their growing financial value [8,9,18,23,24].

In parallel, the growing recognition of murals and site-specific artworks as elements of Public Art has led to the development of dedicated conservation and management programs at an international level. Notable examples include institutional initiatives focused on the documentation, monitoring, and long-term preservation of contemporary public artworks, often involving collaboration between conservators, artists, municipalities, and local communities. These programs reflect a broader shift toward the professionalization of Public Art conservation and provide reference frameworks for addressing the technical, ethical, and social challenges associated with preserving artworks in public space [25–27].

The socio-cultural role of Street Art is equally significant. Art created in public space is now widely recognized as a meaningful component of contemporary

cultural heritage. Murals are closely tied to the urban context and often convey messages of social, political, or ethical relevance, while simultaneously reinforcing community identity and pride [8,10]. They can serve as collective memory, as in the case of the mural *Musica Popolare* in Milan, which embodies the shared historical identity of its neighbourhood [9,17,28–30]. Street Art has also proven to be a powerful tool for urban regeneration, revitalizing neglected areas and transforming them into cultural landmarks. Its origins, however, remind us that Street Art has always been deeply political, born in the 1960s as an act of rebellion and protest. Its large scale and public accessibility make it a particularly effective medium for social commentary [28,29].

To conclude, it must be considered that nowadays Street Art carries an inherently democratic dimension. By existing “outside the borders” of galleries and museums, it breaks away from traditional notions of exclusivity and asserts itself as an art form accessible to all. Regardless of the legal challenges that often accompany its creation, its visibility in everyday spaces and its capacity to be experienced by anyone at any time affirm its status as a form of public art, addressed to society as a whole [9,10].

Despite their growing institutional recognition and socio-cultural relevance, contemporary murals remain materially fragile. Unlike traditional wall paintings executed with mineral-based techniques, Street Art is predominantly realized with industrial spray paints formulated for commercial applications rather than long-term artistic durability. Their exposure to uncontrolled outdoor environments makes them particularly vulnerable to rapid degradation processes, raising urgent conservation concerns that will be discussed in the following sections.

1.2. Street Art as emerging Cultural Heritage

Over the past decade, the perception of Street Art and contemporary muralism has undergone a radical transformation. A form of artistic expression that was once regarded primarily as an act of vandalism is now increasingly recognized as a significant component of contemporary cultural heritage[8,13]. The very term *graffiti* historically carried connotations of damage and illegality, evoking the considerable costs of cleaning and repair that municipalities often faced when heritage buildings were defaced. Today, however, a growing number of works are no longer dismissed as nuisances but are instead being valued as artistic expressions [8,10,11,14,18,19,31].

This shift is the result of two intertwined factors. On the one hand, many urban artworks are now acknowledged as beloved community icons, capable of expressing collective identity and memory. On the other, their social recognition as “testimonies that transmit the values of civilization” has gradually aligned them with broader definitions of cultural heritage [10,11,13,18]. The transition has also been shaped by the trajectories of artists themselves: many who once operated clandestinely as graffiti writers have migrated toward sanctioned forms of Street Art, seeking both public recognition and access to the institutional art world [16].

Despite this cultural revaluation, the conservation of Street Art and contemporary murals remains a challenging and still emerging field. The ephemeral nature of the materials employed, questions of ownership, and the significant costs of intervention have hindered the development of systematic practices [18]. In Italy, for instance, the legal framework of cultural heritage law requires a 70-year threshold from the date of creation (and from the death of the artist) before an object can be formally recognized as of cultural interest [21]. This leaves most recent street works outside official and institutional protection and recognition, although copyright legislation does safeguard the moral rights of artists over their

creations [10,21]. Meanwhile, the academic community has begun to address the issue more actively, stressing the urgent need for methodologies tailored to the specificities of mural painting, ranging from documentation of conservation status to the assessment of protective treatments [8,12,13].

In this context, urban art festivals and regeneration projects have played an important role in raising awareness and embedding Street Art within the cultural landscape. In Italy, the GRAArt project in Rome is emblematic: it aims to narrate the city's history through urban artworks in peripheral neighborhoods, combining social revitalization with heritage-making [9,21]. Other initiatives, such as the EU-funded CAPuS (Conservation of Art in Public Spaces) project, have developed guidelines and glossaries for the conservation of muralism across Europe [9,13]. The PRIN 2020 SUPERSTAR project is similarly focused on creating sustainable conservation strategies, with particular attention to the behaviour of materials and intervention methods [9,32]. Italian examples such as the murals *A Very Long Story* by Blu in Prato (2006), *Musica Popolare* in Milan (Orticanoodles, 2017) or *Ubuntu* in Reggio Emilia (2018) demonstrate both the social significance of such works and the rapidity with which they can deteriorate, making them important case studies for the field [12,29,30,32]. Internationally, cities such as Lisbon, Berlin, and London have also embraced the artistic and cultural potential of muralism, each developing distinct approaches to its promotion, conservation, and commodification [13,15,18].

Yet Street Art's cultural ascent does not erase its intrinsic ephemerality. The scientific community widely accepts that the fleeting nature of urban works stems from both the constant transformations of urban space and the inherent fragility of the materials used [13,29]. Modern paints, particularly acrylics and alkyds in spray formulations, are composed of polymers that are highly susceptible to photochemical and physical degradation when exposed to sunlight, UV radiation, humidity, and pollutants [9,13,22]. For example, murals such as *Ubuntu* have

shown visible fading and chromatic alteration within months, particularly in fluorescent or red-orange hues [9,12,22,28,32]. While this fragility poses a serious conservation challenge, it does not diminish the cultural or artistic value of these works; rather, it highlights the urgency of preventive strategies aimed at mitigating their loss [9,10].

Preventive approaches to conservation are well established in heritage science and have been systematically formalized since the late 20th century as risk management strategies, notably through frameworks such as the ABC Method developed by Michalski and Pedersoli Jr.[33].

Current research increasingly emphasizes preventive conservation over remedial action. Documentation tools have been central in this regard: in Italy, for example, the *SCIMA* (*Scheda Conservativa Informatizzata Mural Art* – transl.: *Digital Conservation Record for Mural Art*) system developed by YOCOCU APS in collaboration with M.U.Ro provides digital records of the socio-cultural significance, materials, environment, and conservation issues of murals. Similar initiatives, such as the CAPuS glossary, contribute to the standardization of terminology and approaches in the field [20,21]. Protective interventions have also been explored, ranging from UV-protective coatings to preliminary surface treatments with lime mortar [9,20,34]. Although such measures may alter the aesthetic qualities of a work, they represent crucial steps in extending durability, as exemplified by the use of an acrylic-alkyd coating in the restoration of Keith Haring's *Tuttomondo* in Pisa [9,13,23,24].

These approaches increasingly recognize the importance of collaboration between artists, conservators, scientists, local authorities, and local communities, particularly in the context of Street Art as a form of living and socially embedded heritage [9,21,34].

1.3. Conservation Challenges in Street Art and Contemporary Muralism

The conservation of Street Art and contemporary muralism presents specific and complex challenges, largely due to both the ephemeral characteristics of the materials employed and the aggressive outdoor environments in which they are displayed [10,19,34]. Unlike traditional mural paintings, such as frescoes, there are no standardized conservation protocols specifically designed for these works. One of the primary issues concerns the materials themselves. Street artists typically rely on synthetic paints, most notably acrylic and alkyd spray paints, that were originally developed for industrial or domestic applications, not for long-term artistic purposes. These spray paints are complex formulations consisting of polymeric binders, synthetic organic pigments, solvents, and a wide range of additives such as fillers, plasticizers, stabilizers, and biocides [8,9,22,34]. Moreover, their exact composition is often undisclosed due to intellectual property rights, which complicates conservation research. The binders most commonly used are alkyd resins, often modified with nitrocellulose or styrene to enhance gloss, hardness, and adhesion, and acrylic resins, also frequently modified with styrene [8,9,18,22,31,32,35]. Additives such as plasticizers are included to provide flexibility, but they tend to migrate or leach out, weakening the paint film over time [8,9,12]. Moreover, synthetic organic pigments, while valued for their brilliant colours, are notoriously unstable under outdoor exposure [9,28].

In addition to the intrinsic vulnerabilities of the paint, the substrates present further complications. Street Art is typically executed on exposed urban surfaces such as concrete walls, plaster façades, or masonry structures. These supports often lack adequate preparation and may already show signs of deterioration, such as rising damp, salt efflorescence, or flaking plaster, all of which compromise adhesion and accelerate the degradation of the paint layer [9,12,13,20,34].

Environmental factors are equally detrimental. Ultraviolet radiation is among the most damaging agents, initiating photochemical reactions that cause oxidation, chain scission, and cross-linking in polymeric binders. Light-induced degradation is commonly evaluated in terms of cumulative radiant exposure (dose), and conservation guidelines often refer to acceptable loss thresholds to balance preservation needs with the unavoidable exposure of artworks, particularly in outdoor or publicly accessible contexts [33,36–39]. These processes lead to embrittlement of the paint film and to chromatic instability, particularly in red, orange, and magenta tones, which are highly prone to fading [9,10,13,20,22,28,30,34]. Certain pigments, such as titanium dioxide in its anatase form, can even catalyze photodegradation reactions, whereas carbon black provides better UV stability [9,13,28,29,31]. Over time, the degradation of binders manifests in phenomena such as chalking, where the surface becomes powdery and loses cohesion [9,12,28]. Fluctuations in temperature and humidity contribute to mechanical stress, inducing cracking, flaking, and delamination, while water promotes hydrolysis, leaching of soluble additives, and salt crystallization at the paint–substrate interface [8,9,12,13,20,22,34]. Pollutants like nitrogen oxides and sulfur dioxide further accelerate chemical degradation, and biological colonization by fungi, algae, or cyanobacteria becomes frequent in humid environments [9,10,20,34]. On top of this, works are exposed to deliberate acts of vandalism such as tagging or overpainting, which are particularly difficult to remove selectively because the intruding layers are often chemically similar to the original ones [10,13,40,41].

Conservation treatments developed for traditional heritage materials are often ill-suited for these contemporary works [9,13,34]. Acrylic resins such as Paraloid B-72, widely employed in conservation, can undergo photodegradation and yellowing under outdoor conditions, while their application may cause changes in gloss, saturation, or even induce craquelure in the paint layer [9,42].

Fluorinated anti-graffiti coatings offer durability but drastically reduce water vapour permeability, trapping moisture within masonry supports and promoting salt crystallization, mechanical stress and consequent cracks and efflorescences formations [9,43]. The ethical principle of reversibility adds another layer of complexity: sacrificial systems such as waxes or organosilane coatings require frequent reapplication, while permanent systems like polyurethanes or fluorocarbons resist cleaning but pose questions regarding their removability and reversibility [14,34,44].

For these reasons, the conservation of Street Art is increasingly oriented toward preventive approaches and the development of innovative protective systems. Documentation tools and standardized glossaries, such as those produced by the CAPuS project, together with digital recording platforms like the SCIMA, are now widely recognized as essential components of conservation strategies. Current research focuses on protective solutions capable of mitigating environmental degradation while respecting material compatibility and ethical constraints, underscoring the need for approaches specifically tailored to contemporary muralism [9,10,12,13,40,45].

Criteria for Protective Strategies
The conservation of contemporary muralism and Street Art in urban environments requires a radical methodological rethinking, due to the complex and often ephemeral nature of the works. Current approaches to conservation are still largely inherited from other areas of cultural heritage and, as such, rely on materials and methods that were not specifically designed for the preservation of Street Art. This lack of tailored solutions highlights the urgency of developing innovative and effective protective strategies [9,18,29,34].

At present, no shared or standardized protocols exist for the conservation or maintenance of murals and street paintings, and the scientific literature repeatedly emphasizes the scarcity of commercial products specifically formulated for these artworks [9,13]. The compatibility and stability of protective materials with

modern spray paints remain critical challenges, and the market offers very limited options. Laboratory and in-situ studies consistently demonstrate that no universal solution exists: no single protective system has yet proven effective across the wide variety of commercial paints employed by street artists [34]. Preventive conservation emerges as a particularly promising approach, as it aims to mitigate future deterioration while preserving the chromatic vibrancy and legibility of the works without undermining their urban and often ephemeral character. Although the transient nature of Street Art can be considered intrinsic to its meaning, there is broad recognition of the need to preserve the artistic and social messages of its most significant examples [10,13]. However, the pace of deterioration in outdoor environments is rapid and often unpredictable. Fading, driven by photodegradation of the organic components of modern paints, is one of the most frequent and alarming manifestations, quickly compromising the visual legibility of murals [13,18,28,34,46]. In certain cases, such as the mural *20 Years of Freedom and Democracy* in Milan, fading has been shown to affect only the uppermost 10 μm of the paint layer, underscoring the importance of developing a deeper understanding of degradation mechanisms as a foundation for conservation strategies [28].

Any protective system applied to outdoor mural surfaces must therefore meet stringent criteria. Transparency and compatibility are fundamental, as coatings must not alter the optical properties or visual perception of the artwork; in this context, compatibility is primarily intended as chemical affinity between the protective system and the underlying paint layers or substrate

The chemical affinity between the coating and the underlying paint strongly influences this impact, and case studies have demonstrated that protective systems can induce significant chromatic shifts, sometimes more noticeable on real murals than on laboratory mock-ups [9,13,47]. Preliminary testing on representative materials and supports is thus indispensable. Durability is another

critical parameter, ideally ensuring stable protection for five to ten years, although most systems currently available require frequent maintenance and reapplication, as in the case of sacrificial wax-based coatings [9].

In the case of organosilane-based protective systems, long-term effectiveness is strongly influenced by environmental exposure and substrate characteristics, and periodic monitoring and maintenance are generally required, rather than one-time application. From a conservation planning perspective, the application of protective coatings to contemporary murals should therefore be conceived within a time-based maintenance framework, rather than as a permanent or definitive intervention. In outdoor contexts, the effectiveness of protective systems inevitably evolves over time as a function of environmental exposure, substrate behaviour, and material ageing.

As a result, protective coatings should be integrated into planned maintenance strategies, based on periodic inspection, monitoring of surface properties (e.g., colour, gloss, cohesion), and timely retreatment when performance thresholds are reached. This approach allows deterioration processes to be mitigated before significant material loss occurs, while reducing the need for invasive remedial interventions.

Within this perspective, durability does not imply permanence, but rather predictable performance over a defined time interval, compatible with regular conservation monitoring. The development of protective systems that can be safely renewed or adjusted over time is therefore essential to introduce a realistic time dimension into the conservation of Street Art and contemporary muralism. Reversibility remains an ethical requirement: coatings should be removable or retreatable, a criterion partly fulfilled by certain organosilane systems, which combine ease of application with long-term reversibility [9,44].

However, the concept of reversibility in conservation requires critical evaluation, particularly in the context of outdoor and contemporary artworks. Complete

removal of protective coatings without any interaction with the original material is often unrealistic, especially after prolonged environmental exposure. For this reason, reversibility is increasingly interpreted as retreatability or controlled removability, whereby a protective system can be safely modified, renewed, or partially removed without inducing unacceptable changes to the substrate.

In the case of Street Art and contemporary muralism, where materials are inherently vulnerable and interventions must be compatible with planned maintenance strategies, a pragmatic approach to reversibility becomes essential. From this perspective, the ethical requirement of reversibility should be balanced against durability, compatibility, and long-term performance, acknowledging that conservation decisions often involve managing acceptable levels of material interaction rather than pursuing idealized, fully reversible solutions.

Finally, sustainability and physical performance must also be taken into account. Protective systems should maintain water vapour permeability, preventing moisture entrapment that could accelerate substrate degradation [9,44]. They must be chemically inert, non-toxic, and environmentally sustainable, in line with contemporary conservation ethics [19]. In this context, the search for suitable protective systems for Street Art represents not only a technical challenge but also an ethical and cultural responsibility, aimed at safeguarding works that, though fragile and ephemeral, have become a significant part of the contemporary urban heritage.

Within this framework, it becomes evident that a significant functional gap persists in the conservation of contemporary muralism. Existing protective systems typically address individual requirements – such as hydrophobicity, durability, or ease of application – but rarely achieve a balanced integration of chemical compatibility with modern spray paints, optical transparency, vapour permeability, reversibility, and environmental sustainability.

The novelty of the approach proposed in this research lies precisely in addressing this gap through the design of a hybrid protective coating that combines an organic biopolymer with an inorganic nanophase. Rather than optimizing a single performance parameter, the chitosan–nanosilica system is conceived to provide multifunctional protection, reconciling material compatibility, controlled interaction with the substrate, and long-term performance under outdoor exposure. This integrated strategy responds to conservation needs that remain largely unmet by currently available commercial products for Street Art and contemporary murals.

1.4. Deontological Code for the Conservation of Material Cultural Heritage
Interventions involving tangible cultural heritage must be framed within a well-established ethical and methodological framework, developed to ensure respect for the material, historical, and cultural significance of artworks and architectural surfaces. In the field of conservation, technical innovation cannot be dissociated from deontological responsibility: any treatment, including the application of protective coatings, must comply with fundamental principles that govern conservation practice and guide professional decision-making.

A cornerstone of modern conservation theory is represented by the principles articulated by the Italian art critic and historian Cesare Brandi (1906–1988) in the mid-20th century. Brandi’s theoretical framework, which remains highly influential in contemporary conservation practice, defines conservation as a critical act aimed at safeguarding the material integrity of the artwork while preserving its aesthetic and historical values [48]. Within this framework, three fundamental principles – recognizability, reversibility, and compatibility – form the ethical basis for any intervention on material cultural heritage.

Recognizability requires that any conservation treatment be distinguishable, at least upon close or analytical examination, from the original material. This

principle does not imply visual intrusion or aesthetic disruption; rather, it ensures intellectual transparency and prevents the falsification of the artwork's historical record. In the context of protective coatings, recognizability entails that the applied material does not alter the visual perception of the artwork and that its presence can be identified through appropriate analytical methods if required.

Reversibility, or more accurately retreatability, refers to the possibility of removing or modifying an intervention without causing damage to the original substrate. While absolute reversibility is often unattainable in practice, especially in polymer-based systems, the principle remains central as a guiding criterion. For protective coatings, this translates into the use of materials that can be removed or significantly reduced using mild and controllable procedures, minimizing chemical and mechanical stress on the underlying paint layers and support.

Compatibility encompasses chemical, physical, and mechanical affinity between the conservation material and the original substrate. A compatible intervention must not induce harmful interactions, such as chemical degradation, differential mechanical stress, or inhibition of natural moisture exchange. In the case of mural paintings and painted architectural surfaces, compatibility is particularly critical due to the heterogeneous nature of substrates, preparation layers, and paint films, as well as their exposure to fluctuating environmental conditions.

Within this deontological framework, the application of protective coatings must be understood not as an isolated technical action, but as part of a broader conservation strategy that prioritizes minimal intervention, long-term stability, and respect for the artwork's material authenticity. The development and assessment of new protective materials must therefore explicitly demonstrate alignment with these principles, ensuring that innovation does not override ethical responsibility.

In recent years, conservation theory has increasingly emphasized the importance of integrating traditional deontological principles with sustainability-oriented approaches. Contemporary conservation practice operates within a global context marked by environmental challenges, resource constraints, and societal responsibility. As such, the ethical framework governing conservation interventions must expand to include considerations related to environmental impact, material sourcing, and life-cycle performance.

This perspective is consistent with the objectives promoted by the United Nations Sustainable Development Goals (Agenda 2030), particularly those addressing sustainable cities and communities, responsible consumption and production, and climate action [49]. In the conservation of material cultural heritage, sustainability should not be regarded as an optional or external criterion, but as an integral component of ethical practice. The selection of conservation materials should therefore consider not only their technical performance and compatibility with heritage substrates, but also their environmental footprint, durability, and potential contribution to reducing the frequency and invasiveness of future interventions.

From this standpoint, sustainable conservation strategies align naturally with the principle of minimal intervention, as materials that exhibit greater stability, lower toxicity, and reduced environmental impact contribute to long-term preservation while minimizing cumulative damage to both heritage assets and the environment. The integration of environmental assessment tools, such as life cycle analysis, represents a valuable extension of traditional conservation ethics, providing a quantitative framework to support responsible material selection.

In the context of contemporary mural paintings and Street Art, these considerations acquire particular relevance. The ephemeral nature of such artworks, their exposure to harsh outdoor environments, and their strong social dimension demand conservation approaches that are both ethically sound and

environmentally responsible. Protective coatings developed for these contexts must therefore be evaluated not only in terms of performance, but also in light of their compliance with deontological principles and their contribution to sustainable conservation practice.

Accordingly, the protective systems investigated in this research are framed within the deontological requirements of recognizability, reversibility, and compatibility, while also addressing the growing need for sustainable conservation solutions. This integrated approach seeks to reconcile material innovation with ethical responsibility, ensuring that advances in chemistry and materials science effectively serve the long-term preservation of material cultural heritage.

1.5. Bridging the Conservation Gap: Towards Hybrid Formulations

This doctoral research is positioned within the current debate on the conservation of contemporary muralism and Street Art, addressing the clear gap between real conservation needs and the absence of specifically tailored protective materials. Despite the increasing recognition of Street Art as a valuable component of cultural heritage, no dedicated protocols or products are yet available for its preservation. The solutions currently on the market, largely inherited from other fields of cultural heritage conservation, remain inadequate for works created with modern spray paints on exposed cementitious supports. The rapid deterioration of these materials under outdoor conditions, caused by sunlight, thermal fluctuations, humidity, pollutants, and biological colonization, highlights the urgency of developing new formulations that meet strict requirements of compatibility, transparency, durability, sustainability, vapour permeability, and neutral pH.

In response to these challenges, this doctoral project proposes a hybrid chitosan–nanosilica (Chs–NS) coating as a novel protective system. Chitosan, a sustainable

biopolymer, offers promising film-forming and optical properties, yet its limitations in mechanical resistance and compatibility with inorganic substrates hinder its application in conservation. The integration of nanosilica into the chitosan matrix is designed to overcome these shortcomings, improving stability, adhesion, and overall performance.

Furthermore, a new preparation strategy has been developed to achieve a final neutral pH, representing a significant methodological advancement in the formulation of chitosan-based protective systems. This aspect is particularly relevant from a conservation standpoint, as acidic formulations are known to increase the risk of chemical interaction with cementitious substrates and preparation layers, potentially promoting salt migration and efflorescence phenomena. By reducing the acidity of the coating, the proposed formulation substantially lowers the risk of substrate alteration, thereby enhancing its compatibility and conservation potential for sensitive painted surfaces.

This research pursues two main goals: first, to formulate and characterize a sustainable hybrid coating tailored to the conservation of Street Art; and second, to assess its protective efficacy through experimental testing. Key parameters such as adhesion, water vapour permeability, hydrophobicity, and long-term stability under accelerated aging conditions were systematically evaluated using representative concrete mock-ups. Beyond laboratory validation, the work is conceived as a methodological step toward real-world applications, in line with the aims of the PRIN 2020 SUPERSTAR project, which supports the development of sustainable conservation strategies for Street Art.

The results demonstrate that the Chs–NS hybrid coating can effectively mitigate degradation under combined environmental stressors while maintaining the visual and physical integrity of the painted surfaces. This outcome suggests the potential of the formulation as a foundation for a new generation of eco-friendly protective systems specifically designed for outdoor murals. Ultimately, this

doctoral project contributes to narrowing the gap between conservation research and practice, offering both methodological insights and practical tools for the sustainable safeguarding of Street Art as an emerging yet fragile cultural heritage.

2. Chitosan and Nanosilica

2.1. Chitosan

2.1.1. General properties

Chitosan is a natural polymer that has garnered increasing interest due to its unique properties and numerous possible applications [7].

Every year, the number of publications and patents based on this polymer increases. Derived from chitin, the most abundant marine biopolymer, chitosan represents a valuable resource that contributes to the circular economy and pollution reduction by utilizing crustacean industry waste [50].

From the chemical point of view, chitosan is a family of linear polysaccharides, not a single polymer with a defined structure, composed of varying amounts of $\beta(1\rightarrow4)$ linked residues of N-acetyl-2-amino-2-deoxy-D-glucose (N-acetylglucosamine, GlcNAc) and 2-amino-2-deoxy-D-glucose (glucosamine, GlcN). It is produced by the deacetylation of chitin – the most abundant biopolymer on Earth, after cellulose – and this process consist in the conversion of some N-acetylglucosamine units into glucosamine units [7]. The main reactive functional groups found in the chitosan structure are a primary amino group (C2) and primary and secondary hydroxyl groups (C6, C3).

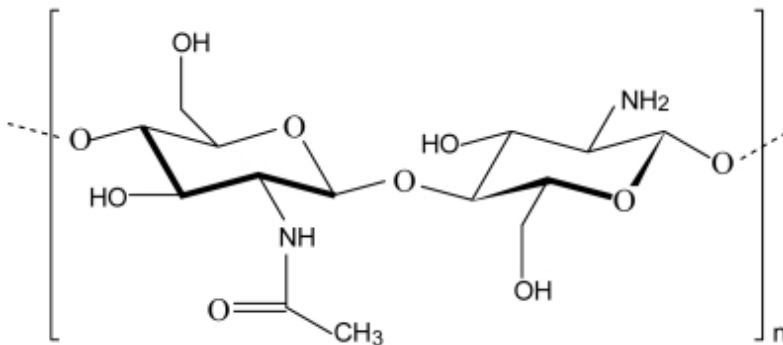


Fig. 1 Molecular structure of chitosan.

Glycosidic bonds and the acetamide group can also be considered functional groups. The presence of these amino groups, which can be protonated, confers chitosan solubility in aqueous acidic media, as its pKa value is around 6.5. Chitosan is the only polycation found in nature, and its charge density depends on the degree of deacetylation (DD) and the pH of the medium. The polymer's solubility depends on its molecular weight (Mw) and degree of deacetylation [50,51]. However, chitosan exhibits poor solubility in neutral and basic media (above pH 6.5), which limits its use under certain conditions [7,51]. This limitation has led to the synthesis of numerous chitosan derivatives with improved solubility. Chitosan, nano-chitosan, and chitosan-ZnO nanocomposites were tested and compared. Accelerate[52,53].

Biodegradability is a fundamental property of chitosan, as it is easily broken down inside the human body through enzymatic hydrolytic degradation mechanisms, particularly those involving lysozymes. This process involves breaking down the glycosidic linkages and releasing saccharides and glucosamine, which are then stored or further metabolized by human tissues [51]. When chitosan-based materials are applied in outdoor environments, such degradation processes can be broadly framed within the concept of weathering, which refers to the progressive physical, chemical, and biological alteration of materials induced by environmental exposure. In this context, factors such as moisture, temperature fluctuations, atmospheric oxygen, pollutants, and biological activity contribute to the gradual modification of polymeric structures over time. Understanding the weathering behaviour of chitosan is therefore essential when considering its application in conservation, as it directly influences long-term stability, performance, and interaction with exposed substrates.

Chitosan degradation can occur through several mechanisms [7]:

- Acid hydrolysis: HCl, for example, hydrolyses both O-glycosidic and N-acetyl linkages [51];
- Oxidative–reductive or nitrous acid depolymerization: Nitrous acid (HNO₂) specifically attacks the primary amine in glucosamine, leading to the cleavage of glycosidic bonds following a D-unit. Hydrogen peroxide (H₂O₂) produces faster, random degradation[54];
- Ultrasonic degradation: This method does not affect the degree of acetylation or polydispersity of the recovered polymers, allowing for moderate degradation [55,56];
- Enzymatic degradation: can be caused by specific and non-specific enzymes. Specific enzymes are called “chitosanases” (EC 3.2.1.132): they hydrolyse the β -1,4-glycosidic bonds of partially acetylated chitosan, releasing chitosan oligosaccharides (COS). Chitinases (GH18 and GH19) degrade A-A and A-D linkages, but not D-D linkages. Proteases (e.g., lysozyme, pepsin, papain, pronase), lipases, cellulases, and hemicellulases are non-specific/promiscuous enzymes that can degrade the biopolymer structure [57–59].

The rate of chitosan degradation can be controlled by various factors such as the degree of deacetylation (DD), molecular weight (Mw), and crosslinking [51,56]. The final degradation products depend not only on the chosen method (physical, chemical, or enzymatic) but also on the specific chemical agent or enzyme used. Chemical modifications can be used to improve chitosan’s biodegradability. Physical or chemical (non-enzymatic) degradation of chitosan is rare due to its highly crystalline nature [51].

Chitosan possesses excellent film-forming ability, making it suitable for a wide variety of applications, particularly in the medical and packaging sectors [7,60,61], typically by solvent-casting methodologies.

Chitosan-based films can be produced by:

- Blending the polymer with others such as pectin [62];
- Creating layer-by-layer films with negatively charged polymers like polyacid, poly(lactic-co-glycolic acid) (PLGA), or polylactic acid [63–65];
- From chitin (chitosan precursor) dissolved in solvents like DMAc/LiCl or NMP/LiCl, or ionic liquids, followed by casting onto a glass plate, coagulation in an antisolvent (e.g., water, ethanol, acetone) to form a hydrogel, and then drying [3,66].

These biopolymer-based films, in addition to their safety, biocompatibility, and biodegradability, are excellent candidates for controlled drug delivery systems, contact lenses, wound dressings, and tissue engineering matrices. They result are particularly promising for packaging and medical devices due to their ability to control water vapour transmission rate (WVTR), preventing both excessive dryness (which causes scarring) and exudate accumulation (which delays healing) in wound dressings. However, chitin films can be fragile and may require plasticization with glycerol to improve mechanical properties. High Mw IL-regenerated chitin has enabled the production of pure and strong chitin films, unlike commercial chitin which often produces fragile, web-like films.

Chitosan's film-forming ability has also been exploited for the fabrication of microneedles (MNs) for transdermal drug delivery and vaccinations, although challenges such as achieving adequate mechanical strength and efficient sterilization methods remain to be addressed [7,67].

2.1.2. Antimicrobial Activity

Chitosan, together with its derivatives and oligosaccharides, is well known for its broad-spectrum antimicrobial activity. It has been shown to inhibit the growth of a wide variety of microorganisms, including both Gram-positive and Gram-negative bacteria, as well as filamentous fungi and yeasts [51,68]. Among Gram-

negative bacteria, species such as *Aeromonas hydrophila*, *Edwardsiella ictaluri*, *Flavobacterium columnare*, *Salmonella typhimurium*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Vibrio parahaemolyticus*, *Enterobacter aerogenes*, and *Vibrio cholerae* are particularly sensitive to chitosan [69]. Similarly, several Gram-positive strains, including *Bacillus cereus*, *Staphylococcus aureus*, *Bacillus megaterium*, *Lactobacillus plantarum*, *Listeria monocytogenes*, *Lactobacillus brevis*, and *Lactobacillus bulgaricus*, have also been reported as susceptible. In addition, antifungal activity has been demonstrated against yeasts such as *Candida albicans*, *Candida krusei*, and *Candida glabrata* [70].

The antimicrobial effectiveness of chitosan depends strongly on its chemical form. For instance, chitosan hydrochloride typically exhibits strong antimicrobial effects, whereas carboxymethyl chitosan is significantly less effective. Chitosan oligosaccharides and N-acetyl-D-glucosamine, on the other hand, generally show little or no antimicrobial activity.

The mechanisms underlying chitosan's antimicrobial action remain the subject of ongoing debate, but several plausible pathways have been proposed. One widely accepted explanation involves the disruption of microbial membrane fluidity. Protonated amino groups ($-NH_3^+$) on chitosan interact electrostatically with negatively charged groups, such as carboxylate ($-COO^-$), lipopolysaccharides, or surface proteins, located on microbial cell membranes [71–73]. This interaction compromises membrane integrity, leading to increased permeability, leakage of intracellular components, nutrient deprivation, and ultimately cell death [51]. Other studies suggest that chitosan can penetrate microbial cells and interfere with genetic processes, either by binding to DNA and inhibiting RNA transcription or by disrupting mRNA translation and protein synthesis [74]. A third mechanism relates to the ability of chitosan's amino groups to chelate essential metal ions, including Ca^{2+} , Mg^{2+} , Fe^{2+} , and Zn^{2+} , thereby limiting

microbial growth. This phenomenon has been reported to be particularly effective at higher pH values [75,76].

Finally, chitosan may act as a physical barrier by forming a dense layer around the microbial cell surface, which blocks porins and prevents nutrient and gas exchange, further hindering microbial proliferation [51].

Several factors influence the antimicrobial activity of chitosan, making it a complex and context-dependent phenomenon. Molecular weight, for example, is often considered important, although its role remains controversial: some studies report enhanced activity at higher molecular weight, while others observe the opposite trend [68]. Similarly, the degree of deacetylation (DD) has been correlated with antimicrobial performance, since lower DD generally increases the availability of free amino groups, but conflicting evidence also exists [7]. The pH of the surrounding medium plays a critical role, as protonation of the amino groups under acidic conditions greatly enhances activity, while at neutral pH the loss of charge significantly reduces efficacy. Concentration is another determinant: at low levels, chitosan primarily interacts electrostatically with cell surfaces, whereas at higher concentrations it can completely coat microbial cells, blocking nutrient exchange and exerting a bactericidal effect [77,78].

Environmental conditions also matter: chitosan tends to show stronger antimicrobial activity at low temperatures, with maximum effects observed at 4 °C compared to 25 °C [51,79]. The type of microorganism is equally relevant: Gram-negative bacteria are generally more sensitive to chitosan than Gram-positive species, while the effect on fungi tends to be fungistatic, hindering growth, rather than strictly fungicidal [51,69,80]. Solvents used for dissolving chitosan, such as acetic or citric acid, can themselves contribute to antimicrobial effects, which complicate interpretation of experimental results [68].

When chitosan-based coatings are applied to outdoor surfaces, the long-term degradation of the polymeric network may lead to the gradual release of low-

molecular-weight fragments and oligomers into the surrounding environment. In the context of mural paintings executed on architectural substrates, these degradation products may potentially reach the underlying soil through runoff or surface leaching.

From an environmental standpoint, such release is generally considered of low ecological concern, as chitosan and its degradation products are biodegradable and naturally occurring compounds that can be further metabolized by soil microorganisms [81]. Nevertheless, the interaction of bioactive polymers with soil microbiota and mineral components should be taken into account when assessing the overall environmental impact of protective treatments, particularly in urban settings. For this reason, the development of conservation materials increasingly requires a balance between antimicrobial efficacy, durability, and environmental compatibility, reinforcing the importance of life-cycle-based evaluation approaches.

As mentioned above, chitosan is poorly soluble in aqueous and alkaline solutions and can be obtained in a broad range of molecular weights (M_w , 10-1000 kDa), degrees of solubility, and degrees of deacetylation (50-95%), by varying its source and extraction methods. Chitosan can be physically or chemically modified thanks to the presence of reactive groups: the amino ($-NH_2$) group, the hydroxyl ($-OH$) group, and the carboxyl ($-COOH$) group, in its backbone. These groups can be modified without interfering with the polymer backbone [82,83]. Chitosan can interact with different hydrophilic molecules through hydrogen bonding or electrostatic interactions, as demonstrated by the formation of complexes with negatively charged DNA and RNA and its metal ion chelating activity [84]. Chitosan can be also modified by grafting, crosslinking, nanoparticles, microspheres, and through the amalgamation with bioactive agents.

Here are reported some of the chemical modifications often employed to obtain specifically designed chitosan derivatives with desired properties: grafting [85,86], crosslinking [87,88], combination with bioactive compounds [89], synthesis of nanoparticles [90], microspheres [91,92], acetylation [93], thiolation [94], phosphorylation [95], carboxylation [96], sulfonation [97], etc. All these kinds of operations not only enhance chitosan existing properties like hydrophilicity, biocompatibility, antimicrobial activity, and mechanical strength but also impart new specific properties to it, according to the specific purposes [83,98]. In particular, some chemical modifications can often enhance chitosan's performances in terms of resistance, and stability. For example, formulations combining chitosan with other active agents, such as essential oils (e.g., clove or oregano oil) or inorganic components like silver and ZnO, have also been reported to display synergistic effects. Moreover, the biological origin of chitosan influences its performance: fungal-derived chitosan generally shows lower antimicrobial activity than crustacean-derived chitosan, although it remains effective against certain Gram-positive strains. Even within crustacean sources, variations between species or anatomical parts can yield differences in activity. Finally, the presence of competing inorganic cations such as Na^+ or Mg^{2+} can reduce antimicrobial performance by interfering with the electrostatic interactions essential to its mode of action [68,75].

Taken together, these aspects highlight the versatility but also the complexity of chitosan as an antimicrobial agent. Its performance depends not only on its intrinsic structural features but also on environmental conditions, microbial species, and formulation strategies, making it a material of high interest for applications in fields such as biomedicine, food preservation, and, more recently, cultural heritage conservation.

2.1.3. Sustainability

Chitin, the natural precursor of chitosan, is one of the most abundant biopolymers on Earth, with an estimated annual production of nearly 100 billion tons [50]. A major source of chitin is the exoskeleton of crustaceans, from which approximately 6–8 million tons of waste are recovered each year [50]. The valorisation of this biomass not only reduces the environmental impact of shellfish industry residues but also enables the recovery of high-value bioproducts, thereby supporting the principles of a circular economy.

Despite this promising potential, conventional methods for producing chitosan from chitin present significant sustainability challenges. The industrial process, which relies on chemical deacetylation, typically requires harsh conditions such as high concentrations of alkaline or acidic reagents (e.g., sodium hydroxide ≥ 40 wt%) and elevated temperatures (≥ 100 °C) maintained for hours or even days [6]. These processes generate large volumes of toxic and corrosive wastewater containing calcium chloride and residual proteins, release greenhouse gases such as carbon dioxide, and lead to the loss of valuable amino acid salts [6]. Furthermore, they are water-intensive, often consuming more than one ton of water for every kilogram of chitin processed. In addition to their environmental impact, such methods frequently compromise product quality, as the severe reaction conditions may cause inconsistent chain scission, uncontrolled molecular weight reduction, and irregular deacetylation patterns, producing polymers with variable properties [4].

In response to these issues, biological methods employing enzymatic deacetylation have been investigated as a more sustainable alternative. Enzyme-based approaches can operate under milder reaction conditions and yield products with more uniform characteristics. However, their large-scale application remains limited by the high cost of enzymes and unresolved regulatory considerations [50].

Recently, attention has shifted towards greener and more efficient methods, in line with the principles promoted by the United Nations Sustainable Development Goals (Agenda 2030), particularly Goal 11 (Sustainable Cities and Communities), Goal 12 (Responsible Consumption and Production), and Goal 13 (Climate Action), which are directly relevant to the sustainable conservation of cultural heritage and the development of environmentally responsible materials [49]. Deep eutectic solvents (DESs) have emerged as particularly promising alternatives, as they enable chitin deacetylation under relatively mild conditions while maintaining high efficiency. DESs such as potassium carbonate, glycerol, choline chloride, acetic acid, and choline chloride, malic acid have been successfully applied, with the latter achieving a degree of deacetylation of 40% within 24 hours at 120 °C. DESs are biocompatible, low-cost, easy to prepare, and highly biodegradable, and they can be recovered and reused over several cycles, thus minimizing waste [5]. Another environmentally friendly approach involves pre-treating prawn shells in hot glycerol. This method eliminates the need for corrosive reagents, reduces CO₂ emissions and water consumption, and enables the recovery of proteins and minerals. Importantly, glycerol can be reused for multiple cycles, particularly when treated with activated charcoal to remove impurities [6]. Ionic liquids (ILs) represent an additional avenue of research, as they permit chitin extraction without significant degradation, thus preserving both molecular weight and degree of deacetylation. Nevertheless, challenges remain with respect to their cost, biodegradability, and large-scale applicability [4,5].

From this perspective, a significant knowledge gap persists regarding the environmental and financial sustainability of chitosan production, particularly when comparing conventional chemical deacetylation with emerging greener alternatives. While several processes have been proposed as environmentally

improved, systematic and comparable data on their life-cycle impacts, resource consumption, scalability, and cost-effectiveness are still limited [66,78,81].

This uncertainty directly affects the downstream application of chitosan-based materials in conservation, where sustainability is increasingly considered a key criterion alongside technical performance. The present research is positioned within this context, acknowledging these upstream limitations and addressing sustainability at the formulation and application level, rather than at the raw-material production stage. By integrating material performance evaluation with environmental assessment tools, this work contributes to bridging the gap between material innovation and realistic conservation practice.

2.1.4. Applications of Chitosan

In recent years, chitosan has attracted remarkable attention across multiple fields, including cosmetics, medicine, food technology, and materials science owing to its unique combination of biological and technological properties. The number of publications and patents dedicated to this polymer continues to increase each year, underscoring its scientific and industrial relevance. One of the main reasons for such widespread interest lies in its abundance and sustainability. Chitosan is derived from chitin, the second most abundant natural biopolymer after cellulose, commonly found in the exoskeletons of crustaceans, insect cuticles, and fungal cell walls [5,7,51].

The valorisation of crustacean shell waste, amounting to several million tons annually, not only mitigates environmental pollution but also enables the recovery of high-value-added materials, thereby supporting circular economy models. Chitin and chitosan belong to a family of linear polysaccharides, and although chitosan has traditionally been produced through chemical deacetylation of crustacean-derived chitin, more recent strategies have expanded

its extraction to alternative biomass sources, often with improved purity and yield [5].

Beyond its availability, chitosan's biological properties make it an exceptionally versatile material. It is inherently non-toxic, biocompatible, and biodegradable, and can be enzymatically degraded in the human body, primarily by lysozymes, into saccharides and glucosamine, which can be metabolized or stored as proteoglycans [4,5]. These characteristics have paved the way for a wide range of biomedical applications. Chitosan also demonstrates antimicrobial activity against both Gram-positive and Gram-negative bacteria, filamentous fungi, and yeasts, a property that has been widely explored in the food, textile, cosmetic, and medical industries [7,51]. Several mechanisms of action have been proposed, including disruption of microbial membranes, interference with genetic transcription and translation, chelation of essential metal ions, and the formation of impermeable surface layers that inhibit nutrient transport. Its antioxidant capacity, attributed to the presence of amino and hydroxyl groups capable of scavenging free radicals, further enhances its biomedical potential, as do its anti-inflammatory properties, which modulate cytokine activity and promote tissue regeneration. Chitosan is also widely recognized for its ability to promote wound healing, encouraging dermal regeneration and supporting mammalian cell adhesion and proliferation. Hydrogels based on chitosan are particularly valuable in this respect, providing a moist wound environment and acting as a barrier to bacterial contamination. Furthermore, its hemocompatibility, including the ability to stimulate blood clotting and activate the complement system, broadens its medical applications [4,51,99,100].

At the molecular level, chitosan owes much of its versatility to its chemical functionality and modifiability. Its structure contains reactive amino ($-NH_2$) and hydroxyl ($-OH$) groups, which can undergo a wide range of chemical modifications, such as acetylation, thiolation, phosphorylation, carboxylation,

sulfonation, alkylation, grafting, and crosslinking. These modifications not only improve intrinsic properties such as solubility and mechanical strength but can also impart entirely new functionalities. Native chitosan is poorly soluble in neutral and basic media, which can limit its physiological applications. However, solubility may be enhanced through protonation of amino groups under acidic conditions or through the synthesis of water-soluble derivatives. For example, homogeneous deacetylation produces polymers soluble in aqueous acetic acid solutions even at relatively low degrees of deacetylation, while quaternised chitosan derivatives are permanently cationic and thus highly soluble in water [7,51].

These intrinsic and engineered properties have enabled chitosan to serve as a platform for a wide range of technological applications. In the biomedical field, it is extensively studied for controlled drug delivery and gene therapy, taking advantage of its cationic nature, mucoadhesive properties, and ability to form polyelectrolyte complexes with negatively charged nucleic acids [101]. Chitosan can be processed into diverse forms: films, scaffolds, nanoparticles, hydrogels, aerogels, microspheres, fibers, and microneedles, each of them tailored to specific uses. In medicine, it is also applied in wound dressings, bone substitutes, diagnostic devices, biosensors, and as scaffolding for tissue engineering. In the food industry, chitosan functions as an antimicrobial and antioxidant agent and as a component of active packaging materials designed to prolong shelf life. Its physicochemical properties further make it attractive for cosmetic formulations ranging from gels and scrubs to oral care products. Additionally, chitosan has been widely explored in the synthesis of metallic nanoparticles, where it acts as a stabilizing and sometimes reducing agent, and in biocatalysis, serving as an efficient support for enzyme immobilization.

Finally, chitosan's scientific and commercial appeal is reflected in its growing market presence. The global market, valued at 1.7 billion USD in 2019, is

projected to reach 4.7 billion USD by 2027, driven by applications in water treatment and expanding use in pharmaceuticals, cosmetics, biomedicine, and food technology. Regulatory agencies currently recognize chitosan and its hydrochloride as excipients, though not yet as therapeutic agents, yet its potential clinical applications continue to attract intense research efforts [4,51].

2.1.5. Chitosan in Cultural Heritage Conservation

In recent years, chitosan has attracted remarkable attention across multiple fields, including cosmetics, medicine, food technology, and materials science, owing to its unique combination of biological and technological properties. Derived from chitin, one of the most abundant natural biopolymers, chitosan is valued for its sustainability, versatility, and ease of chemical modification, which have contributed to its growing scientific and industrial relevance. The polymer also possesses distinctive functional properties, including film-forming capacity, antimicrobial and antifungal activity, and a strong chelating ability toward metal ions. These characteristics, coupled with its structural affinity to polysaccharides such as cellulose, have motivated extensive research on its potential in conservation science.

One of the earliest and most thoroughly explored applications of chitosan concerns the stabilization of paper documents and papyri [102–104]. Derivatives such as carboxymethyl chitosan, alkyl chitosan, and quaternised chitosan have been investigated for their ability to improve tensile strength, folding endurance, and barrier properties of aged paper. Beyond mechanical reinforcement, these treatments have been shown to be effective in enhancing the resistance to microbial attack. Chitosan-based consolidants have similarly proven effective for the preservation of ancient papyri, where formulations enriched with nanoparticles such as zinc oxide further improve both mechanical stability and protection against biodeterioration. Despite these advantages, challenges remain

regarding yellowing, pH compatibility, and solubility under neutral conditions, which require careful optimization, as discussed in the literature [102–104].

In many studies related to the conservation of archaeological wood, it was found that chitosan acts as a multifunctional agent, simultaneously strengthening degraded structures and mitigating catalytic degradation by chelating reactive metal ions [105]. Aqueous solutions of chitosan have shown promising penetration into waterlogged wood, improving cohesion without excessive clogging of pores. Modified derivatives, such as tert-butyldimethylsilyl chitosan soluble in organic solvents, have been proposed for highly acidic alum-treated wood, where non-aqueous approaches are essential. These treatments not only enhance mechanical stability but also enable future retreatments, highlighting the adaptability of chitosan in addressing the complex challenges posed by archaeological substrates [105,106].

Chitosan has also been studied as a protective coating for metals such as bronze and silver [107,108]. Transparent, colourless, and easily removable chitosan films create a protective barrier while maintaining the aesthetic integrity of cultural heritage objects. Incorporation of corrosion inhibitors, notably benzotriazole, enhances anticorrosive performance, although pure chitosan often performs equally well under museum storage conditions. Its ability to coordinate with metal ions contributes to surface passivation and the formation of stable protective layers.

Stone conservation represents another significant area where chitosan-based systems have demonstrated potential. By inhibiting salt crystallization within porous matrices, chitosan coatings limit structural damage and promote efflorescence at the surface rather than destructive subflorescence [109,110]. Hybrid formulations that combine chitosan with inorganic consolidants, such as hydroxyapatite or silane-polysaccharides, have shown particular promise, combining consolidation with antimicrobial activity [110–114]. Recent research

developments also include nanocomposite coatings incorporating halloysite nanotubes, antioxidants, and metal oxide nanoparticles to enhance durability, resistance to photo-oxidation, and antimicrobial performance, all while maintaining permeability to water vapour [112–117].

Further applications have been reported in the stabilization of textiles and cartonnage [114,118]. For example, carboxymethyl chitosan has improved the mechanical properties and thermal stability of historic silk [119], while chitosan–silver nanocomposites have been successfully applied to ancient Egyptian linen without significant alterations to appearance. In cartonnage, chitosan has offered effective consolidation and microbiological protection, though aesthetic issues such as yellowing remain a concern [106].

On the other hand, antifungal formulations based on low molecular weight chitosan have been explored for tempera paintings, demonstrating strong bioactive performance at low concentrations without significant optical changes [120].

While chitosan presents significant advantages as a multifunctional and environmentally friendly material, its application in conservation still poses challenges related to molecular weight, penetration, compatibility with original substrates, and long-term stability. These aspects require careful formulation design and remain the focus of ongoing research [7,121].

In this broader perspective, the growing interest in chitosan reflects a more general need within conservation science for green, multifunctional materials capable of addressing multiple requirements simultaneously. Contemporary conservation challenges increasingly demand products that combine mechanical stabilization, chemical compatibility, antimicrobial activity, durability, reversibility, and reduced environmental impact, rather than single-function solutions. Biopolymer-based systems, and chitosan in particular, offer a versatile

platform that can be chemically tailored and hybridized to meet these complex demands.

Beyond the specific applications discussed in this work, the multifunctional nature of chitosan-based formulations opens promising perspectives for the development of next-generation conservation materials, including hybrid coatings, smart or responsive systems, and formulations designed to integrate preventive conservation and planned maintenance strategies. Such approaches may find application not only in mural painting conservation, but also in broader areas of built heritage, archaeological materials, and outdoor cultural heritage exposed to aggressive environmental conditions. In this sense, chitosan-based systems can be regarded not merely as alternative materials, but as part of a wider methodological shift toward sustainable, multipurpose solutions in heritage conservation [127,128].

2.1.6. Molecular Mechanisms of Chitosan exploited in Cultural Heritage Conservation

The effectiveness of chitosan in cultural heritage conservation can be traced to its distinctive molecular structure. As a cationic polyelectrolyte bearing both amino and hydroxyl groups, chitosan is capable of establishing a wide range of interactions with organic and inorganic substrates, including hydrogen bonding with polysaccharide matrices, coordination with transition metal ions, and ionic interactions with soluble salts. Depending on its formulation, molecular weight, and application mode, these interactions can support two distinct conservation functions: consolidation and surface protection. When applied as a consolidant, chitosan penetrates the porous or fibrous structure of degraded materials, where it contributes to restoring mechanical cohesion through intermolecular bonding and reinforcement of weakened networks. In this role, its effectiveness is primarily related to penetration depth, molecular affinity with the substrate, and the formation of stabilizing interactions within the bulk material.

In contrast, when applied as a protective coating, chitosan primarily acts at the surface, forming a thin, continuous film that reduces the interaction between the artwork and external environmental agents such as moisture, pollutants, and biological contaminants. In this case, the key functional requirements shift toward optical transparency, vapour permeability, chemical compatibility, and controlled interaction with the underlying layers, rather than bulk mechanical reinforcement.

This functional distinction is particularly relevant for contemporary mural paintings, where the use of chitosan as a surface protective coating aims to mitigate environmental degradation while preserving the visual appearance and material integrity of modern paint films, rather than consolidating structurally degraded substrates.

One of the most important interactions occurs with cellulose, the dominant component of paper and many historical textiles. Owing to their structural similarity (chitosan is composed of glucosamine and N-acetylglucosamine units, which closely resemble the glucose units of cellulose) the two polymers are able to form extensive hydrogen bonding networks [105,130]. The amino and hydroxyl groups of chitosan readily bind to the hydroxyl groups of cellulose, creating intermolecular bridges that enhance fiber cohesion. This interaction not only increases the mechanical resistance of degraded cellulosic materials, such as ancient papyri, but also facilitates the formation of continuous chitosan films that act as consolidants [104,105,130]. In the case of silk, the incorporation of carboxymethyl-chitosan has been shown to establish hydrogen bonds with fibroin chains, leading to significant improvements in both tensile strength and thermal stability [131].

The high degree of chemical compatibility between the chitosan and cellulose further ensures that consolidation occurs without adverse side effects, while the

cationic nature of chitosan under mildly acidic conditions enhances its binding to negatively charged substrates such as degraded archaeological wood [104,130]. A second crucial mechanism involves the chelation of metal ions. Archaeological wood, particularly when waterlogged, often contains transition metals such as iron and copper that catalyze degradation processes. Chitosan, through the lone electron pairs on its amino and hydroxyl groups, is able to coordinate these metal ions and immobilize them. This chelating activity is pH dependent but remains effective even under acidic conditions, making it highly suitable for archaeological contexts. By binding such ions, chitosan reduces their catalytic activity and mitigates their detrimental effects on both the wooden matrix and any applied consolidants. On metallic artifacts themselves, the ability of chitosan to coordinate with surface cations contributes to the formation of passivating layers. For example, its strong affinity for copper ions supports the development of stable polymer–metal complexes, which act as protective barriers. The incorporation of corrosion inhibitors such as benzotriazole can further stabilize these interactions, preventing ion migration and maintaining the transparency and integrity of the chitosan coating on bronzes and silver alloys [105,108,126] .

Chitosan also plays a significant role in addressing salt-induced damage in stone and brick structures, where crystallization of salts within porous matrices can lead to severe deterioration. Thanks to its cationic character, chitosan interacts with anionic species such as sulphates, effectively sequestering them from solution and thereby inhibiting the crystallization of sodium sulphate [109]. When adsorbed onto porous mineral surfaces, chitosan can redirect crystallization to occur externally, forming less harmful efflorescences rather than destructive subflorescence. Pre-treatments that modify the substrate, such as the deposition of hydroxyapatite layers, have been shown to improve the anchoring of chitosan films, enhancing their protective effect. Moreover, crosslinked formulations – for instance, those obtained with citric acid or sodium

tripolyphosphate – exhibit controlled swelling and water solubility while preserving water vapour permeability, features particularly desirable for breathable stone conservation treatments.

Taken together, these mechanisms demonstrate that the molecular versatility of chitosan underlies its broad potential in cultural heritage applications. By forming hydrogen bonds with cellulosic substrates, chelating catalytic metal ions, and interacting with harmful salts, chitosan provides both structural reinforcement and chemical protection. Understanding these interactions at a molecular level is key to optimizing chitosan formulations and tailoring them to the specific needs of different heritage materials, ultimately enabling more durable and sustainable conservation strategies.

2.1.7. Formulation and Application Techniques of Chitosan in Cultural Heritage Conservation

The efficacy of chitosan in cultural heritage conservation is closely linked to the methods used for its formulation and application, which directly influence penetration, adhesion, and overall performance. Various strategies have been employed depending on the material type and the intended treatment outcome. For paper-based artifacts, carboxymethyl-chitosan (CMCH) is typically applied by brush on both sides of the sheet, allowing uniform consolidation [102].

In the case of waterlogged archaeological wood, immersion in chitosan solutions has been shown to achieve penetration within two weeks, while partially submerged treatments have been used for stone surfaces with ammonium phosphate and chitosan solutions over 24 hours [105,109]. Spray-coating techniques are increasingly employed, particularly for metallic artifacts such as silver objects or outdoor stone sculptures. For instance, ZnO/CuO@chitosan hydrogels have been optimized for spray application on granite and marble, with viscosity adjustments facilitating even deposition [108,114]. Similarly, chitosan

nanoparticles loaded with natural biocides, such as thymol, can be sprayed on stone surfaces to provide controlled release of the active compound while minimizing application frequency [132]. Drop-casting techniques are applied for thin chitosan films on bronze and silver alloys, allowing precise volumetric deposition and ambient drying [107,108]. Solvent casting is used to fabricate bio-nanocomposite films of chitosan and pectin incorporating natural antioxidants and reinforcing fillers, as well as hybrid silane-chitosan formulations [115,116]. Hydrogels, meanwhile, are synthesized to achieve a balance of viscosity and mechanical stability suitable for targeted application on complex surfaces [114].

The chemical environment of chitosan solutions is critical for their performance. Solubility is ensured in mildly acidic aqueous solutions below pH 6, where amino groups are protonated, while viscosity reaches a minimum between pH 3 and 4, optimizing penetration into porous substrates such as degraded wood [107,109,128]. For acid-sensitive materials like stone, solutions are initially prepared at acidic pH to dissolve chitosan, then adjusted to neutral conditions (pH 5–7) with bases such as NaOH or NH₄OH to avoid substrate damage [109,110]. For metal treatments, maintaining a slightly acidic to neutral pH (~6) prevents surface corrosion while ensuring chitosan remains soluble [107]. The choice of solvent also plays a pivotal role: acetic acid is widely used for general solubilization, while D-(+)-gluconic δ -lactone (GDL) is preferred for metallic applications due to its gradual acidification, yielding homogeneous, transparent films and avoiding the formation of lead-rich deposits on bronze alloys [107,108,117]. Water/ethanol mixtures are employed to optimize wettability and polymer solubility, and in cases where aqueous treatments are unsuitable, such as alum-treated archaeological wood, tert-butyl-dimethylsilyl chitosan (TBDMS-chitosan) dissolved in organic solvents like ethyl acetate/toluene enables

penetration without swelling the wood, preserving the possibility of future retreatments [107,108,129].

Molecular weight further modulates chitosan's effectiveness. Lower molecular weight chitosan (e.g., 12–25 kDa) demonstrates superior penetration into degraded wood matrices and exhibits enhanced antifungal activity on sensitive surfaces such as historic paintings. Conversely, higher molecular weight forms penetrate less effectively, limiting their applicability in certain substrates. Depolymerization techniques, such as nitrite treatment, can be employed to fine-tune molecular weight, marginally improving uptake while maintaining the intrinsic chelating and antimicrobial capabilities of the polymer [105,129].

Nanotechnology has significantly advanced the application of chitosan in conservation, enhancing delivery, adhesion, and overall performance [118,120,127,133]. Chitosan nanoparticles penetrate damaged zones more effectively, ensuring internal reinforcement where bulk polymers may fail [104]. Nanocomposites, including chitosan-ZnO and chitosan-cellulose combinations, improve interfiber cohesion, tensile strength, and optical properties in paper and textile substrates. The incorporation of inorganic nanocarriers, such as halloysite nanotubes loaded with natural antioxidants, stabilizes bionanocomposite films, enhancing their long-term durability and resistance to photooxidation. Furthermore, nanostructured systems allow controlled release of biocides, as seen with thymol-loaded chitosan nanoparticles for stone conservation, mitigating volatility issues and reducing the frequency of application [117,132].

Nanocomposites also confer enhanced antimicrobial, mechanical, and optical properties, crucial for the protection of diverse cultural heritage objects. Methods such as ionic gelation, sonication, emulsification-gelation, and blend mixing are routinely employed to synthesize well-dispersed chitosan nanoparticles and nanocomposites suitable for targeted application [104,106,117,132].

In general, the careful selection of application techniques, control of pH, solvent choice, and molecular weight, in combination with the incorporation of nanotechnologies, is essential for optimizing and tailoring chitosan-based conservation treatments. These parameters ensure effective penetration, adhesion, and performance while preserving the integrity and long-term stability of cultural heritage artifacts, supporting the development of sustainable, multifunctional conservation strategies.

From a research perspective, these considerations directly inform the present study. In particular, the relationship between chitosan depolymerization, molecular weight reduction, and penetration depth is central to the research questions addressed in this thesis, especially in relation to the interaction between protective coatings and modern painted substrates. Understanding how controlled depolymerization and formulation parameters influence penetration and surface interaction is essential for tailoring chitosan-based systems to contemporary mural paintings, where surface protection rather than bulk consolidation is required.

2.1.8. Case Studies on the Application of Chitosan in Cultural Heritage Conservation

Chitosan has been the main subject of numerous studies and practical applications in cultural heritage conservation, with several documented case studies highlighting its potential effectiveness, albeit with variable outcomes depending on the substrate and formulation used. One notable example involves the consolidation of an ancient Egyptian funerary shroud, dating to approximately 1850 BCE and belonging to Hatnofer, the mother of Senenmut, currently preserved at the Egyptian Museum in Cairo. The shroud, composed of plain-weave linen with inscriptions in carbon and metallic ink from the Book of the Dead, was treated using a nanocomposite of crosslinked chitosan (CCTS)

coated with Ag-loaded nano-SeO₂ (CCTS-SLS) [118]. This formulation was selected due to its superior physico-mechanical, chemical, and antimicrobial properties compared to conventional chitosan. The application involved “polymer reactivation,” in which silk supports reinforced with the polymer (10% concentration in acetic acid) were dried and then placed beneath the shroud, followed by paper pulp impregnated with diluted acetic acid to gently reactivate the polymer, limiting adhesion forces between the support and the artifact. Accelerated aging tests and in-situ monitoring using artificially aged linen samples inoculated with fungi and bacteria isolated from the ancient shroud demonstrated that the CCTS-SLS maintained its properties without critical deformation, in contrast to standard chitosan, which exhibited complete deformation. The nanocomposite also conferred significant antibacterial resistance, enhancing the long-term durability of the linen.

In contrast, the consolidation of archaeological cartonnage, composed of textile supports, a calcium carbonate preparation layer, and pigments such as Egyptian blue and red ochre, yielded less favourable results [106]. Chitosan solutions (3–5% in ethanol), alone or combined with nano-calcium hydroxide and compared to Klucel G, were applied using Japanese paper strips. Accelerated aging under simulated Egyptian burial conditions (80 °C, 65% relative humidity for 264 hours) revealed significant yellowing correlated with concentration. The addition of nano-calcium hydroxide partially mitigated the effect, but optical and SEM analyses indicated severe surface staining, agglomeration, and fissuring, rendering chitosan unacceptable for this material.

Chitosan’s effectiveness is further illustrated in outdoor stone conservation. At Feilaifeng, Hangzhou, China, limestone surfaces were treated with thymol-loaded chitosan nanoparticles via spray application (10 mL of 0.1% solution over 10×10 cm areas) [132]. Both accelerated aging and in-situ monitoring

demonstrated superior performance against *Aspergillus niger* compared to free thymol, with controlled biocide release significantly reducing microbial activity, as evidenced by ATP measurements.

Moving to metal artifacts conservation, Boccaccini et al. conducted a study on sterling silver discs replicating the chemical composition and microstructure of historical objects comparing pure chitosan coatings, chitosan with benzotriazole (BTA), and a commercial acrylic resin (Incral 44) [108]. Accelerated aging under ammonium sulphide vapours showed that the chitosan/BTA coating performed comparably to Incral 44 for up to 10 hours, whereas pure chitosan exhibited slight green-yellowing due to copper-sulfur compound formation. Long-term in-situ monitoring over 30 months revealed that pure chitosan more effectively preserved silver surfaces than the BTA-containing film, with yellowing less pronounced and linked to nanoparticle migration and nucleation.

Finally, the consolidation of aged papyrus from Al-Qaramous, Egypt, demonstrated the advantages obtained through the use of nanomaterials [104]. Traditional chitosan, nano-chitosan, and chitosan-ZnO nanocomposites were tested and compared. Accelerated thermal aging showed that chitosan-ZnO nanocomposites significantly improved tensile strength and antibacterial properties. Nano-chitosan achieved better distribution and surface coverage than conventional chitosan, while the ZnO component enhanced antibacterial efficacy and reduced biodeterioration. These studies collectively highlighted the promising properties of chitosan and its derivatives for cultural heritage conservation, while emphasizing the necessity of careful formulation and application to avoid adverse effects such as yellowing and to ensure long-term compatibility with different substrates.

2.1.9. Limitations and Open Questions in the Use of Chitosan for Cultural Heritage Conservation

Despite its promising potential, the application of chitosan in cultural heritage conservation presents several limitations and unresolved issues that warrant further investigation. One primary concern is yellowing, which has been observed in some cases as a significant colour change towards yellow, often increasing with higher chitosan concentrations, as exemplified in archaeological cartonnage [106]. Similarly, prolonged exposure of silver artifacts under simulated museum conditions (up to 30 months) resulted in yellowing of both pure chitosan and chitosan/benzotriazole coatings, with the effect more pronounced in the latter [108]. This phenomenon has been linked to the migration and nucleation of silver nanoparticles within the polymeric film. For papyrus, traditional chitosan showed a greater tendency to yellow during thermal aging compared to nano-chitosan and nanocomposites, while on stone, although visible chromatic alterations were not apparent, detailed colorimetric analyses remain necessary to confirm stability [104,112]. The issue of compatibility also persists: although chitosan exhibits structural affinity with cellulose and is generally considered compatible with stone, many concerns remain regarding its interactions with other paper components, inks, and decorative elements, as well as its actual deposition and adhesion on mineral surfaces [102,103,109,113].

Reversibility represents another critical aspect. Conservation principles dictate that treatments should allow for safe removal or re-treatment. As a biodegradable biopolymer, chitosan is expected to degrade naturally without leaving harmful residues, permitting future interventions and re-treatments. On metals such as silver or copper-based alloys, chitosan coatings have been shown to be easily removed with water or ethanol without visible residues, and the incorporation of corrosion inhibitors like BTA or MBT can further facilitate removability [107,108]. However, accelerated corrosion tests on bronze revealed that pure

chitosan may leave residues after removal, indicating incomplete detachment under aggressive conditions. For archaeological wood, ideal consolidants should preserve an open structure to enable future treatments; in this context, both standard chitosan and tert-butildimethylsilyl-chitosan (TBDMS-chitosan) demonstrated the ability to coat cell walls without fully filling lumina, allowing for straightforward re-treatment [105,128,129]. In stone sculptures, crosslinked chitosan formulations have exhibited partial solubility and water vapour permeability, suggesting potential reversibility under controlled conditions. However, studies on chitosan coatings applied to calcite-based substrates indicate that adsorption phenomena and formulation-dependent interactions may locally reduce water transport. These apparently divergent observations reflect the strong influence of substrate mineralogy, formulation parameters, and crosslinking degree, highlighting the need for careful case-by-case evaluation rather than representing a true contradiction [109,113]. Carboxymethylated chitosan, being water-soluble, facilitates removal in aqueous systems [102].

Long-term stability is aspect that requires attention. Accelerated aging tests and exposure to environmental stressors such as UV light, humidity cycles, and pollutants reveal that chitosan may undergo degradation. On silver, extended storage showed yellowing linked to nanoparticle migration, suggesting that time significantly influences film alteration [108]. The stability of metal-inhibitor complexes (e.g., Cu-BTA, Ag-BTA) may decrease, leading to migration of elements within the polymeric matrix. For archaeological wood, TBDMS-chitosan appears stable under moderate pH conditions, whereas pure chitosan on bronze demonstrated polymer degradation likely due to acid-catalyzed hydrolysis of the pyranose ring [105,129]. Photo-oxidation of chitosan/pectin bio-nanocomposites is another concern, mitigated through the incorporation of halloysite nanotubes and natural antioxidants [115,116]. The release of active agents remains a challenge for nanocomposites; encapsulation strategies, such as

thymol-loaded chitosan nanoparticles, have proven effective in controlling release and enhancing long-term efficacy [127,132]. Nonetheless, onsite durability, particularly given chitosan's biodegradability, still requires extensive field evaluation [109].

Moreover, the lack of standardized protocols complicates reproducibility. Testing for salt crystallization damage in porous substrates, commonly used to evaluate chitosan efficacy, often varies between studies, with no universally accepted method to quantify damage reliably [109]. Similarly, antimicrobial activity assessments are inconsistent due to differences in microorganisms and testing conditions [113]. For chitosan-cellulose composites, the absence of agreed analytical protocols limits broader implementation [130]. All these challenges underscore the need for further research to address long-term durability, colour stability, and methodological standardization, ensuring that chitosan-based treatments are both effective and sustainable in cultural heritage conservation.

2.1.10. Future Directions for the Use of Chitosan in Cultural Heritage Conservation

Future prospects for the use of chitosan in cultural heritage conservation are moving toward the development of innovative systems that combine its sustainable nature with advanced functionalities, aiming to provide smart, multifunctional, and monitorable protection [128]. In particular, research is focused on creating hybrid composite materials capable not only of consolidating and protecting artifacts but also of actively responding to environmental changes. Among the most promising strategies is the incorporation of nanoclays, such as halloysite nanotubes (HNTs), which act both as physical compatibilizers and as carriers for natural antioxidant molecules (vanillic acid and quercetin), enhancing the durability and photo-oxidation resistance of chitosan/pectin nanocomposites [115,116].

Further developments involve the use of reactive nanoparticles for self-healing systems, such as the supramolecular PolyCatNap polymer network based on chitosan and guar gum, crosslinked with cucurbituril, which simultaneously addresses chemical, biological, and mechanical challenges [116,128]. Functionalization with catechol units enables the capture of iron ions responsible for degradation, increasing the dimensional stability of the polymer network within wooden materials and paving the way for active, adaptive treatments. Similarly, integrating corrosion inhibitors such as benzotriazole (BTA) or mercaptobenzothiazole (MBT) into chitosan coatings for copper alloys exemplifies hybrid approaches aimed at active protection of metals [107,127]. Sustainability remains a guiding principle, in these developments, supported by the use of renewable resources and greener extraction processes, including deep eutectic solvents and enzymatic methods. In parallel, bio-inspired approaches and lignin-derived materials are being explored to ensure high compatibility with heritage substrates and to promote the formation of environmentally responsible hybrid systems [128–130].

[109,115,116,128,129][103] Digital monitoring and portable analytical techniques play an increasingly important role in evaluating in-situ performance and understanding degradation processes over time. The intrinsic fluorescence of chitosan is under investigation as a potential indicator of dispersion and penetration within treated substrates, while tools such as the Drill Resistance Measuring System (DRMS) allow the assessment of salt distribution in porous materials. While chitosan's biodegradability supports reversibility, it also highlights the need for long-term monitoring to assess durability and to inform future maintenance strategies [109,112].

2.2. Nanosilica

2.2.1. General properties

The general properties of nanosilica (SiO_2 nanoparticles) are widely documented in the literature, with particular emphasis on their application in the field of conservation and protective coatings. These properties can be considered under four main aspects: structure, mechanical resistance, surface characteristics, and chemical stability.

Nanosilica consists of SiO_2 nanoparticles dispersed in silicon-based products and represents one of the most important recent nanomaterials [134]. Colloidal silica is typically composed of amorphous spherical particles with diameters ranging from 5 to 100 nm [135,136]. XRD pattern is most common, different morphologies have been reported [136,137]. For example, rice husk ash-derived nanosilica presents rigid spherical particles in the range of 50–200 nm, while commercial products such as Sigma (10–20 nm) or Arosil (7–12 nm) supply porous nanosilica [135,137]. Elongated morphologies have also been documented [135]. Depending on synthesis and product type, typical particle sizes range from below 50 nm up to about 200 nm, with smaller diameters (7–12 nm) being preferred for transparent coatings and resin formulations, especially when combined with high solid content (30–40 wt%) [134,137–139].

One of the most important contributions of nanosilica is the improvement of mechanical performance in host materials [140]. By nature, SiO_2 nanoparticles possess high hardness (approximately 5.5 on the Mohs scale), toughness, and strength [139]. When incorporated into polymers or composites, they act as reinforcement agents, increasing compressive strength and abrasion resistance [137]. For example, coatings exhibit significantly enhanced wear resistance when nanosilica is introduced. This reinforcing action is generally attributed to cross-linking interactions between the inorganic SiO_2 phase and the surrounding organic matrix, leading to more robust composite films [134,137,139,140].

2.2.2. Surface Properties

The effectiveness of nanosilica also derives from its high specific surface area (SSA) and the reactivity of its surface chemistry [135,141]. Spherical particles can exhibit SSA values of around 360 m²/g, while elongated morphologies can reach up to 1100 m²/g [135]. The surface of silica sols is fully hydroxylated and characterized by silanol (Si–OH) groups, which impart strong polarity [44,141,142]. The surface charge of nanosilica depends strongly on pH: in aqueous sols at pH values above 8, particles are typically stabilized by strong electrostatic repulsion, being negatively charged due to deprotonated silanols [141,142]. At lower pH (around 3), the charge is only weakly negative [135,143]. Commercial products are available in different surface states: unmodified (weakly anionic), strongly anionic, or cationic, the latter often obtained through surface modification with aluminium-based species [135,141]. Surface functionalization is crucial for tuning dispersion and compatibility; silanization, for example, reduces the number of surface charges and silanol groups, improving sol stability [134–136,141,142]. Hydrophobic nanosilica (HNS), in particular, is produced by modifying the surface with hydrophobic groups, thereby extending its applicability in systems where water resistance is required [136].

2.2.3. Chemical Stability

Nanosilica is highly valued for its chemical robustness and stability under aging. SiO₂ is thermally stable and resistant to high temperatures. The incorporation of nanosilica into polymer matrices enhances both the thermal stability and the weathering resistance of coatings, helping to mitigate degradation caused by acids, salts, or atmospheric erosion [134,137,140]. In terms of colloidal stability, silica sols are generally sensitive to electrolytes and prone to aggregation; however, surface silanization introduces steric hindrance that, combined with

electrostatic repulsion, greatly improves resistance against gelation induced by salts or freezing [142].

2.2.4. Other Relevant Properties

Amorphous silica displays some degree of water solubility, particularly under acidic conditions, where colloidal silica may become metastable and gel within days if not stabilized. SiO_2 also possesses a low refractive index (1.45), which makes it especially useful for optical applications. In aqueous formulations, nanosilica can be employed to produce single-layer antireflective coatings with excellent performance, combining transparency with durability [134,142,143].

The combination of structural characteristics, mechanical reinforcement, surface reactivity, and chemical stability makes nanosilica a particularly attractive nanomaterial for use in conservation science and advanced protective systems.

2.2.5. Nanosilica applications in coatings and composites

The widespread use of nanosilica (SiO_2) in coatings and composite materials can be attributed to its peculiar combination of chemical, physical, and mechanical properties, which substantially enhance the performance of host matrices. These improvements align closely with contemporary demands for durability and sustainability, particularly in fields such as cultural heritage conservation and construction materials.

A primary advantage of nanosilica lies in its reinforcing capacity, which imparts superior mechanical properties compared to conventional fillers [134,136,137]. Due to its intrinsic hardness, strength, and toughness, nanosilica enhances the resistance of polymeric matrices to abrasion and scratching [136,137,139,140,142,144]. For instance, the incorporation of Levasil nanoparticles into aqueous silica sols has been shown to increase pencil hardness up to 3H while maintaining optical transparency [139].

Similarly, nanosilica contributes to the compressive strength of polymer composites and promotes cross-linking interactions between the organic and inorganic phases, thereby improving structural cohesion [134,136,137,140].

Beyond mechanical reinforcement, nanosilica plays a crucial role in enhancing the durability and stability of materials under harsh environmental conditions. Its natural resistance to corrosion, weathering, and thermal degradation prolongs the service life of composites [134,137,139,140]. Hybrid systems such as SiO₂/fluoroacrylate coatings demonstrate improved water resistance and atmospheric stability, while the incorporation of nanosilica in acrylic matrices enhances resistance to solvent penetration and moisture absorption [140]. Moreover, nanosilica can improve thermal stability, confer UV resistance, and strengthen chemical resilience, making it especially advantageous for outdoor applications [136,137,140,142,144].

In the context of mural preservation, these properties are particularly relevant for mitigating weathering phenomena such as moisture ingress, UV-induced degradation, and pollutant-driven deterioration of modern paint films.

Equally important is the versatility of nanosilica, which can be tailored for diverse functional roles. Its surface can be chemically modified to improve dispersion and compatibility with polymer matrices, as well as to introduce specific functionalities [134–136]. For example, functionalized silica nanoparticles can act as active molecules, illustrating the broader multifunctional potential of nanosilica-based hybrid systems. While such approaches are extensively explored in corrosion protection, in the context of mural conservation this concept is primarily relevant as a model for controlled interaction with the environment and long-term durability, rather than for corrosion inhibition in the strict sense.[111,136,141]In addition, nanosilica's low refractive index (1.45 for SiO₂) makes it an ideal component in transparent coatings and resins [142]. Within the field of heritage conservation, nanosilica is widely employed as a

consolidant for porous materials, filling voids and densifying structures to restore their mechanical and physicochemical integrity [134]. In treatments based on tetraethyl orthosilicate (TEOS), the addition of silica nanoparticles has been shown to reduce gel cracking during drying, thereby improving the efficacy of the consolidating system [134,136,138,144,145]. In hybrid protective coatings for contemporary murals, nanosilica primarily contributes to improving cohesion, durability, and compatibility of surface treatments, rather than acting as a bulk consolidant.

From an environmental and practical perspective, nanosilica also offers notable benefits. Colloidal silica nanoparticles are readily available and relatively inexpensive, supporting their broad industrial application [142]. Furthermore, water-based formulations containing nanosilica contribute to greener production practices by minimizing the use of volatile organic compounds (VOCs) [137,139]. Nanosilica is generally associated with low toxicity, and its hydrophobic variants are particularly valuable for enhancing the moisture resistance of polymers such as hydroxypropylcellulose, thereby improving their performance as consolidants [134,135].

In summary, nanosilica enables the development of multifunctional hybrid systems with improved mechanical strength, environmental resistance, and thermal stability. In the specific framework of mural preservation, its role is not linked to corrosion inhibition, but rather to the enhancement of durability, transparency, and resistance to weathering processes. These characteristics support the design of sustainable hybrid coatings capable of protecting contemporary painted surfaces under outdoor exposure while maintaining their visual and material integrity.

2.2.6. Applications of nanosilica in cultural heritage

The application of nanosilica (SiO_2 nanoparticles) in the field of cultural heritage conservation has advanced considerably over the past decades, owing to the unique chemical, mechanical, and surface properties of these nanomaterials. Their use has opened new perspectives for the consolidation, protection, and stabilization of both inorganic and organic cultural substrates, and they have proven particularly valuable when employed in hybrid materials designed to merge the advantages of organic and inorganic components [111,134].

One of the most widely explored applications is the consolidation of lithic materials, such as sandstones and limestones, which often lose cohesion as a result of prolonged exposure to weathering and other deterioration processes [138,146]. Ethyl silicate (TEOS)-based treatments are among the most traditional consolidants for siliceous stones, but they frequently suffer from limitations, including the formation of brittle gels prone to cracking during drying [145,146]. The incorporation of nanosilica into TEOS formulations has been shown to mitigate these shortcomings. The resulting nanocomposites exhibit enhanced compressive strength, greater resistance to erosion, acids, and salts, and improved pore-filling capacity, while maintaining compatibility with the stone substrate [145,146]. Furthermore, the addition of oligomeric silica precursors and surfactants such as n-octylamine allows the formation of homogeneous, crack-free coatings with superior durability compared to commercial products [134]. Beyond stone, nanosilica has also been tested for the consolidation of cementitious heritage materials, such as mortars and concrete. When used alone or in combination with nanolime or TEOS, nanosilica contributes to improved pore filling, slight increases in mechanical strength, and stabilization without perceptible changes in porosity or colour [134,146].

In addition to consolidation, nanosilica plays a crucial role in the development of protective coatings. Owing to its ability to enhance hydrophobicity, thermal

resistance, and self-cleaning activity, it has been integrated into a range of multifunctional formulations. Hybrid nanocomposites based on nanosilica and fluoroacrylates (SiO_2/FPA), for instance, have been successfully applied to the preservation of stone surfaces, such as the inscriptions of the Jiaoshan Steles Grove in China, where they improved water resistance, weathering stability, adhesion, and hardness [140]. Similarly, the incorporation of nanosilica into polydimethylsiloxane (PDMS) matrices generates superhydrophobic coatings (contact angle $>150^\circ$), where the dual-scale surface roughness created by the nanoparticles entraps air beneath water droplets, thus providing strong repellency against water, the primary vector of degradation in building materials [146]. These coatings also show promise as anti-graffiti barriers, provided they remain transparent, aging-resistant, and reversible. Moreover, composites of TiO_2 and SiO_2 nanoparticles act as photocatalytic self-cleaning agents, coupling hydrophobic properties with enhanced mechanical resistance [147].

The versatility of nanosilica extends to its compatibility with both inorganic and organic cultural substrates. In fibrous cellulose-based supports such as canvas paintings, nanosilica has been employed to reinforce degraded fibers and simultaneously act as a deacidifying agent, due to its intrinsic alkalinity. More complex hybrid systems, combining silica nanoparticles with polyelectrolytes and cellulose nanofibers (CNF) or nanocrystals (CNC), have been developed to provide both rigidity and ductility, yielding a balanced consolidating effect [111,148,149]. This dual approach, where nanosilica stabilizes the substrate while CNF or CNC preserve flexibility, is particularly valuable for the long-term stabilization of acid-degraded iron-gall ink manuscripts and canvases [111,148,149]. For ceramic artifacts, nanosilica has been used in combination with hydroxypropylcellulose (HPC) to improve mechanical stability and water resistance. In particular, the incorporation of hydrophobic nanosilica (HNS) transforms the inherently hydrophilic HPC into a hydrophobic consolidant,

protecting ceramics against moisture while minimizing unwanted colour changes such as yellowing under sunlight [136,149].

The importance of nanosilica is further amplified in the context of hybrid organic–inorganic materials, where it acts as a reinforcing and performance-enhancing agent. Its high intrinsic hardness and toughness contribute to increased abrasion resistance and scratch durability of composite films [137,140]. The strong reinforcement effect often derives from cross-linking between the organic polymer phase and the inorganic silica phase, leading to improved cohesion and mechanical stability [137,140]. In addition, hyperbranched polysiloxane-silica systems (HB-PolySi) have been explored to reduce viscosity, facilitating better penetration into porous substrates while maintaining effective reinforcement [150]. From a chemical standpoint, nanosilica improves resistance to weathering, solvents, and thermal stress, while also preserving the vapour permeability of treated substrates, a critical requirement in conservation practice [134,137,138,140,150]. Importantly, nanosilica displays low toxicity and can be readily functionalized with specific molecules, allowing fine-tuning of surface interactions for particular applications. Compared to purely organic polymers, silica-based systems also demonstrate superior resistance to aging and enhanced compatibility with siliceous substrates [134,141].

In conclusion, nanosilica has emerged as a key nanomaterial in cultural heritage conservation, offering significant advantages for the consolidation of porous materials, the development of protective and functional coatings, and the design of advanced hybrid systems. By combining mechanical reinforcement, chemical durability, surface tunability, and environmental compatibility, it provides a versatile and sustainable strategy to address the challenges posed by the preservation of diverse cultural substrates.

3. Chitosan–Nanosilica hybrids

3.1. Rationale for combining the two materials.

The integration of chitosan with nanosilica or silica precursors within organic–inorganic hybrid materials has attracted increasing attention due to the wide range of synergistic effects that arise from their combination [151–153]. This strategy is motivated by the need to enhance the physical, mechanical, chemical, and biological performance of the resulting composites, and has been explored extensively in fields such as biomedicine, environmental science, and material engineering. In the context of cultural heritage preservation, and particularly for the conservation of street art, this kind of hybrids are especially promising because they combine mechanical strength, adhesion, stability, and sustainability, all those qualities that are often difficult to achieve simultaneously in a single material system [152,154].

From a structural perspective, the incorporation of nanosilica serves as an effective reinforcement strategy for chitosan, addressing one of the main limitations of the pure biopolymer: its insufficient mechanical strength. The rigidity of the inorganic phase counterbalances the elasticity of the organic component, resulting in hybrids with markedly improved compressive strength and elastic modulus [154–157]. In some systems, the addition of silica has been reported to increase the elastic modulus by up to two orders of magnitude compared to unmodified chitosan, while also imparting superior thermal stability [155]. The nanoparticles act as barriers to volatile and degradable organic compounds, thereby reducing thermal degradation [151,152,158]. Another critical improvement lies in dimensional stability: nanosilica reduces the excessive swelling and hydrophilicity typical of chitosan films, ensuring enhanced water resistance and lower moisture uptake [152]. This property is particularly advantageous for applications in humid or outdoor environments,

where hybrid networks absorb significantly less water than their individual components [154,155,158].

The biological properties of these hybrids are equally compelling. Chitosan is inherently biocompatible, biodegradable, and non-toxic, supporting cell adhesion and proliferation, whereas silica contributes decisive bioactivity. In biomedical studies, silica-containing chitosan hybrids have demonstrated rapid hydroxyapatite formation in simulated body fluids, confirming their potential for biomineralization [159]. Moreover, covalently or electrostatically bound hybrids promote the adhesion and proliferation of osteoblastic cells far more effectively than pure chitosan membranes [154–156,160]. Other applications include oxygen-permeable membranes for wound healing and multifunctional drug-delivery carriers, further underscoring the versatility of these hybrid systems [160,161]. While these examples derive from the biomedical domain, they highlight the broader principle that the hybridization of chitosan and silica produces materials that are at once stable, bioactive, and adaptable.

The interactions underlying this synergy are both chemical and electrostatic. Silane coupling agents, such as γ -glycidoxypyriltrimethoxysilane (GPTMS), enable the formation of covalent bonds between silica and the amino groups of chitosan, leading to homogeneous dispersions and thermally stable nanocomposites [154,155,158–160,162]. In parallel, electrostatic attraction plays a central role: the cationic nature of chitosan in acidic environments allows it to interact strongly with the negatively charged silanol groups on the nanosilica surface [151,163–165]. These interactions can be harnessed to tailor the morphology of the resulting materials, ranging from well-defined porous structures to hybrid nanofibers with core–shell architectures [159,160,163]. The main goal, in general, in this kind of applications, is to create a homogeneous or interpenetrating network, especially under weak acidic conditions [156].

Beyond biomedical contexts, chitosan–silica hybrids offer additional functionalities with direct relevance to cultural heritage conservation. Their intrinsic antimicrobial activity is enhanced when combined with inorganic additives, providing protection against bacterial and fungal colonization [158,162,166–168]. In construction materials, hybrid nanocomposites have been shown to improve compressive and tensile strength, reduce shrinkage, and enhance durability [157]. In papermaking, similar systems improve fiber retention and drainage through the formation of semi-reversible electrostatic flocs [163]. Even in photoprotection, mesoporous silica coated with chitosan has been investigated as a plastic-free platform for encapsulating UV filters, preventing the formation of reactive oxygen species and enhancing light stability [164].

3.2. Overview of advantages for Street Art preservation: mechanical strength, adhesion, stability, sustainability.

From the standpoint of environmental stability, nanosilica plays a crucial role in reinforcing the hybrid matrix. Thermal analyses consistently show that nanosilica enhances the mechanical and thermal stability of chitosan films, as the inorganic nanoparticles act as effective barriers against volatile or degradable organic compounds, thereby slowing down thermal degradation and improved resistance to compression, elongation and elastic modulus [151,152,154,155,158–160,165,169,170]. Equally important is the resistance to water: the addition of nanosilica mitigates the excessive swelling and hydrophilicity typical of pure chitosan, conferring improved water resistance and dimensional stability [155,156,158]. This reduction in water uptake is vital for ensuring the long-term integrity of coatings exposed to outdoor conditions. In conservation of porous substrates such as limestone, nanosilica-based systems have further been associated with enhanced resistance against salt crystallization processes, a key

mechanism of weathering, thereby improving the durability of treated surfaces. Moreover, the presence of the inorganic phase contributes to the high chemical resistance of these hybrids, ensuring their protective performance under chemically aggressive conditions [171,172].

In addition to stability and durability, the chitosan–silica combination aligns with the growing demand for sustainable conservation materials. Chitosan itself is an ecological and renewable biopolymer, naturally biodegradable, non-toxic, and non-antigenic, derived primarily from chitin extracted from crustacean shell waste. Its use not only reduces reliance on synthetic polymers but also promotes circular economy principles by valorizing industrial by-products. When combined with nanosilica, these hybrids open pathways for environmentally friendly alternatives to conventional plastic-based coatings [155,157,158,160]. For instance, chitosan–silica composites have been explored as “plastic-free” platforms for encapsulating UV filters, offering ecologically safe solutions that prevent marine and coastal pollution associated with synthetic polymers [164]. Equally relevant are the green preparation routes commonly employed for such hybrids. The sol–gel process, widely used to synthesize silica and silica-containing composites, can be conducted under mild conditions, often at low temperature and in aqueous media, thus reducing the environmental footprint of the synthesis [158,166]. Even in construction-related contexts, where nanosilica–chitosan systems have been tested in cementitious mortars, their environmental impact remains competitive: the incorporation of chitosan has been reported to increase the global warming potential by only around 1.3% compared to control samples [173]. This suggests that, despite the slight additional footprint associated with nanosilica synthesis, the overall sustainability of these hybrids compares favourably to conventional alternatives.

In sum, the chitosan–nanosilica hybrid approach not only enhances mechanical strength and stability but also satisfies emerging requirements for

environmentally responsible conservation strategies. These features are particularly relevant for street art preservation, where protective materials must combine robustness with eco-sustainability to meet the challenges posed by urban outdoor environments.

Taken together, the combination of chitosan and nanosilica in hybrid materials provides a platform that unites the flexibility, adhesion, and antimicrobial properties of the biopolymer with the rigidity, thermal stability, and chemical durability of the inorganic phase. For the conservation of street art, these properties are especially valuable: improved mechanical strength and adhesion address the fragility and heterogeneity of spray paint layers; enhanced stability and resistance to water or pollutants counteract the challenges of outdoor exposure; and the renewable origin and biodegradability of chitosan align with the increasing demand for sustainable conservation treatments. These hybrid systems thus represent a promising direction for the development of protective coatings tailored to the unique demands of street art preservation, providing the conceptual and material foundation for the experimental work presented in the next section of this thesis. In light of the literature reviewed, it is worth noting that the combined potential of chitosan and nanosilica is particularly relevant for the conservation of outdoor mural artworks. Street Art and contemporary murals are exposed to continuous weathering, solar radiation, moisture, pollutants, and mechanical stress, conditions under which protective materials must simultaneously ensure adhesion, durability, vapour permeability, and environmental sustainability. The complementary properties of chitosan and nanosilica therefore suggest a promising material platform specifically suited to the protection of modern painted surfaces in urban outdoor environments.

3.3. From State of the Art to Research Objectives: Towards a Sustainable Hybrid Coating for Street Art

The literature reviewed so far clearly highlights the potential of both chitosan and nanosilica as conservation materials. Chitosan, with its biocompatibility, antimicrobial properties, and renewable origin, has attracted considerable attention as a “green” alternative to synthetic polymers, although limitations such as swelling, colour alteration, and variable long-term stability remain unresolved. Nanosilica, by contrast, offers mechanical reinforcement, chemical stability, and compatibility with porous substrates, making it highly effective in protective coatings and consolidants. Importantly, the integration of these two materials into hybrid organic–inorganic systems has emerged as a promising strategy to combine their respective strengths while mitigating individual weaknesses.

Despite these advances, the application of such hybrid systems to the preservation of contemporary urban artworks – particularly street art – remains relatively underexplored. While outdoor sculptures, monuments, and built heritage have been investigated for decades in order to improve protection and conservation treatments, contemporary street art introduces additional complexities linked to the nature of modern spray paints, heterogeneous substrates, and the socio-cultural context of public art. Environmental fluctuations also affect indoor collections; however, in outdoor contexts these factors – solar irradiation, temperature excursions, relative humidity variations, atmospheric pollutants, and biological colonization – act simultaneously and often with greater intensity. In the specific case of the mural investigated in this study, located in the area of Sesto Fiorentino (Tuscany), exposure conditions include high seasonal solar irradiance, marked summer temperatures, urban–peri-urban pollutant loads, and moisture cycles associated with rainfall and substrate water dynamics. Such a combination of environmental stressors accelerates

weathering processes and highlights the need for protective systems specifically tailored to modern painted surfaces under real outdoor conditions.

The present work aims to fill this gap by formulating and characterizing a new sustainable hybrid coating based on chitosan and nanosilica, designed specifically for the protection of street art surfaces. The research objectives are threefold: (i) to optimize the formulation of the hybrid coating and evaluate its physicochemical properties; (ii) to assess its protective performance in terms of adhesion, mechanical resistance, and durability under accelerated aging; and (iii) to investigate its compatibility with representative street art substrates and pigments. By doing so, this study aims not only to advance the field of hybrid materials in cultural heritage conservation but also to provide a practical, eco-sustainable solution for safeguarding an increasingly valued yet highly vulnerable form of contemporary art.

PART B

Building on the considerations presented in Part A, this section introduces a chitosan–nanosilica hybrid formulation specifically designed for the protection of Street Art surfaces.

Chapter 4 focuses on the experimental formulation and physico-chemical characterization of the hybrid system, detailing the preparation procedures and analytical techniques used to evaluate its film-forming properties and compatibility with painted surfaces.

Chapter 5 reports the results of the application tests conducted on concrete mock-ups painted with acrylic spray paints, in order to assess the hybrid coating's protective performance, optical stability, and durability under different accelerated ageing conditions.

Finally, Chapter 6 provides an overview of the Life Cycle Assessment (LCA) carried out in collaboration with Dr. Sarah Nunber, PhD candidate in Heritage Science at Sapienza University of Rome, who included the chitosan–nanosilica hybrid among the case studies analysed in her research. This chapter discusses the environmental performance of the hybrid coating and identifies the main hotspots and opportunities for improvement, thus integrating the technical evaluation with a broader sustainability perspective.

4. Hybrid Formulation and characterization

The present chapter focuses on the formulation and characterization of a new hybrid chitosan–nanosilica system specifically designed for the conservation of modern outdoor cultural heritage, with particular emphasis on street art murals executed on inorganic wall supports such as concrete. Street art is particularly challenging to preserve due to the intrinsic vulnerability of its materials: pigments and dyes dispersed in synthetic organic binders are typically applied onto porous inorganic substrates and are continuously exposed to fluctuations in light, temperature, and humidity, as well as to pollutants and biological agents that accelerate their degradation.

The hybrid coating was designed to exploit the favourable film-forming ability, optical transparency, antimicrobial activity, and sustainability of chitosan, while enhancing its performance through the addition of nanosilica, which improves the mechanical strength, dimensional stability, and environmental resistance of the polymer matrix. The compatibility of the hybrid films with spray paint layers and concrete substrates was a central aspect of this work, as ensuring both adhesion and reversibility is essential in conservation practice.

Further evaluations regarding the performance of the hybrid coating, such as adhesion to spray-painted concrete mock-ups, water vapour permeability, hydrophobicity, and long-term stability under accelerated aging conditions, were also carried out to simulate real conservation scenarios. Since these investigations relate directly to the practical behaviour of the coating on representative substrates, they are presented and discussed in detail in Chapter 5.

4.1. Materials and methods

4.1.1. Chemicals

From an experimental standpoint, chitosan powder of medium molecular weight (Mw) was selected for this study, as it represents a suitable compromise between penetration ability, film-forming properties, and mechanical stability. In conservation applications, molecular weight plays a critical role in governing viscosity, processability, and interaction with the substrate. While low Mw chitosan generally promotes deeper penetration into porous materials and high Mw grades provide stronger mechanical reinforcement, medium Mw chitosan offers adequate solubility and manageable viscosity, enabling the formation of continuous and homogeneous films while maintaining sufficient affinity for inorganic and painted substrates. Previous studies have also reported that chitosan within this Mw range exhibits favourable chemical interactions with metal ions and mineral surfaces, as well as antimicrobial potential, although the latter was not specifically investigated in the present work [103,108,128,133].

On this basis, medium Mw chitosan was considered the most appropriate choice for the development of hybrid coatings aimed at cultural heritage conservation. Specifically, chitosan (Chs; medium Mw, viscosity 200–800 cP, degree of deacetylation 75–85%) was purchased from Sigma Aldrich, together with D-(+)-gluconic δ -lactone (GDL; purity $\geq 99.9\%$) and high-retention seamless cellulose dialysis tubing (MWCO 14,000, 99.9% retention). Prior to use, chitosan was washed in boiling water for 1 h, filtered, and rinsed with distilled water to remove residual impurities, following the protocol proposed by Giuliani et al., and then left to dry at room temperature for 48 h. [107].

The selection of D-(+)-gluconic δ -lactone (GDL) as the acidifying agent for chitosan dissolution was informed by both experimental trials and prior literature. Preliminary tests with acetic acid, the most commonly employed chitosan solvent, and with hydrochloric acid produced films that were fragile, prone to

yellowing, and exhibited surface patinas, compromising their transparency and uniformity. In contrast, GDL offered clear advantages in film quality and suitability for cultural heritage applications. Upon hydrolysis in water, GDL gradually generates gluconic acid, inducing a controlled decrease in pH that promotes progressive protonation of chitosan amino groups. This slow acidification ensures homogeneous dissolution, minimizes aggregation, and enables the formation of uniform coatings. Consequently, films cast from GDL-based solutions are typically colourless, transparent, and smooth—essential aesthetic requirements for conservation treatments. Moreover, unlike acetic acid, gluconic acid does not facilitate the formation of acetate crystals, such as Pb acetate observed on copper alloys containing lead, a phenomenon particularly undesirable in conservation contexts [107].

The use of hydrochloric or other inorganic acids, while capable of dissolving chitosan, is limited by solution instability and the potential for chloride-induced corrosion. Similarly, acetic acid, although widely used, tends to produce inhomogeneous films and can interact adversely with metal substrates, making it less suitable for the present application. Within this framework, GDL emerges as a more sustainable and effective choice, allowing the preparation of transparent, chemically stable, and aesthetically compatible coatings, albeit requiring careful pH control to ensure substrate safety.

Regarding water, ultrapure Milli-Q water (resistivity $18.2 \text{ M}\Omega \cdot \text{cm}$ at 25°C) was employed in all relevant experimental procedures.

For the inorganic component, Levasil CC301 was selected as the silica source for the hybrid formulation. Nano-silica dispersion (NS) Levasil® CC301 (Nouryon) was used as received. It is a neutral aqueous dispersion of colloidal silica ($\sim 30 \text{ wt}\%$) with an anionic surface modified by epoxy-silane groups. This selection was driven by structural, chemical, and application-oriented considerations. While sol–gel precursors such as tetraethyl orthosilicate (TEOS) or organically

modified silanes (e.g., GPTMS) are commonly employed to induce covalent cross-linking between organic and inorganic phases in chitosan–silica hybrids, these methods often require alcohol-based solvents or conditions incompatible with conservation sustainability goals. In contrast, Levasil CC301 provides a ready-to-use, water-based alternative, ensuring both procedural simplicity and environmental compatibility.

Structurally, Levasil CC301 contains silica nanoparticles of approximately 12 nm, stabilized at 30 wt% in water. Surface modification with sodium aluminate reduces the zeta potential below -10 mV in the pH range 2–6, enhancing particle stability in mildly acidic conditions and mitigating excessive electrostatic repulsion with protonated chitosan. This facilitates electrostatic interaction without uncontrolled aggregation, resulting in homogeneous, stable hybrid dispersions.

Functionally, the incorporation of colloidal silica nanoparticles enhances the thermal stability of the hybrid coatings by acting as barriers to volatile degradation products, while reducing water uptake and swelling, which are typical in pure chitosan films. These properties are critical for outdoor conservation, where coatings are exposed to humidity fluctuations and require dimensional stability. Additionally, Levasil CC301 improves hardness and elastic modulus, reinforcing the chitosan matrix and producing films that are less brittle and more durable on rough inorganic substrates such as concrete.

Finally, the commercial availability, reproducibility, and established use of Levasil colloidal silicas in coatings and consolidation treatments make CC301 particularly suitable for cultural heritage applications. Compared to TEOS or hydrochloric/acetate-based systems, preliminary trials indicated that films prepared with Levasil CC301 were more transparent, homogeneous, and resistant to yellowing or surface patina formation, thus satisfying the stringent aesthetic and functional requirements of heritage conservation.

4.1.2. Coatings preparation

Chitosan powder with a 0.6% w/v concentration was dissolved in aqueous 0.05 M gluconic acidic solution. The solution was heated at 30 °C for 24h under continuous stirring, reaching a pH of approximately 3.5. Then, to remove the insoluble residues, the solution was centrifuged at 4500 rpm twice for 5 minutes. The pH adjustment of the centrifuged solution was achieved by dialysis, using a membrane cell for 24 h against 1 L water. This operation was chosen to avoid the addition of alkaline solutions that lead to the formation of salts which could be hazardous for the application of the coating on porous substrates. After dialysis, the Chs aqueous solution resulted clear and transparent, and its pH was about 6.0. As the final concentration is calculated gravimetrically, the desired final concentration was adjusted for the analysis or the application on the mock-ups according to the values reported in Table 2. The chitosan-nano silica (Chs-NS) hybrid solution was prepared by mixing and magnetically stirring the Chs-based solution and NS at the selected ratios (Table 2).

	Chs - Chitosan	NS - Levasil® CC301	Chs-NS hybrid
Concentration %ww	0.5	0.5	0.25/0.25

Table 2 Chitosan, nanosilica, and Chs-NS hybrid concentrations.

A portion of each resulting solution was cast on a glass plate and let dry at room temperature for at least 48 hours to obtain coating films for the characterization analysis and film's aging tests (par. 4.1.3). The remaining portion of each solution was kept at room temperature for 24h before the application on the mock-ups to evaluate the performances of the formulations.

4.1.3. Accelerated artificial aging tests

To evaluate the chemical stability of the Chs-NS-based films and to compare this property with that of films composed solely of chitosan, several accelerated aging tests were performed. Replicates of both Chs and Chs-NS coatings were cast

directly onto glass Petri dishes, and each set of samples was subjected to a specific aging protocol for 20 days to investigate the effects of aging on the physical and molecular structure of the films. The different aging conditions are described below:

- *A1 – Photo-oxidative aging*

Although standardized artificial ageing protocols are widely available (e.g., ASTM G154 and ASTM G155 for UV exposure of polymeric materials; ISO 4892 series for plastics under laboratory light sources; ISO 16474 for coatings and varnishes), these standards are primarily designed for industrial coatings and construction materials subjected to controlled and repeatable exposure cycles.

In the present research, the objective was not to certify durability according to industrial performance benchmarks, but rather to perform a comparative assessment between pure chitosan (Chs) and chitosan–nanosilica (Chs–NS) films under simplified, easily-reproducible and controlled stress conditions. For this reason, tailored ageing protocols were adopted to isolate specific degradation factors (photo-oxidative, hydrothermal, and thermal stress), allowing clearer interpretation of molecular and physico-chemical changes in relation to conservation-oriented applications. Moreover, standardised protocols often require xenon-arc or fluorescent UV weathering chambers with cyclic irradiation/condensation systems, which were not available within the laboratory facilities at the beginning of this doctoral project. The selected experimental setup, while simplified, ensured controlled and reproducible exposure conditions suitable for comparative material evaluation in a conservation science context.

Films were exposed to UV–visible light to induce photo-oxidative degradation. Samples were placed in a closed chamber equipped with a Neon Light Color 765 Basic daylight Beghelli® Lamp (380–700 nm, 160 mW/lm). Temperature and relative humidity inside the chamber ($T = 36 \pm 2$ °C, $RH = 40 \pm 5\%$) were monitored using a digital thermohygrometer (Gauge). The samples were

positioned approximately 10 cm from the lamp, receiving an estimated illumination of 11,000 Lux uniformly across their surfaces.

- *A2 – Hydrothermal aging*

Chs and Chs-NS films were sealed in hermetic vessels containing a vial of saturated KCl solution and placed in an oven at 60 °C to maintain a constant relative humidity of 80% inside the vessels.

- *A3 – Thermal aging*

Chs and Chs-NS films were subjected to a constant temperature of 60 °C in a dry environment (RH $\approx$ 40%). The relative humidity value was not intended to reproduce specific local environmental conditions; rather, it was selected to simulate relatively dry conditions that may occur during summer periods or under intense solar exposure. This choice allowed the evaluation of the coating's behaviour under combined photo-oxidative and low-humidity stress, representing a potentially critical scenario for outdoor mural surfaces.

4.1.4. ATR-FTIR

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy was employed to characterize the coating films. Measurements were carried out using a Thermo Nicolet Nexus 870 spectrometer equipped with a liquid nitrogen-cooled HgCdTe detector and a single-reflection diamond crystal ATR unit. Spectra were collected in the 4000–650 cm^{-1} range, acquiring 128 scans per spectrum with a spectral resolution of 4 cm^{-1} .

This technique was applied to characterize both the individual components—namely, chitosan-only films and solidified nanosilica—as well as the hybrid film, in order to investigate molecular interactions between the organic and inorganic phases. Moreover, ATR-FTIR was used to assess molecular-level changes induced by accelerated aging in both the Chs-only and Chs-NS films.

4.1.5. Field emission scanning electron microscopy (FE-SEM)

Field Emission SEM (FE-SEM) images were recorded with a Sigma scanning electron microscope (Carl Zeiss Microscopy Deutschland GmbH, Germany). The images were acquired at a working distance of 1.8 mm playing with an acceleration potential of 10 kV using a secondary electron detector as well as an in-lens secondary electron detector with an acceleration potential of 5 kV. The Chs and Chs-NS films were gold coated with an automatic sputter coater (Agar Scientific Ltd, UK).

4.1.1. Size distribution and zeta potential

Dynamic light scattering (DLS) measurements at $\theta = 90^\circ$ and the ζ -potential determination was performed using a Brookhaven Instrument 90 Plus (Brookhaven, Holtsville, NY). Each measurement was an average of 10 repetitions of 1 min each, and measurements were repeated 10 times. 3 repeats were carried out for each sample. 659 nm laser light radiation. The measurements were carried out at 25 °C. Particle size distributions were obtained from the fitting of the measured autocorrelation functions using the CONTIN method [174].

4.2. Results and discussion

4.2.1. Coating preparation

The Chs coating prepared through the protocol described in the previous section (par. 4.1.2) results in a transparent and colourless solution. In particular, the washing procedure of the chitosan powder already described previously [107] had a positive impact on the clear and colourless appearance of the solution. Chs is soluble in acidic media and, usually, after its solubilization its pH is raised using NaOH aqueous solutions [109]. In this study, we opted for a dialysis process to avoid the introduction of other materials into the solution which would lead to the formation of harmful salts for the conservation of stones and building materials in general. Also, Chs films obtained after the evaporation of the solution

are transparent and colourless, as well as the Chs-NS ones. The Chs-NS mass ratio equal to 1 resulted in the most suitable composition to have a transparent solution and film.

4.2.2. Exploring the interactions of chitosan and nanosilica

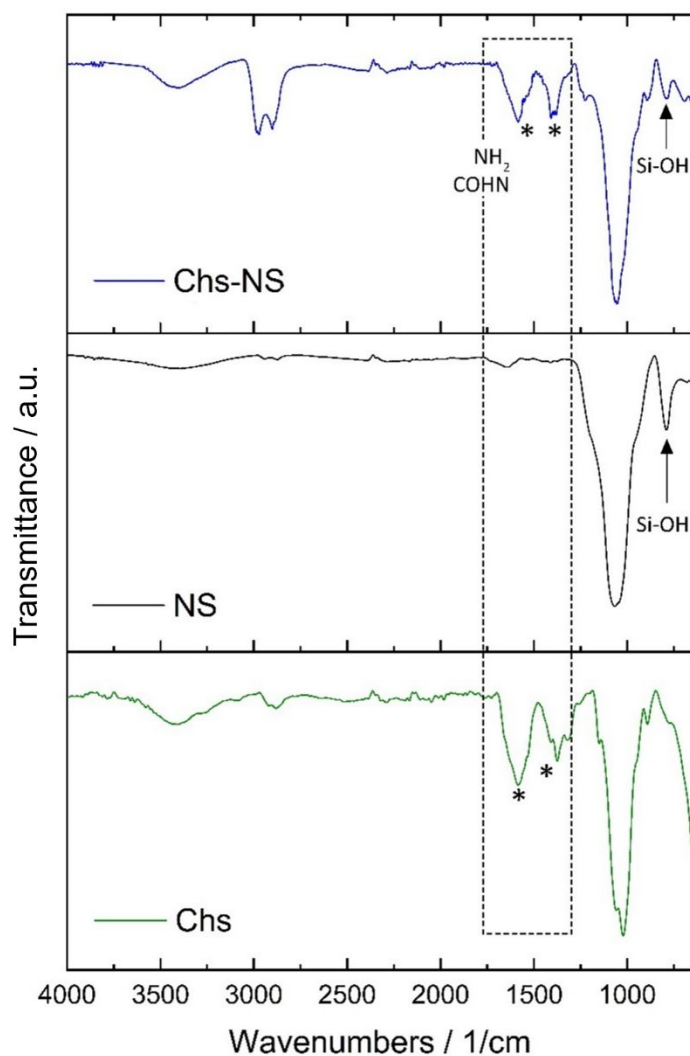


Fig. 2 ATR-FTIR spectra of the coating films.

The chemical structure of the films obtained by the single components (Chs and NS) and the hybrid one, were studied by ATR-FTIR spectra (Fig. 2). The spectrum referred to the Chs-based film presents the following typical functional group of the polysaccharide: a broad band at 3435 cm^{-1} due to the stretching vibration of O–H groups which almost overlaps with the stretching vibration of N–H in the $3300\text{--}3150\text{ cm}^{-1}$ region [175]; the bands at 2922 and 2877 cm^{-1} attributed to the C–H symmetric and asymmetric stretching, respectively; a shoulder at 1655 cm^{-1} due to the C=O stretching of the secondary amide in acetylated units of chitosan; a broad band at 1590 cm^{-1} attributed to N-H bending of the primary amine [176]; the bands at 1411 cm^{-1} , 1378 cm^{-1} , and 1322 cm^{-1} are attributed to the C–H₂ bending, the asymmetrical C–H bending of the C–H₂ group, and the amide III band, respectively. The shoulder at 1153 cm^{-1} is attributed to the C–O–C glycosidic bond of the pyranose ring; the peaks at 1064 and 1020 cm^{-1} are due to the vibrations of C–O, C–OH, C–OC, CH₂OH, and C–O–C functional groups.

The NS spectrum presents a peak at 1050 cm^{-1} attributed to the Si–O–Si internal asymmetrical stretching; a peak at 955 cm^{-1} due to the vibration of the silanol groups Si–OH, and a peak at 808 cm^{-1} attributed to the symmetric stretching of Si–O–Si bonds [177].

As shown in Fig. 2, the spectrum of the hybrid film is likely the overlapping of the spectra of the single components, matching most of the absorption values described above and confirming the loading of NS in the Chs matrix. However, some changes are detectable in the $1700\text{--}1400\text{ cm}^{-1}$ range, due to the angular deformations of the NH₂ group at 1590 cm^{-1} and CONH group at around 1400 cm^{-1} , respectively. This phenomenon can be explained by the variation of the electric dipole moment of the NH₂ and CONH groups due to the angular deformation due to the hydrogen bonding between the silanol groups of silica and amine groups of chitosan [178]. Moreover, the decrease of the silanol groups

signal at 808 cm^{-1} in the hybrid film if compared to the NS spectrum can corroborate the hypotheses of a hydrogen bonding interaction between the two components [177]. Additionally, the intense band in the $950\text{-}1190\text{ cm}^{-1}$ range in Chs spectrum becomes broader in the Chs-NS due to the Si–O–Si and Si–OH vibrations [179].

The presence of epoxy silane structures [142] on the NS surface was considered to describe the interaction between Levasil CC301 and Chs. It is well known that chitosan may give covalent bonds with epoxy silanes through a sol-gel method [180]. Moreover, several possible mechanisms may occur when chitosan and GPTMS interact. These mechanisms may include: (i) the covalent coupling of the epoxide ring to the primary amine, which forms a secondary amine; (ii) covalent coupling between the hydroxyl groups of the chitosan via the epoxy ring; (iii) condensation of silane groups with hydroxyl groups of Chs; (iv) hydrogen bonding which can occur between amine, amide, and hydroxyl groups; (v) ionic bonding between positively charged amine groups of Chs and the negatively charged silanes, and finally (vi) ionic bonds between protonated amines and negatively charged oxygen of the epoxide group [181]. For clarity, the possible interaction mechanisms between chitosan and nanosilica are summarized in Table 3.

Mechanism	Type of interaction	Functional groups involved	Expected relevance at pH $\approx$ 6
(i) Epoxide ring opening by amine	Covalent	$-\text{NH}_2$ and epoxy group	Limited
(ii) Epoxide ring opening by hydroxyl	Covalent	$-\text{OH}$ and epoxy group	Limited
(iii) Silane condensation	Covalent	$\text{Si}-\text{OH}$ and $-\text{OH}$ groups	Possible
(iv) Hydrogen bonding	Non-covalent	$-\text{NH}_2$, $-\text{OH}$, amide groups	Highly probable
(v) Electrostatic interaction	Ionic	$-\text{NH}_3^+$ and $\text{Si}-\text{O}^-$	Highly probable
(vi) Protonated amine-epoxide interaction	Ionic	$-\text{NH}_3^+$ and epoxy oxygen	Possible

Table 3 Possible interaction mechanisms between chitosan (Chs) and nanosilica (NS).

As indicated in Table 3, under mildly acidic conditions ($\text{pH} \approx 6$), the interaction between Chs and NS is expected to be predominantly governed by hydrogen bonding and electrostatic attraction, whereas extensive covalent coupling reactions are less favoured. The reaction between primary amines with the epoxy groups on GPTMS is known to occur under acidic conditions – as the epoxy rings open and react with hydroxyl groups of chitosan to form $\text{C}-\text{O}-\text{C}$ bonds, or with the protonated $-\text{NH}_3^+$ groups [182,183]. However, considering that the pH of the Chs solution upon addition of NS is approximately 6, the formation of stable

covalent bonds is likely limited. Therefore, the interaction between NS and Chs can reasonably be attributed mainly to ionic interactions and hydrogen bonding [184].

The Chs, NS, and Chs-NS solutions were analysed using DLS and zeta potential measurements, investigating concentration values of 0.2% for each component. The DLS Intensity plots (Fig. 3) show that Chs exhibits a wide distribution of dimensions in the nanoscale in the 235-370 nm range, with the presence of some smaller structures in the 20-30 nm range. NS shows a monodisperse and narrow size distribution at about 10 nm, according to the data provided by the producer. The hybrid solution has a size distribution like the Chs solution with polydisperse structures in the 50-70 nm and 200-590 nm ranges. This increase of the size distribution in the hybrid system can be better explained by the data obtained by the zeta potential measurements which highlighted the positive charge of the Chs solution and the negative of the NS alone, +51.40 mV and -11.00 mV, respectively (Table 4). The hybrid solution has a positive charge which results higher than the value measured in Chs. This phenomenon can be explained by hypothesizing that the biopolymer, once combined with NS, rearranges itself surrounding the silica particles increasing the exposition of the positive charges of the protonated amine groups. As shown above, Chs and NS can interact with each other by hydrogen bonding, thus decreasing the contribution of the negatively charged OH groups.

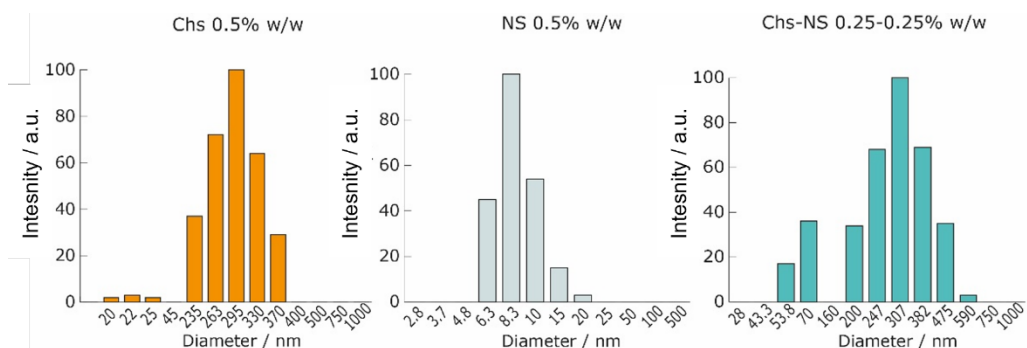


Fig. 3 DLS intensity-weighted plots measured for Chitosan (0.5% ww), Nanosilica (0.5% ww), and Chs/NS (0.25%/0.25% ww).

ζ-Potential	Chs	NS	Chs-NS
Mean (mV)	51.40 ± 1.35	-11.00 ± 0.41	62.64 ± 2.55

Table 4 Zeta-potential of Chs, NS and Chs-NS solutions.

The surface morphology of chitosan-based and hybrid films was observed by SEM analyses (Fig. 4). The Chs-based films show a compact, smooth, and homogeneous structure (Fig. 4a), without defects. These characteristics are also detected macroscopically as a transparent and homogeneous film is obtained. The surface of the hybrid films (Fig. 4b-d) shows a homogeneous distribution of NS within the polymeric matrix.

4.2.3. Accelerated artificial aging effect

The long-term durability of Chs-NS and Chs-based coatings was studied through three kinds of accelerated aging tests described in paragraph 4.1.3. The

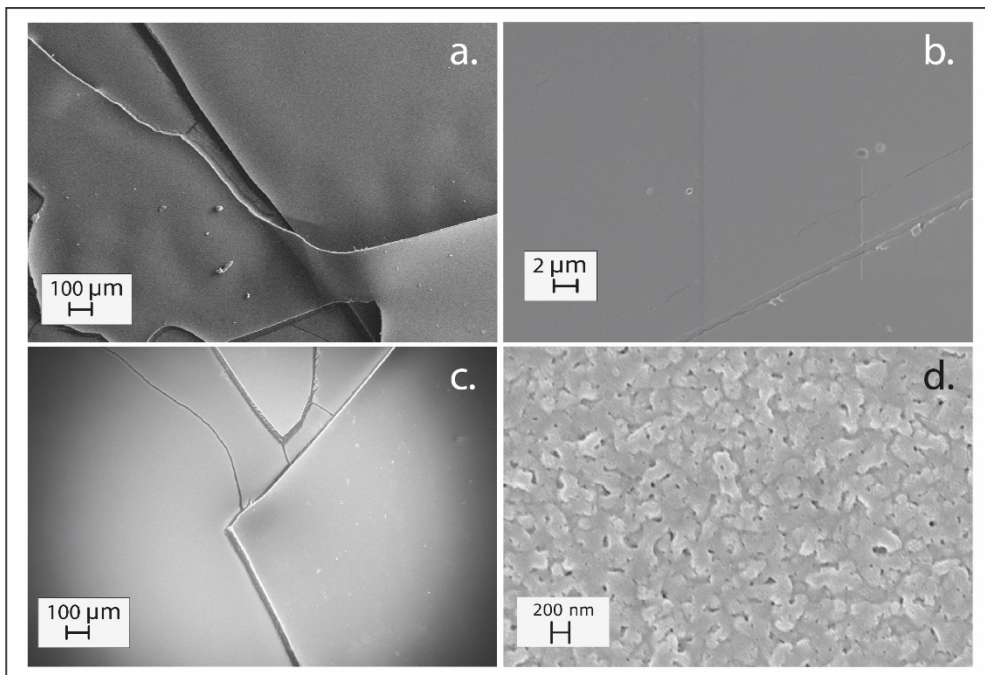


Fig. 4 SEM images of the Chs-based coating (a), and the Chs-NS film (b-d).

degradation effects were analysed by FTIR-ATR analysis on Chs and Chs-NS films aged for 20 days, to detect any variation in the molecular structure of the materials. According to the literature, the main degradation phenomena that may affect Chs are depolymerization followed by deacetylation, oxidation, and interchain crosslinking [185]. Considering Chs-based film, the spectra reported in Fig. 5 show a good resistance of the polysaccharide film toward photo-oxidative degradation (A1), and thermal degradation (A3) since the comparison between the aged and unaged films does not highlight any significant variation of the signals. The spectrum of the Chs exposed to hydrothermal degradation (A2) shows many variations in the signals attributed to the N–H and amide II vibrations. These phenomena can be ascribed to the interaction of the Chs with

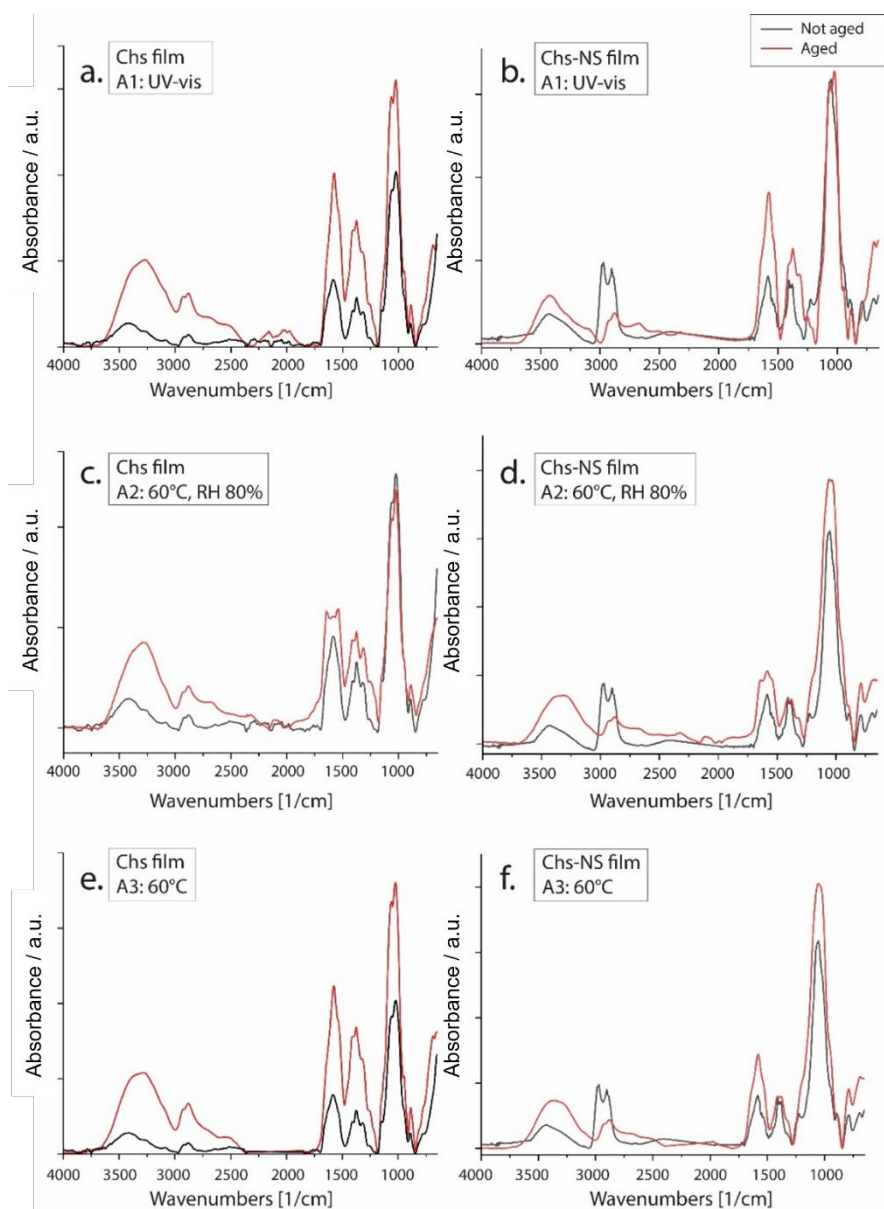


Fig. 5 ATR-FTIR spectra of Chs (left side) and Chs-NS films (right side) under different aging conditions: Chs and Chs-NS films subjected to photo-oxidation - A1 (a, b), hydrothermal aging (c,d) and thermal aging (e, f) respectively.

the moisture water. It is important to note that in the A2 setup, RH is 80% and Chs as a hydrophilic polymer can undergo structure reorganization of the molecules due to the plasticizing effect of the water molecules which can also

determine the crystalline-amorphous transition impacting the molecular mobility of Chs [186,187].

In natural outdoor conditions, chitosan depolymerization is not associated with a well-defined timescale, as it strongly depends on environmental variables such as relative humidity, temperature, solar irradiation, pH, and biological activity. Available literature indicates that, in the absence of strong acidic or oxidative conditions, chitosan degradation in ambient environments generally occurs over long periods (years), often through slow hydrolytic or photo-oxidative pathways rather than rapid depolymerization [81,188,189].

As mentioned in 3.2, Chs-NS spectrum has numerous peaks and, considering the overlapping of some signals and the complexity of the possible degradation phenomena that can affect the biopolymer, the study of the Chs-NS behaviour towards accelerated aging is a very complex issue. Moreover, the spectra of the aged hybrid films exposed to the different conditions (A1-3) only showed a slight shift in the 3000-2800 cm^{-1} range, while any significant variations of the spectra are reported in the other ranges. It is important to observe that the absorption bands in the 1260–800 cm^{-1} range belonging to the glycosidic ring, particularly the band at about 1150 cm^{-1} corresponding to the glycosidic bond - do not show any significant variation, thus it can be confirmed that no depolymerization phenomena are observed when the Chs and hybrid films are aged. Within the 20-day accelerated aging time scale investigated, this indicates that no measurable depolymerization phenomena occur in either the Chs or Chs-NS films. These results suggest good short- to medium-term chemical stability of the coatings under simulated aging conditions. However, longer exposure times would be required to fully assess potential long-term depolymerization processes under real outdoor conditions.

Therefore, the Chs and hybrid films can be considered chemically stable for their application as protective coatings on outdoor mural paintings. SEM images

recorded after the aging test on the Chs and Chs-NS based films did not show any significant change in the morphology of the surface, and they can be observed in Fig. 7.

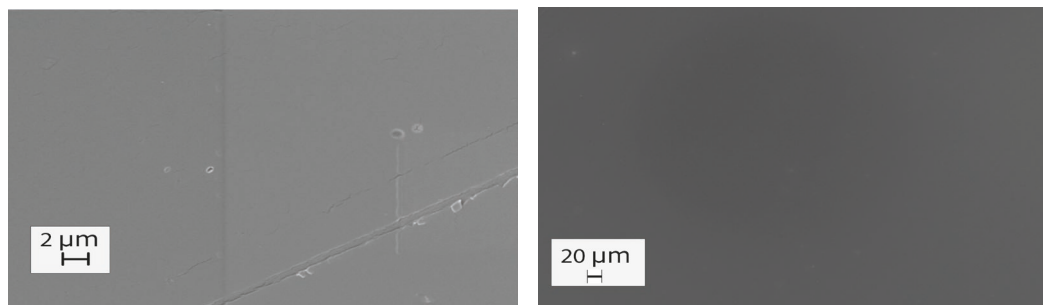


Fig. 7 SEM images of aged Chs-based films subject to photo-oxidative aging tests.

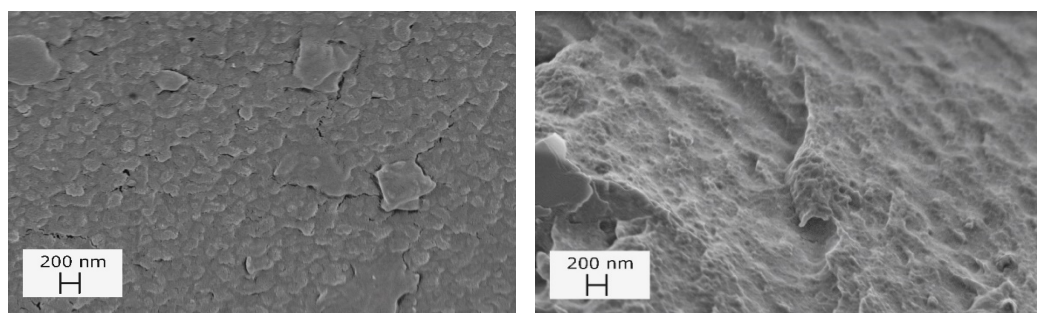


Fig. 7 SEM images of aged Chs-NS hybrid films subject to photo-oxidative aging tests.

4.3. Conclusions

In this chapter, the formulation and the characterization of a novel chitosan–nanosilica (Chs-NS) hybrid coating are presented, with the aim of developing a sustainable protective system for contemporary outdoor cultural heritage, particularly street art murals on inorganic substrates. The hybrid system was designed to combine the film-forming ability, optical transparency, flexibility, and potential antimicrobial properties of chitosan with the mechanical reinforcement, adhesion, and aging resistance provided by colloidal nanosilica, while maintaining breathability and compatibility with painted surfaces.

The chitosan-based formulation was prepared using a controlled pH approach via D-(+)-gluconic δ -lactone (GDL) combined with a dialysis step, avoiding the conventional neutralization with alkaline solutions such as NaOH. This approach prevented salt formation, which is reported in the literature as potentially harmful for historic and artistic wall surfaces, and enabled the preparation of clear, homogeneous, and chemically stable hybrid solutions forming transparent and flexible films.

Levasil CC301 colloidal nanosilica was incorporated as the inorganic phase, improving mechanical performance and resistance to thermal, hydrothermal, and photo-oxidative aging, while preserving permeability and aesthetic compatibility. ATR-FTIR spectroscopy, DLS, zeta potential measurements, and FE-SEM analyses confirmed a uniform dispersion of nanosilica within the chitosan matrix, and the formation of a stable nanostructured hybrid material.

Accelerated aging tests indicated that the Chs-NS films largely retain their chemical integrity and morphology under conditions representative of outdoor exposure, with no evidence of significant depolymerization or degradation. These results support the potential durability of the hybrid system for application as a protective coating on outdoor painted surfaces. No significant depolymerization or degradation was observed, suggesting that the hybrid system could offer

adequate chemical stability and durability for potential outdoor applications of protective coatings.

These results provide a basis for the next stage of this research, which focuses on the practical application of the Chs-NS coating. In the following chapter, the hybrid. On this basis, the following chapter focuses on the application of the Chs-NS coating on concrete mock-ups painted with acrylic and alkyd spray paints, in order to evaluate its protective performance, optical stability, and interactions with representative substrates under simulated outdoor conditions.

5. Application test of the hybrid formulation on concrete

5.1. Introduction

Following the structural and physico-chemical characterization of the chitosan–nanosilica hybrid formulation described in Chapter 4, the next step was to evaluate its performance under conditions that more closely simulate real conservation scenarios. Since street art is typically executed on inorganic substrates such as concrete, brick walls, and masonry, mock-ups reproducing spray paint on concrete were prepared to serve as representative test supports. The application of the hybrid coating on these mock-ups enabled the assessment of key functional parameters, including adhesion to painted surfaces, water vapour permeability, and hydrophobicity, since all of which directly influence the protective capacity and compatibility of the treatment with outdoor murals.

To further investigate the durability of the proposed formulation, accelerated ageing protocols were employed in order to simulate the main environmental stressors affecting outdoor murals, namely humidity fluctuations, temperature variations, and daylight exposure. In particular, light ageing was designed to reproduce visible and near-UV irradiation comparable to natural daylight, with controlled irradiance and cumulative dose selected to represent prolonged outdoor exposure within a reduced experimental timeframe. The resulting changes in surface properties and appearance were monitored by means of colorimetric analyses, providing a quantitative assessment of the coating's stability and long-term protective efficacy.

In a preliminary phase of the study, the aging parameters were maintained identical to those adopted in Chapter 4, allowing direct comparison between pure chitosan and chitosan–nanosilica hybrid films. Subsequently, however, a single combined ageing protocol was implemented, integrating controlled cycles of light irradiation, temperature, and relative humidity. This approach was adopted

following the inclusion of a real case study in this project (to be discussed in Part C), where direct collaboration with the street artist provided both valuable information on the painting process and a selection of original spray cans used in the artwork. As a result, these specific paints were therefore included in the mock-ups application tests campaign, and subjected to the unified ageing protocol, in order to better approximate the cumulative daylight exposure and environmental conditions experienced by outdoor murals.

5.2. Materials and methods

5.2.1. Mock-ups preparation

White concrete (Knauf, Germany) and silica sand (SiO_2 , 50–70 mesh particle size, Sigma Aldrich, USA) were used as raw materials for the preparation of mock-ups. Samples with dimensions of $5.5 \times 5.5 \times 1 \text{ cm}^3$ were fabricated by mixing concrete, sand, and water in a 2:5:2 volume ratio, as recommended by the manufacturer. The resulting paste was cast into wooden moulds and allowed to cure for two weeks at room temperature. Once hardened, the exposed surface of each mock-up was spray-painted with acrylic paints to reproduce the typical appearance of street art murals. Replicates were produced for each selected colour to ensure consistency in subsequent analyses.

Two acrylic spray paints were selected from the Kobra Low line (Low Kobra, Italy) and used as received: LOW1171 “Strong Blue” and LOW001 “Pure White”. The chosen colours, white and blue, were selected to better detect the colour variations both as the coatings are applied, and during the aging processes, i.e. yellowing or formation of whitish residues. Once coloured, the mock-ups were left set for a week at room temperature before the coating treatment and the consequent colour measurements, film analysis, and aging tests.

The chitosan-based coating and the hybrid system were applied on concrete mock-ups by brush.

In a subsequent phase of the study, additional sets of concrete mock-ups were prepared. Each set was painted with one of the thirteen spray colours provided directly by the artist who created the case study mural discussed in Part C. These paints, which belong to the MTN94 line (Montana Colors, Barcelona, Spain), were selected to reproduce the actual materials employed in the original artwork. Their characterization and the molecular analysis of their deterioration under accelerated ageing will be presented in detail in Part C. The full list of spray paints provided by the artist is reported in Table 5, including their names and catalogue codes, to facilitate reproducibility and future conservation studies. The specific ageing protocols, tailored to the different categories of mock-ups and to the objectives of each experimental phase, are presented in the following section (5.2.2).

Sample ID	Colour	Code Name
W	White	<i>Matt White</i> ; R-9010
Bk	Black	<i>Matt Black</i> ; R-9011
Y	Yellow	<i>Light Yellow</i> ; RV-1021
O	Orange	<i>Kalani Orange</i> ; RV-2004
R	Red	<i>Light Red</i> ; RV-3020
P	Pink	<i>Tutti Frutti</i> ; RV-115
LV	Light Violet	<i>Community Violet</i> ; RV-171
DV	Dark Violet	<i>Ultraviolet</i> ; RV-173
LB	Light Blue	<i>Electric Blue</i> ; RV-30
DB	Dark Blue	<i>Dark Blue</i> ; RV-5005
G	Green	<i>Mystic Green</i> ; RV-271
LBr	Light Brown	<i>Inca Brown</i> ; RV-136
DBr	Dark Brown	<i>Mole Brown</i> ; RV-140

Table 5 Spray paints provided by the artist and analysed in this study.

5.2.2. Accelerated artificial aging tests

To evaluate the colour stability of both treated and untreated mock-ups, accelerated ageing protocols were employed. A 200-day exposure period was selected to induce measurable chromatic variations while avoiding unrealistically severe degradation. Although accelerated ageing cannot be directly correlated in a linear manner with natural exposure, this duration was considered adequate to simulate medium-term outdoor stress under controlled laboratory conditions. Concrete mock-ups coated with acrylic spray paints from the Kobra series were subjected to three distinct ageing protocols (A1, A2, A3), in order to isolate the contribution of individual environmental stressors and better understand specific degradation mechanisms affecting modern spray paints. The conditions corresponding to A1, A2, and A3 are described in section 4.1.3. Alkyd-based spray paints - introduced into the research at a later stage to reflect the real case study - were instead subjected to a single combined ageing protocol. This integrated approach was designed to reproduce simultaneous fluctuations in irradiation, temperature, and relative humidity, thereby providing a more realistic simulation of the complex environmental stressors typically affecting outdoor murals. The shift toward a combined protocol reflects the methodological transition from controlled mechanistic evaluation to case-study-oriented validation. A summary of the prepared mock-ups, including paint types and the specific ageing protocols applied, is provided in Table 6. Table 7 details the parameters defining the unique accelerated ageing protocol applied to the alkyd-based mock-ups, which was designed to replicate, in a condensed timeframe, the natural degradation processes affecting original murals due to environmental factors such as light exposure, humidity, temperature fluctuations, and rainfall. Deionized water was employed to control relative humidity and simulate rainfall events. The artificial ageing parameters were set following the methodology described by Lamuraglia et al. [190], who investigated the performance of

chitosan-based protective coatings for outdoor wall paintings through accelerated ageing tests. The sequential steps listed in Table 7 were repeated to achieve a total exposure of 100 hours.

Binder	Colour	Not treated	Treatment	
			Chs 0.5%	Chs-NS 0.25/0.25%
Acrylic	White	Not aged, A1, A2, A3.	Not aged,	Not aged,
	Blue		A1, A2, A3.	A1, A2, A3.
Alkyd	White	Not aged, Combined aging protocol.	Not aged, Combined aging protocol.	
	Yellow			
	Orange			
	Red			
	Pink			
	Light Violet			
	Dark Violet			
	Light Blue			
	Dark Blue			
	Green			
	Light Brown			
	Dark Brown			
	Black			

Table 6 Overview of the prepared concrete mock-ups, paint types, and the corresponding accelerated ageing protocols applied to evaluate colour stability.

Step	Time (min)	Radiance (W/m ²)	Temperature (°C)	Relative Humidity (%)	Dry/wet
1	30	65	50	20	dry
2	30	0	25	40	dry
3	30	65	50	20	dry
4	30	0	25	40	dry
5	30	65	50	20	dry
6	30	0	25	40	dry
7	30	65	50	20	dry
8	30	0	25	40	dry
9	1	65	50	100	rain
10	1	0	25	100	rain

Table 7 Steps and parameters set for the accelerated artificial ageing of spray paint mock-ups.

5.2.3. Colour measurements

Colour measurements on treated mock-ups, before and after aging, were performed using an X-rite SP60 spectrophotometer equipped with an integrating sphere having a circular sampling spot (diameter = 1.5 cm). Colorimetric coordinates were obtained using standard illuminant D65 and a standard observer at 2°. The untreated mock-ups were taken as control. Each measurement was an average of 5 acquisitions taken in 5 different spots on each mock-up surface (30.25 cm²).

The colour difference (ΔE), according to the CIELab equation, and its standard deviation ($\sigma_{\Delta E}$) was obtained using the equations below, respectively:

$$\Delta E = \sqrt[3]{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (\text{equation 1})$$

$$\sigma_{\Delta E} = \sqrt{\left(\frac{\Delta L}{\Delta E}\right)^2 \cdot (\sigma_{L_1}^2 + \sigma_{L_0}^2) + \left(\frac{\Delta a}{\Delta E}\right)^2 \cdot (\sigma_{a_1}^2 + \sigma_{a_0}^2) + \left(\frac{\Delta b}{\Delta E}\right)^2 \cdot (\sigma_{b_1}^2 + \sigma_{b_0}^2)} \quad (\text{equation 2})$$

where ΔL , Δa , and Δb are the differences between the values obtained on the same sample before and after each step, and L_0 , A_0 , b_0 correspond to the values obtained before the application or aging, while L_1 , a_1 , b_1 are referred to the colorimetric coordinates obtained by measuring the mock-ups after the application or the aging. The ΔE^*_{ab} (1976) formulation was selected for the laboratory ageing experiments in order to maintain consistency with widely adopted methodologies in conservation science, where threshold values for perceptibility and acceptability are frequently reported using this metric. Although more recent formulations have been developed, ΔE^*_{ab} remains extensively used in artificial ageing studies, allowing direct comparison with previous research and established evaluation criteria.

In the Heritage Science field, a ΔE value of approximately 2 CIELAB units is generally considered perceptible to the human eye under controlled conditions,

while values above 3 CIELAB units are commonly regarded as visually significant and potentially unacceptable in conservation practice, depending on the context of intervention [13,191].

5.2.4. Gloss measurements

The gloss of the unaged, aged, treated and untreated mock-ups was evaluated using a glossmeter (Novo-Gloss Trio 20/60/85 Glossmeter, Rhopoint Instruments Ltd., UK). The measurement area is 4.4 mm x 44 mm. Gloss is measured in gloss units (GU). Initially, the specular reflection was measured at an incident angle of 60°, which is the standard measurement angle. However, since the gloss values for each sample were below 10 GU, the measurement angle of 85° was selected, as this angle is known to provide better resolution for low gloss surfaces [192]. Measurements were conducted three times for each of the three replicates of each mock-up.

5.2.5. Film properties

The hydrophobicity of the coating was measured on the mock-ups following the UNI EN 15802 standard [193], by measuring the static contact angle formed by a water droplet on the surface. The procedure is recorded by a Canon EOS 60D camera, with a 100 mm f/2.8 Macro lens. The image processing was carried out with *ImageJ* software by using the *Contact angle* plug-in. The results are presented as the mean of 10 repetitions conducted on each sample, with the data dispersion calculated as the standard deviation. The water capillary absorption of both treated and untreated mock-ups was measured following the procedure outlined in the UNI EN 15801 regulation [194]. The results reflect the mean value obtained from three replicates of each sample.

Additionally, the water vapour permeability was measured on concrete mock-ups according to the steps specified in the UNI EN 15803 standard [195]. Even in

this case, the results reflect the mean value obtained from three replicates of each sample.

The Scotch Tape Test [58,59] was conducted on the surface of various concrete mock-ups to assess the adhesion of the Chs and Chs-NS films once applied on the mock-ups. A 3M Magic tape™ was employed, and each strip was weighed using an analytical scale and then applied to cover 10 cm² of the mock-up's surface. The tape was peeled off at a 90° angle one minute after application and weighed again. The decohesion factor (DCF) was calculated to assess the adhesion properties of the coating films on the concrete surfaces using the following equation:

$$DCF = \frac{W_1 - W_0}{S} \quad (\text{equation 3})$$

where W_0 and W_1 are the weights (in mg) of the same strip before and after application on the surface, respectively, and S is the area (in cm²) of the tape application. The results were calculated as the mean value of the measurements on three replicates of each sample. On each replicate, 3 measurements were performed. The uncertainty of the measurement is represented as the standard deviation.

5.3. Results and discussion

5.3.1. Film properties evaluation

The properties of Chs and Chs-NS films were evaluated through colorimetric measurements on the concrete mock-ups, and in terms of adhesion, contact angle, capillary water absorption, and water vapour permeability. The colorimetric tests were performed on both the acrylic and alkyd spray-painted concrete mock-ups to better assess the colour changes that occur after the application of the coatings. The calculation of the ΔE through the equation reported in par. 5.2.3 allows to

compare the values L, a, b coordinates of the paint colours before and after the treatment. The values obtained are reported in Fig. 8.

These results demonstrate that both the coating solutions do not significantly alter the colour appearance of the acrylic and alkyd spray paints applied on the mock-ups, since the ΔE always results lower than 3 CIELAB units, which makes the potential application of these coatings on street artworks safe, from the aesthetical point of view [13,191]. decohesion factor (DCF) (par. 5.2.5) was calculated and reported as the average of five measurements for each specimen in Table 8.

The Scotch tape test [196,197] was conducted on the surface of the various concrete mock-ups – both treated and untreated – to evaluate the dark adhesion of the coating to the substrate, and the consolidating effect of the formulations. The comparative measurement of the effects of applying the Chs and Chs-NS coatings highlighted an effective performance of the treatments in terms of consolidation of the substrate. Specifically, the hybrid formulation demonstrated the best performance on both the coloured and pristine concrete specimens, followed by the Chs-based coating. The DCF in untreated concrete results were about twice

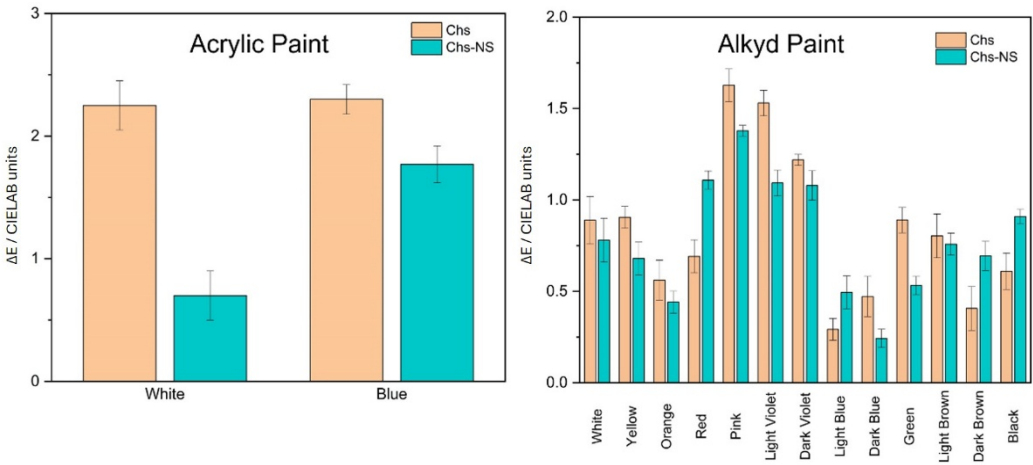


Fig. 8 Colour variations after the application of the films on the mock-ups.

as high compared to the values measured on the Chs-NS-treated mock-ups. These results confirm the improved adhesion of the coating to the substrate due to the addition of NS to the Chs solution

Mock-ups		DCF (mg/cm ²)	Standard deviation
Pristine concrete	Not treated	6.86	0.01
	Chs 0.5%	4.62	0.01
	Chs-NS 0.25-0.25%	3.26	0.01
Acrylic Spray	White Spray		
	Not treated	4.58	0.05
	Chs 0.5%	2.58	0.01
	Chs-NS 0.25-0.25%	1.86	0.01
	Blue Spray		
	Not treated	4.7	0.01
	Chs 0.5%	3.22	0.01
Alkyd spray	Chs-NS 0.25-0.25%	2.18	0.04
	White Spray		
	Not treated	4.94	0.02
	Chs 0.5%	3.13	0.03
	Chs-NS 0.25-0.25%	2.88	0.01
	Blue Spray		
	Not treated	4.87	0.04
	Chs 0.5%	3.26	0.01
	Chs-NS 0.25-0.25%	2.94	0.03
	Chs-NS 0.25-0.25%	4.87	0.04

Table 8 Decohesion factors measured for the different concrete mock-ups.

Furthermore, the tests conducted to investigate the interaction between the mock-ups, and the water highlighted the promising performance of the films. By comparing the results of the treated and untreated mock-ups (Fig. 9) the coatings based on Chs or Chs-NS do not impact the breathability of the substrate and its interaction with water. More in detail, the contact angle of the surface of the mock-ups slightly decreases due to the Chs and NS slight hydrophilicity (Fig. 9a). Even the water vapour permeability (Fig. 9b) does not significantly change after the application of the treatments. It can be noted that the exchange of water between Street-Art substrates and the environment, is already strongly impacted by the synthetic paints employed by the street artists. Thus, the application of protecting coatings that do not further affect these aspects would be preferred. Indeed, the capillary water absorption values are very similar in treated and untreated mock-ups, while the highest impact on hydrophobicity and breathability of the porous substrate is due to the application of the synthetic paint, as can be observed in Fig. 9c, by comparing the uncoloured concrete with the coloured and untreated mock-ups. In general, the application of Chs and Chs-NS coatings would not lead to further waterproofing of the substrate, leaving the permeability of the Street-Art walls unaltered. This finding is particularly relevant for mural conservation, as maintaining vapour permeability prevents moisture entrapment and salt crystallization within the wall substrate.

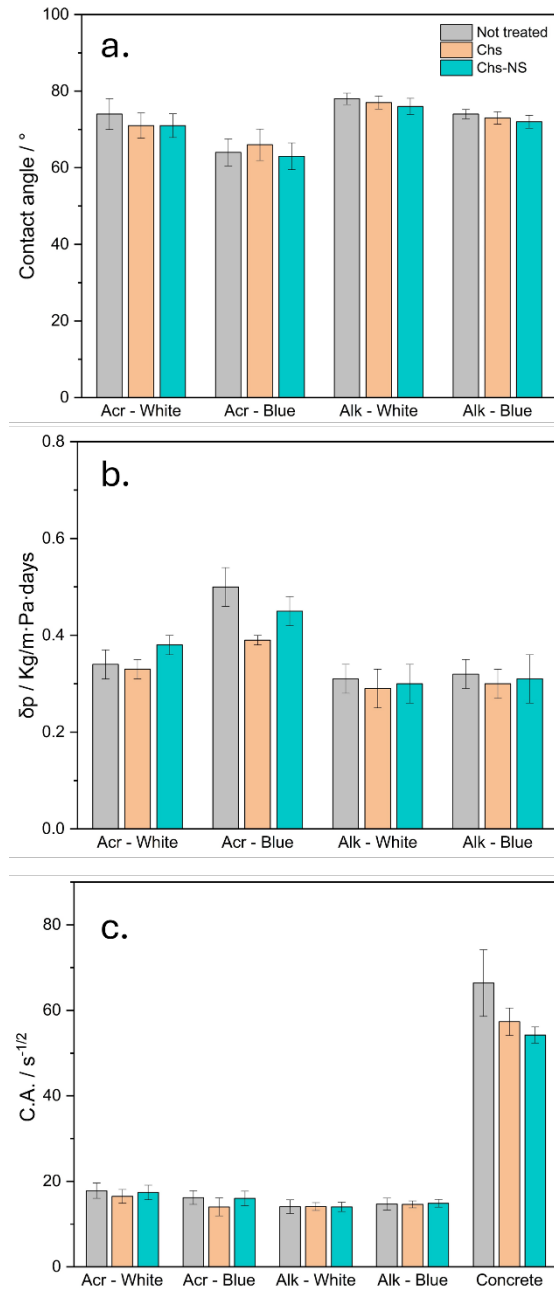


Fig. 9 Film properties measured on the mock-ups: contact angle (a.), water vapour permeability (b.), and capillary water absorption (c.).

As mentioned above (par. 4.2.1), the obtained films resulted transparent and very stable also when applied on the spray-painted mock-ups [195]. The colour variation of the coated and aged samples was monitored by comparing the results with the colour variation detected on aged and untreated mock-ups used as a control. The coloured concrete samples did not exhibit any visible changes after the application of coatings, even after the accelerated aging tests. The ΔE values calculated by the comparison of the colorimetric coordinates of unaged and aged samples are shown in Fig. 10 for the acrylic spray painted mock-ups – aged through the three different protocols – while the results about the alkyd-painted mock-ups – aged through the unique combined aging protocol – are shown in Fig. 12

The difference in ageing protocols reflects the distinct experimental phases of the study. Acrylic mock-ups were initially subjected to three separate ageing conditions in order to isolate and evaluate the individual effects of photo-oxidative, hydrothermal, and thermal stress on the coating performance. In contrast, alkyd-based paints were introduced at a later stage of the research, in connection with the real case study, and were therefore exposed to a single combined ageing protocol designed to better reproduce the simultaneous environmental stressors typically affecting outdoor murals. This methodological adjustment aimed to enhance the representativeness of the ageing conditions rather than to alter the evaluation criteria.

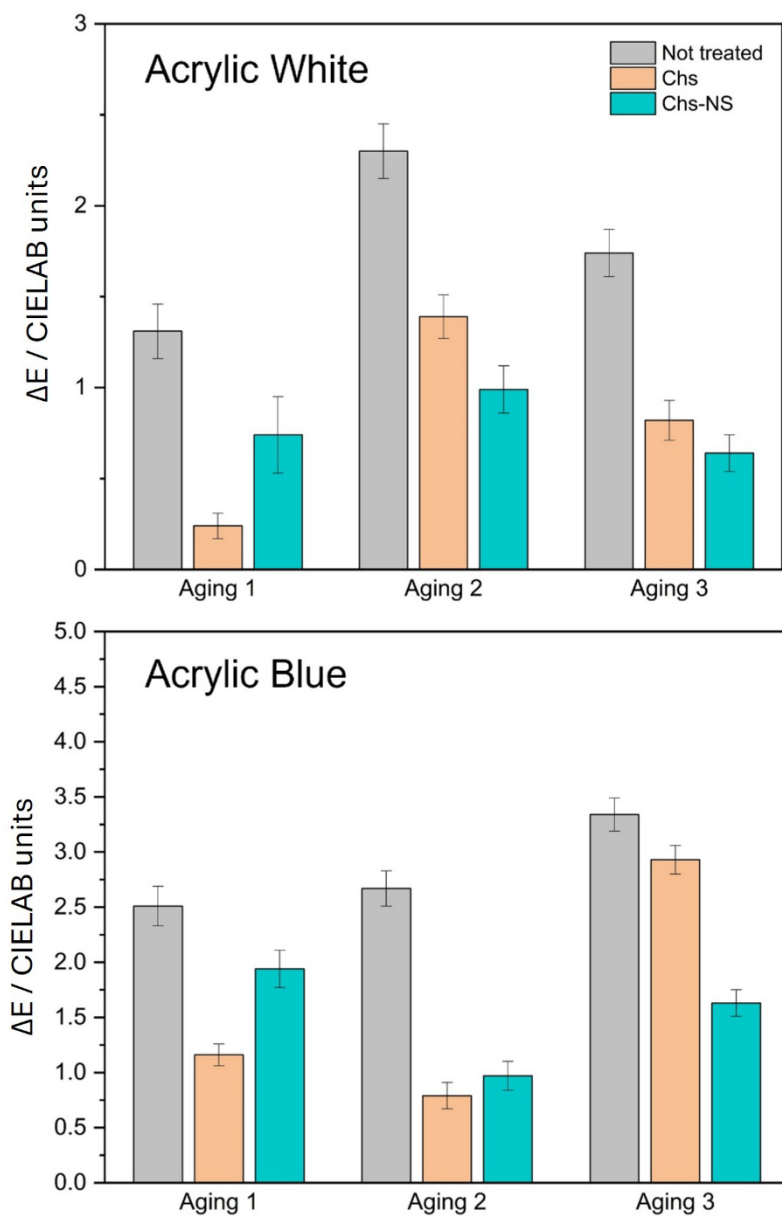


Fig. 10 Colour variation (ΔE) after the three aging tests (A1: UV-vis radiation; A2: 60 °C, 80% RH; A3: 60 °C) of the untreated and Chs or Chs-NS-treated spray-painted mock-ups.

More specifically, the untreated control mock-ups consistently exhibited higher ΔE values, indicating a more pronounced colour alteration induced by the accelerated artificial aging conditions on the uncoated acrylic and alkyd paints. Concerning the white and blue acrylic spray mock-ups aged under the three different protocols (A1, A2, and A3), comparison between the two colours shows that the white samples generally displayed lower ΔE values. This behaviour can reasonably be ascribed to the presence of titanium dioxide as the primary pigment on the white spray. Titanium dioxide is widely employed in modern spray paint formulations, predominantly in the rutile crystalline form, which is generally preferred for its higher photostability and lower photocatalytic activity. However, TiO_2 -based pigments can still influence paint degradation processes. In particular, the anatase polymorph, although less commonly used in commercial coatings, exhibits higher photocatalytic activity and has been widely reported to promote photo-oxidative degradation of organic binders under UV exposure, potentially contributing to colour changes during ageing [9].

[9] Both Chs and hybrid coatings demonstrated a protective action under the different aging conditions. Under UV-vis radiation (A1), Chs-based films showed lower ΔE values compared to untreated samples, without evidence of yellowing or crack formation. This behaviour contrasts with observations reported by Bussiere et al., who documented thermo-photo-oxidative degradation phenomena in chitosan films under different experimental conditions. [198]. Under hydrothermal aging (60 °C, RH 80%), both Chs and Chs-NS coatings showed similar reduced ΔE values relative to uncoated aged, coloured samples, confirming their ability to mitigate chromatic variation under combined temperature and humidity stress. In the case of thermal aging (A3), the hybrid coating yielded the lowest ΔE values among the tested systems, highlighting its enhanced resistance to temperature-induced colour alteration. The aesthetic changes on the treated and untreated mock-ups after thermal aging are shown in

Fig. 11. The Chs and Chs-NS coatings remained visually stable when applied to acrylic spray-painted concrete substrates. After accelerated ageing, all treated samples exhibited ΔE values below the commonly accepted perceptibility threshold for the human eye [13,191]. These findings support the potential application of Chs and Chs-NS formulations in the development of new environmentally friendly protective products specifically tailored for street art surfaces.

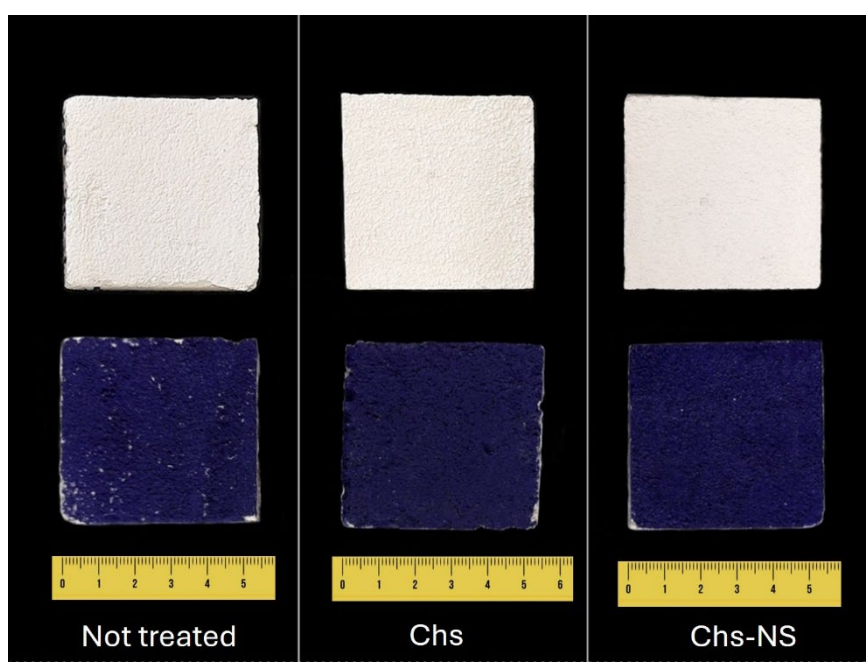


Fig. 11 White and blue acrylic paints mock-ups treated and untreated after 200 days of thermal aging (A3).

Regarding the mock-ups painted with the thirteen alkyd-based spray paints and subjected to the 100-hour artificial ageing protocol combining fluctuations of irradiation, temperature, and humidity, the ΔE values varied significantly among the different colours. In general, the orange paint proved to be the most sensitive to ageing conditions, as the untreated sample reached a ΔE value of 10.35 ± 0.55

CIELAB units. Other colours also exhibited considerable variation, such as Dark Blue (5.26 ± 0.26 CIELAB units), Dark Brown (4.50 ± 0.12 CIELAB units), and Light Brown (3.61 ± 0.25 CIELAB units).

As illustrated in Fig. 11, despite the diverse chromatic responses of the various paints, the mock-ups treated with Chs or Chs-NS coatings consistently showed lower ΔE values overall, indicating reduced colour variation after the accelerated ageing test.

An exception was observed for the black-painted mock-ups, where the samples treated with the Chs-NS coating displayed a slightly higher ΔE (1.46 ± 0.31 CIELAB units) than their untreated counterparts ($\Delta E 0.69 \pm 0.25$ CIELAB units).

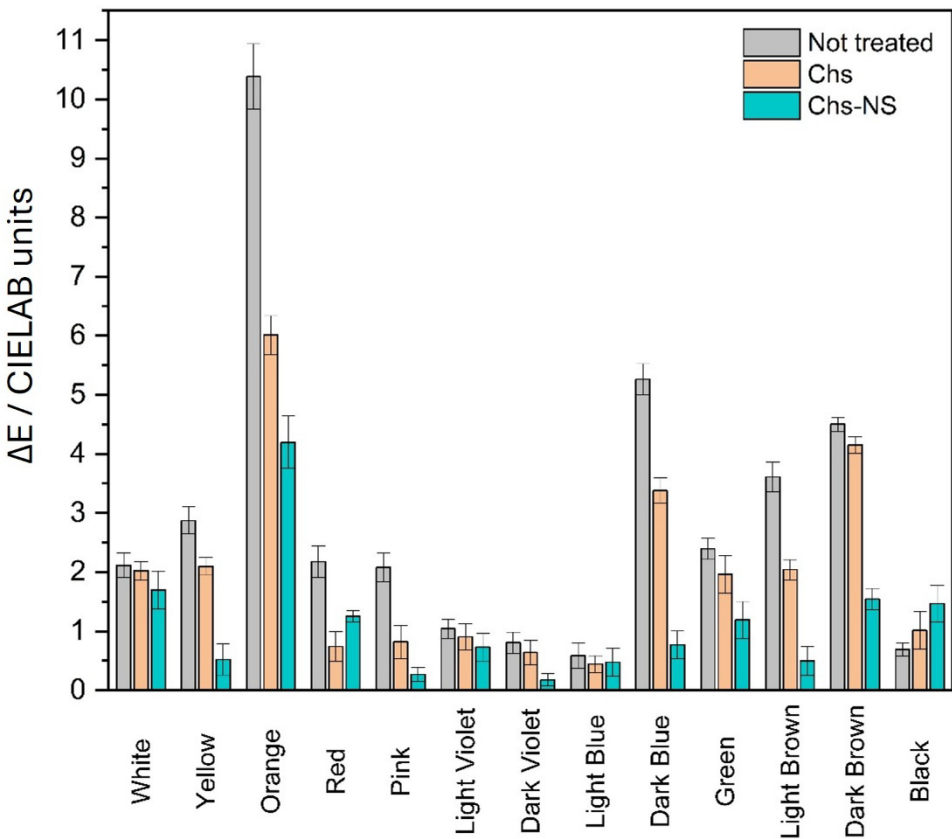


Fig. 12 Colour variation (ΔE) after the aging test conducted on the untreated and Chs or Chs-NS-treated concrete mock-ups, coloured with alkyd spray paints.

Similarly, for White, Light Violet, and Light Blue paints, no significant difference was observed between treated and untreated mock-ups.

These minor variations may be attributed to slight non-uniformities in brush application, potentially affecting local film thickness and ageing behaviour. Nevertheless, most treated mock-ups exhibited improved chromatic stability, with the hybrid formulation generally providing the most consistent mitigation of colour change. Beyond colour stability, one of the most relevant outcomes for conservation purposes is the exceptional optical transparency of both Chs and Chs–NS films. In all cases, the coatings remained visually undetectable on the painted surfaces, preserving the original chromatic saturation and surface appearance. This high transparency represents a critical advantage in conservation practice, where any perceptible alteration of tone, brightness, or surface character may compromise the aesthetic integrity of the artwork. The gloss values measured on treated, untreated, aged, and unaged mock-ups all resulted to be 0 GU. These data confirm that all mock-ups exhibit a matte appearance due to their inherently rough concrete surfaces, and that neither ageing nor the application of the Chs and Chs–NS coatings altered this characteristic. The absence of gloss variation further supports the suitability of these formulations as protective systems that respect the original visual qualities of contemporary mural paintings.

5.4. Conclusions

The application tests conducted on concrete mock-ups demonstrate the promising performance of the chitosan–nanosilica hybrid coating as a protective system for contemporary murals. Both the chitosan-based and hybrid coatings show excellent optical compatibility with the painted surfaces, as indicated by ΔE values consistently below the perceptibility threshold ($\Delta E < 2$) and well under the commonly accepted conservation acceptability limit ($\Delta E = 3$). The coatings

do not alter the surface gloss or the breathability of the substrate, maintaining water vapour permeability and hydrophilicity at levels comparable to untreated samples.

The adhesion tests demonstrate a significant consolidating effect, particularly for the hybrid system, which enhanced cohesion and surface resistance of the painted concrete. Furthermore, the accelerated ageing experiments revealed that both coatings effectively limited chromatic alterations over time, with the hybrid formulation achieving the best overall performance across diverse pigment types and ageing conditions.

From a conservation perspective, these findings position the Chs–NS system primarily within a preventive conservation framework, aimed at mitigating environmental degradation before substantial material loss occurs. At the same time, the improvement in surface cohesion suggests potential applicability within minimally interventive conservation strategies, where stabilization is required without compromising aesthetic integrity.

Importantly, the durability results obtained under accelerated ageing provide a preliminary basis for integrating this coating into planned maintenance strategies, in which periodic monitoring and, if necessary, controlled reapplication could ensure long-term preservation while reducing the need for more invasive interventive treatments.

These results validate the chitosan–nanosilica system as a viable, sustainable, and aesthetically compatible option for the preventive conservation of street artworks. The findings also provide a solid foundation for extending the tests to real case studies, discussed in Part C, and for integrating environmental assessment through the Life Cycle Analysis presented in Chapter 6.

6. Life Cycle Assessment of the Chitosan–Nanosilica Hybrid Coating

6.1. Introduction

In the previous chapters, the chitosan–nanosilica hybrid formulation was developed and evaluated in terms of its structural, physico-chemical, and protective performance on mock-ups reproducing contemporary mural paintings. However, the conservation of Street Art today requires not only the validation of new materials from a technical perspective but also a thorough understanding of their environmental impact and potential for contributing to resource depletion, airborne particulate matter, and greenhouse gas emissions, among others.

In addition, the growing demand for innovative and sustainable conservation strategies inevitably implies the manufacturing of new protective coatings. The development of such materials must therefore be accompanied by a critical reflection on their production processes, raw material sourcing, energy consumption, and scalability. Introducing new coatings into conservation practice is not environmentally neutral: even formulations conceived as “green” alternatives may entail significant impacts during synthesis, processing, and distribution. For this reason, environmental assessment becomes an integral component of responsible material innovation, ensuring that technical improvements are not achieved at the expense of increased ecological burdens.

Within this framework, Life Cycle Assessment (LCA) provides a systematic and quantitative approach to evaluate the environmental footprint impacts of newly developed conservation materials and to identify critical stages (“hotspots”) in their production and use.

This study was conducted in collaboration with Ms. Sarah Nunberg, PhD candidate in Heritage Science at Sapienza University of Rome, who included the chitosan–nanosilica hybrid coating developed during this doctoral project among the case studies analysed in her research on the environmental sustainability

impacts of conservation materials. This collaboration enabled the integration of the hybrid formulation into a broader comparative framework, combining methodological rigor with cross-disciplinary expertise in conservation science and life cycle thinking.

The aim of this chapter is to assess the environmental performance of the chitosan–nanosilica hybrid coating developed in this doctoral project through a screening LCA. The study investigates whether the proposed formulation can be considered a sustainable alternative for conservation practices and identifies the production stages where optimization efforts should be focused.

6.2. Goal and Scope of the Study

The main goal of this LCA was to evaluate the environmental impacts associated with the production of the hybrid coating, comprising chitosan, glucono- δ -lactone (GDL), and nanosilica (Levasil CC301). The focus was on the production phase, from raw material extraction to laboratory preparation, adopting a cradle-to-gate approach.

The functional unit was defined as 1 litre of hybrid coating solution, representing the relevant quantity for potential conservation applications. The study aimed to compare the relative contributions of raw material extraction, component production, and laboratory energy consumption, highlighting the most significant environmental contributors [199–204]. All laboratory-scale preparation was conducted in the Chemistry Lab at the University of Florence, with energy consumption calculated based on equipment specifications (watts, amperage, and duration of use of devices such as ovens and hot plates).

6.3. Methodology

The analysis was conducted using the LCA software SimaPro in combination with the Ecoinvent 3.6 database. The impact assessment method selected was ReCiPe 2016, considering both midpoint and endpoint indicators.

The system boundaries included:

- Production of chitosan from chitin (derived from crustacean shell waste).
- Production of GDL (modelled as citric acid due to data limitations).
- Production of nanosilica and silane-modified precursors (modelled on available nanosilica processes).
- Laboratory-scale preparation and mixing of the coating solution.
- Transport of raw materials.

The study was conceived as a screening LCA, meaning that certain assumptions and proxies were adopted when specific industrial data were not available. This inevitably introduces uncertainties but still provides a valuable first insight into the lower impact, emissions related to production, use, and disposal of the proposed coating.

6.4. Life Cycle Inventory (LCI)

Chitosan – The chitosan life cycle was modelled from shrimp shell waste, representing a by-product valorisation route that aligns with circular economy principles. Despite being renewable, its extraction typically involves chemical-intensive steps using NaOH and HCl, which are recognized hotspots due to their ecotoxicity and fossil fuel resource use. However, recent studies suggest that alternative processes - such as high-pressure-assisted (HPP) or microwave-assisted deacetylation - can significantly reduce the overall impacts (up to 60–90% lower than conventional processes) thanks to improved yield and lower energy demand.

Glucono- δ -lactone (GDL) – As no specific LCI dataset exists, GDL was modelled using data for citric acid fermentation, both being organic acids produced by *Aspergillus niger*. The impact sustainability of this process depends on the source of glucose feedstock (typically from corn or fruit residues), the

energy mix for fermentation and purification, and the use of auxiliary chemicals such as NaOH and HCl. Agricultural inputs (fertilizers, land use, and eutrophication potential) also represent potential environmental hotspots.

Nanosilica (Levasil CC301) – Nanosilica was modelled as colloidal silica produced by the precipitation of sodium silicate, including a surface modification step with silane coupling agents (e.g., GPTMS). The production of nanosilica is highly energy-intensive, mainly due to drying, dispersion, and silane treatment stages, which substantially contribute to climate change and resource depletion categories. Its energy demand and dependence on inorganic chemicals make it the dominant hotspot in most categories.

Energy Use and Transport – Electricity consumption during the laboratory preparation was included, and modelled according to the European electricity mix, which still includes a significant share of fossil-based energy. Transport of raw materials (average 500 km by truck) was included but contributed marginally to the total impact.

6.5. Results

The results of the impact assessment highlight clear differences in the contribution of the individual components:

- Nanosilica emerged as the dominant contributor across most impact categories, due to its highly energy-demanding production process. Its contribution was particularly significant in categories such as global warming potential (GWP), human toxicity, (both cancer and non-cancer effects), and resource use (fossil fuels). The human toxicity category deserves particular attention, as it reflects the cumulative impacts associated with energy-intensive synthesis, precursor chemicals, and potential emissions during production. This hotspot indicates that,

although nanosilica enhances the technical performance of the coating, its production stage represents a critical environmental burden that must be carefully considered in future optimization strategies.

- Energy consumption during laboratory preparation was also a relevant hotspot, especially under the European electricity mix, which still includes a substantial share of fossil-based sources. This result emphasizes the importance of energy source selection in future scale-up scenarios.
- Chitosan, despite requiring chemical processing, showed a relatively lower environmental burden, especially when modelled as a by-product valorisation pathway from crustacean waste. This represents one of the advantages of using biopolymers in sustainable “green” conservation. However, the environmental benefit depends on the choice of deacetylation method, as NaOH-intensive processes can increase impacts in marine ecotoxicity and human toxicity categories.
- GDL (modelled as citric acid) contributed moderately to the overall impact. Being derived from fermentation, its impact is lower than nanosilica, but not negligible, particularly in land use and eutrophication categories.

Considering all these aspects, the nanosilica content and the electricity used in the preparation phase were identified as the main hotspots of the hybrid coating production.

From a conservation perspective, it is also essential to relate these environmental hotspots to the functional durability of the coating. If film decohesion, cracking, or premature degradation were to occur, leading to more frequent reapplication, the cumulative environmental impact would significantly increase over time. Therefore, ensuring long-term film cohesion and resistance to environmental

stress is not only a technical objective but also a sustainability requirement. Durability directly influences the life-cycle performance of the coating, reducing the need for repeated manufacturing and application cycles.

Moreover, it has to be highlighted that the modified epoxy component was excluded due to lack of quantitative data and time constraints; future studies should incorporate it for completeness.

6.6. Discussion

The results highlight a paradox often encountered in sustainable material development: although the chitosan–nanosilica hybrid is based on a renewable, biodegradable biopolymer, its environmental performance is strongly influenced by the nanosilica component, which is energy-intensive to produce. This calls for a more detailed evaluation of alternative sources of silica, such as biogenic silica from agricultural residues (e.g., rice husk ash), which could reduce the environmental burden.

Another critical factor is the scale of production. Laboratory-scale preparation tends to show higher relative impacts due to small-scale inefficiencies and high energy demand. On an industrial scale, impacts could be distributed more evenly, potentially lowering the relative contribution of energy consumption.

From a conservation perspective, the hybrid coating still offers advantages compared to traditional synthetic polymers such as acrylic resins, which are derived entirely from fossil resources and show poor long-term stability outdoors. The hybrid's combination of renewable chitosan and inorganic nanosilica opens a pathway towards sustainable, functional coatings, provided that the environmental hotspots are properly addressed.

Future work should include a comparative LCA between the chitosan–nanosilica hybrid and commercial protective coatings (e.g., acrylic varnishes, anti-graffiti

fluoropolymers) to better contextualize the sustainability of the proposed formulation.

6.7. Conclusions and Future Perspectives

This screening LCA provides a first evaluation of the environmental profile of the chitosan–nanosilica hybrid coating. The analysis highlights that:

- Chitosan contributes positively to sustainability, being derived from renewable by-products.
- GDL has a moderate environmental burden, but its contribution is secondary.
- Nanosilica production and energy consumption during preparation are the main environmental hotspots.

Despite these critical aspects, the hybrid formulation remains promising as a sustainable protective system for Street Art, particularly when considering its performance advantages demonstrated in previous chapters. By addressing the high-impact stages—especially nanosilica sourcing and energy optimization—the coating could achieve a favourable balance between functionality and sustainability.

This side project contributes not only to highlighting the environmental aspects of formulating a new protective coating for contemporary muralism, but also to advancing the field of green conservation science, where environmental considerations are integrated with technical performance.

Future work should focus on:

- Scaling up production to evaluate industrial scale impacts.
- Comparative studies with existing commercial coatings.
- Exploration of alternative low-impact silica sources.

- Incorporating more primary data and relying less on proxies for increased accuracy.
- Including analysis of the modified epoxy component, which was excluded in this study due to lack of quantitative data.

Such efforts are critical to provide a more accurate and comprehensive understanding of the environmental profile of the hybrid coating, while maintaining its effectiveness as a conservation material.

PART C

This section of the thesis expands the scope of the research from laboratory formulation to real-world application, focusing on the study of materials, degradation processes, and collaborative approaches within the context of contemporary muralism.

It begins with the integrated chemical characterisation of 13 alkyd-based spray paints provided by the artist whose mural “Anna Maria” became the central case study.

Using a combination of ATR–FTIR, Raman, SEM–EDX, FORS, and TGA analyses, the study identified the main organic binders, pigments, and inorganic fillers, revealing the complexity and heterogeneity of modern commercial paints. Building upon these analytical results, the following chapter presents the monitoring of the Anna Maria mural over two years of natural outdoor exposure. Colorimetric, thermographic, and visual assessments documented significant chromatic variations, surface cracking, and efflorescence formation, highlighting the influence of environmental factors and substrate interactions.

These observations informed the controlled ageing experiments reported in Chapter 9, where the same spray paints were subjected to accelerated degradation protocols.

The comparison between natural and artificial ageing enabled the identification of consistent molecular and chromatic changes, providing a robust interpretative framework for understanding photochemical and oxidative degradation mechanisms in modern paints.

The experimental research concluded with the application of the chitosan–nanosilica hybrid coating on ETICS mock-ups, representing contemporary architectural substrates.

The results confirmed the coating’s transparency, stability, and compatibility under both accelerated artificial ageing conditions.

The correspondence between field and laboratory data also contributed to defining a reliable accelerated ageing protocol capable of reproducing, with good approximation, the degradation behaviour observed on the real mural.

Although this method may not be universally applicable, it offers valuable guidance for future studies aimed at developing predictive ageing procedures to evaluate restoration and protective materials for Street Art and contemporary muralism.

Finally, the collaborative work with the street artist SKIM and with the Anna Maria Enriques Agnoletti High School demonstrated the relevance of integrating conservation science with artistic practice and education.

These activities promoted awareness of Street Art preservation and fostered interdisciplinary dialogue between researchers, artists, and students.

In summary, this section consolidates the experimental and theoretical outcomes of the research, linking the molecular study of materials to the broader cultural, environmental, and methodological dimensions of conservation.

It illustrates how sustainable material development, analytical investigation, and community engagement can converge to support the long-term safeguarding of contemporary murals as a living and evolving form of cultural heritage.

7. Chemical characterization of spray paints

7.1. Introduction

The understanding of the chemical composition of modern spray paints is a crucial prerequisite for developing appropriate conservation strategies for contemporary mural art. These materials are highly complex multicomponent systems that combine organic binders, synthetic pigments and dyes, and various inorganic fillers and additives. Their chemical and physical behaviour, as well as their long-term stability, are strongly influenced by formulation parameters, environmental exposure, and interactions with the substrate, including cementitious supports, preparatory layers, and thermal insulation systems. While degradation mechanisms of modern paint films – particularly photo-oxidation and pigment instability – have been widely investigated in the literature [12,205,206], the role of substrate–paint interfacial interactions remains comparatively less explored, especially in the context of contemporary mural paintings. In outdoor wall paintings, substrate porosity, alkalinity, moisture transport, and salt migration may significantly affect adhesion, cohesion, and chromatic stability of the paint layers. However, systematic studies addressing these interfacial phenomena in commercial spray paints are still limited, representing a relevant knowledge gap in conservation science.

In conservation science, this complexity poses significant analytical challenges, as the heterogeneous and often proprietary nature of commercial spray paints requires the integration of multiple complementary techniques.

This chapter focuses on the chemical characterization of a set of thirteen alkyd-based spray paints from the MTN94 series (Montana Colors, Barcelona, Spain), directly provided by the artist responsible for the mural investigated in this research. The aim was to identify the main constituents - namely binders, pigments, dyes, and inorganic filler - and to assess their potential role in the

degradation phenomena observed on the original artwork. Particular attention was devoted to the identification of the binding medium and to the recognition of the specific chromophoric systems responsible for the wide colour range used in the mural.

A multi-analytical approach was adopted, combining Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR–FTIR), Micro-Raman Spectroscopy, Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM–EDX), Fibre Optic Reflectance Spectroscopy (FORS), and Thermogravimetric Analysis (TGA). Each technique was selected to provide complementary information that could not be obtained through a single analytical method. ATR–FTIR allowed the identification of organic functional groups and provided insight into the nature of the binding medium and major additives; however, its spectral overlap and limited spatial resolution make it less effective for the unequivocal identification of specific pigments. Micro-Raman spectroscopy, by contrast, enabled the characterization of crystalline pigments and fillers at a micrometric scale, though fluorescence phenomena and laser sensitivity may limit its applicability in certain coloured samples. SEM–EDX provided elemental composition and morphological information, essential for detecting inorganic fillers and pigment elements, but does not directly identify organic compounds. FORS contributed non-invasive optical information related to chromophoric systems and helped distinguish pigments and dyes based on reflectance features, although it cannot provide molecular-level structural data. Finally, TGA supplied quantitative information on thermal stability and organic/inorganic fraction ratios, which cannot be inferred from spectroscopic techniques alone.

The integration of these techniques was therefore necessary to overcome the intrinsic limitations of each individual method and to build a reliable compositional framework. Moreover, the selected analytical protocol was

designed to balance scientific robustness with practical constraints, including available instrumentation, research time, and training scope within the doctoral project. The chosen methods represent a compromise between high-resolution laboratory analyses and techniques that are realistically applicable within conservation research contexts, where cost, accessibility, and reproducibility are key considerations.

ed methodology allowed for a comprehensive characterization of both the organic and inorganic components, offering complementary molecular, elemental, and optical information.

The results presented in this chapter provide a detailed compositional framework for the alkyd spray paints employed in the case study, establishing a necessary foundation for understanding their material properties and guiding subsequent evaluations of ageing behaviour and protective coating performance, which will be discussed in Chapter 9.

7.2. Materials and Methods

7.2.1. Original spray paints

The artist provided 13 spray paint cans in different colours to characterize the materials used for a substantial portion of the mural. The spray paints, manufactured by Montana Colors (Barcelona, Spain), belong specifically to the MTN94 line.

To support their characterization and enable molecular analysis of their deterioration following accelerated artificial ageing tests (Chapter 9), the paints were applied directly onto glass slides and left to dry at room temperature for at least 10 days prior to analysis.

Additionally, each of these colours was applied to the surface of the ETICS mock-ups (Chapter 10).

The exact names and codes of the spray paints analysed correspond to those used in the application study of the Chs- and Chs-NS-based coatings reported in Chapter 5. For convenience, the colours are listed in the table below (Table 5).

Sample ID	Colour – Commercial Name
W	White – <i>Matt White</i> ; R-9010
Bk	Black – <i>Matt Black</i> ; R-9011
Y	Yellow – <i>Light Yellow</i> ; RV-1021
O	Orange – <i>Kalani Orange</i> ; RV-2004
R	Red – <i>Light Red</i> ; RV-3020
P	Pink – <i>Tutti Frutti</i> ; RV-115
LV	Light Violet – <i>Community Violet</i> ; RV-171
DV	Dark Violet – <i>Ultraviolet</i> ; RV-173
LB	Light Blue – <i>Electric Blue</i> ; RV-30
DB	Dark Blue – <i>Dark Blue</i> ; RV-5005
G	Green – <i>Mystic Green</i> ; RV-271
LBr	Light Brown – <i>Inca Brown</i> ; RV-136
DBr	Dark Brown – <i>Mole Brown</i> ; RV-140

Table 9 Spray paints provided by the artist and analysed in this study.

7.2.2. ATR–FTIR spectroscopy – Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR–FTIR) analyses were performed on fresh and artificially aged spray paints, as well as on efflorescences and the inorganic substrate sampled from the mural wall two years after its creation. Measurements were conducted using the same instrument and setup described in section 4.1.4. The analyses aimed to characterize the composition of the materials. Efflorescence samples and fragments of the inorganic substrate were directly collected from the mural surface two years after its execution. About 5 mg of each efflorescence and substrate sample were carefully scraped using a sterile scalpel and analysed by ATR without further chemical treatment. This small amount was sufficient to ensure adequate contact with the diamond crystal while minimizing invasiveness, in line with conservation sampling principles.

7.2.3. Micro-Raman spectroscopy

Micro-Raman spectroscopy was used for the complementary identification of pigments and dyes in the spray paints, as FTIR spectroscopy provides limited information due to the overlapping absorption bands of various components [35]. Each spray colour was deposited onto clean glass slides ($109 \times 22 \times 2$ mm) by spraying from a distance of approximately 20 cm in a vertical orientation for 2 seconds per sample, in order to obtain a homogeneous and sufficiently thick paint layer. The application parameters were kept consistent across samples to ensure reproducibility of the analytical conditions. The painted slides were left to dry for two weeks at room temperature before analysis, in order to simulate a fully dried paint film comparable to mural paints after curing on the wall surface. This precaution minimizes interference from residual solvents and allows a more realistic assessment of the binder–pigment system in its stabilized state. Glass was selected as a support because it produces only a broad and weak Raman

signal in the investigated spectral regions and does not interfere significantly with pigment identification, as commonly reported in Raman studies of artists' materials [207,208]. For each colour, three different measurement spots were analysed to account for possible heterogeneity in pigment dispersion and to obtain representative spectral data.

Raman spectra were acquired using a Horiba XploRA Plus confocal Raman microscope (Horiba UK Ltd, Northampton, UK) equipped with 532 nm and 785 nm excitation lasers. The laser light was focused through the microscope lens ($\times 50$, Olympus, 0.25 NA) onto the spray paint sample. Each spray colour was directly deposited onto a glass slide and left to dry for two weeks at room temperature before measurements. From each sample, three individual point spectra were recorded. Raman scattering was collected within a spectral range of 100–3500 cm^{-1} for the 532 nm laser and 100–2000 cm^{-1} for the 785 nm laser.

The choice of excitation wavelength was guided by the chromatic properties of the pigments to exploit resonance or pre-resonance effects when possible. In particular, the 532 nm laser was preferentially used for yellow, orange, and green paints, where electronic absorption in the visible region may enhance Raman scattering through resonance effects. Conversely, the 785 nm excitation was selected for red, pink, and some darker tones to reduce fluorescence phenomena and avoid excessive background, while still allowing the identification of characteristic vibrational modes. This approach optimized signal-to-noise ratio and improved pigment discrimination across the different colour formulations.

The exposure time for each signal acquisition was adjusted between 1 and 10 accumulations of 1–60 s, depending on CCD saturation levels, with laser power adjusted in the 0.25–10% range.

Spectral acquisition was performed using Labspec 6 software, while smoothing (applying the Savitzky–Golay algorithm), baseline correction, and peak analysis (Lorentzian fitting profile) were conducted using OriginPro 2023 software (v.

10.0.0.154, OriginLab Corporation). 532 nm laser was used to analyse yellow, orange, light and dark violet, light and dark blue, green, and dark brown spray paints, whereas white, red, pink, green, and light brown samples were examined using a 785 nm laser.

7.2.4. SEM-EDX analysis

Scanning electron microscopy (SEM) images were recorded using a Carl Zeiss Supra scanning electron microscope, operating at accelerating voltages in the range of 5–15 keV. Elemental characterization was carried out with an X-Max 50 energy-dispersive X-ray spectroscopy (EDX) detector connected to the SEM (Oxford Instruments, Ltd.). SEM/EDX images and spectra of the spray paints were obtained by depositing the samples onto glass slides, which were then coated with an ~10 nm AuPd film (90% Au, 10% Pd) prior to analysis.

This technique was employed both to investigate the elemental composition of the 13 spray paint colours provided by the artist and to characterize the inorganic substrate of the mural painting, as well as the patina that developed on its surface two years after completion.

7.2.5. Fiber Optic Reflectance Spectroscopy - FORS

Fiber Optic Reflectance Spectroscopy measurements, in the 350–2200 nm range, were performed using the portable spectrophotometer Zeiss equipped with two single-beam spectroanalyzers, the MCS601 UV-NIR (190–1015 nm range) and MCS611 NIR 2.2WR (910–2200 nm range). The data acquisition step for the MCS601 silicon photodiode array detector is 0.8 nm/pixel and 6.0 nm/pixel for the MCS611 InGaAs diode array detector. The radiation source is a 10W tungsten-halogen lamp (model CLH600) with a spectral emission range of 320–2700 nm. The radiation was both conveyed to the sample and collected back from it by means of quartz optical fibers bundle. The fibers were provided with a probe-head with 2x45°/0° geometry and the measure spot diameter was about 2

mm. Calibration was done using a 99% Labsphere Spectralon diffuse reflectance standard. The acquisition and data-processing were done using Aspect Plus software. This technique was employed for the non-invasive characterization of spray paint colours on the mock-ups.

Beyond its non-destructive nature, FORS was selected because it enables rapid in-situ identification of pigments and chromophoric systems through their characteristic electronic absorption features in the visible and near-infrared regions. The method allows comparison with existing spectral databases of modern pigments and paint materials, which is particularly valuable in the study of contemporary commercial spray paints [209–211]. Moreover, FORS provides complementary information to Raman and ATR–FTIR analyses, especially in cases where fluorescence or complex mixtures limit molecular identification. Its portability, low operational cost, and suitability for large-area screening make it particularly appropriate for mural paintings and outdoor artworks.

7.2.6. TGA – Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed on all the 13 spray paints using a SDT Q600 TA Instrument (New Castle, USA), operating from 25 to 700 °C at a heating rate of 10 °C/min under a nitrogen flow of 100 mL/min. Approximately 7 mg of dried spray paint fragments were placed in an open alumina pan for each measurement. Data acquisition and processing were performed using TRIOS software (ver. 5.1.1.46572). This analysis allowed an approximate estimation of the relative amounts of organic components (e.g., binder, stabilizers, organic dyes) and inorganic components (e.g., fillers, inorganic pigments), considering the higher thermal stability of the inorganic fraction.

7.3. Results and discussion

Artists' spray paints are complex organic–inorganic systems, and their complete characterization requires a combination of complementary techniques. In this study, spectroscopic analyses were performed on a selected set of paint samples provided by the artist in 2023, immediately after the creation of the mural. An extensive characterization of the MTN94 spray paints was conducted using a multi-analytical approach that combined ATR–FTIR, Raman, Energy Dispersive X-ray Spectroscopy (EDX), and Fibre Optic Reflectance Spectroscopy (FORS). Due to the very low pigment concentrations in many of the paint formulations, ATR–FTIR spectroscopy primarily allowed for the identification of the binder fillers, and provided partial information about the pigments and fillers, whereas more sensitive techniques such as Raman spectroscopy were essential for detecting the main pigments and dyes.

This integrated methodology enabled the identification of both organic and inorganic components, including binders, pigments, and fillers, across the full range of colours investigated.

7.3.1. Binder

FTIR analysis consistently indicated the presence of an alkyd resin modified with styrene and nitrocellulose as the primary binding medium. Vibrational bands corresponding to esters, aliphatic chains, and aromatic groups were observed in all samples. The representative FTIR spectrum of the black spray paint is shown in Fig. 13, highlighting the main vibrational bands associated with the binder. The characteristic signals are summarized in Table 10.

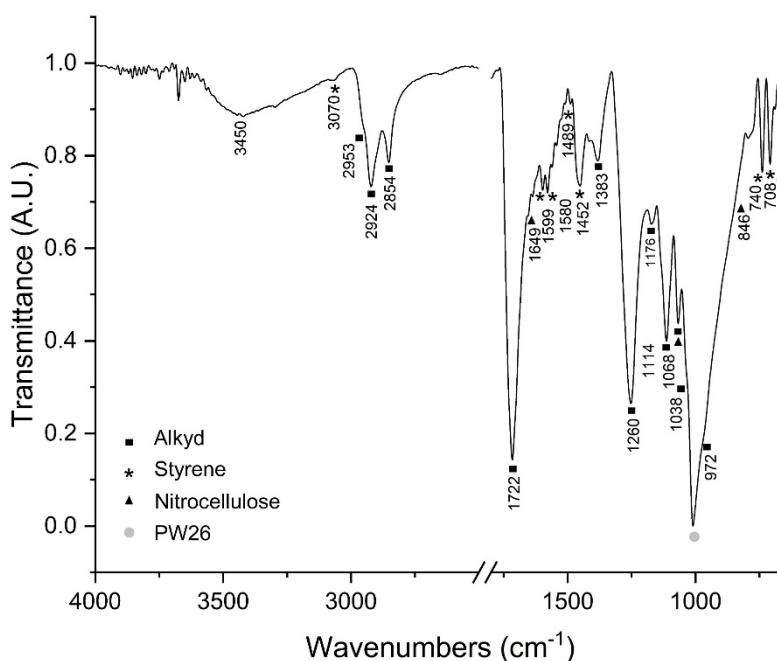


Fig. 13 ATR-FTIR spectrum of the black spray paint, showing the vibrational bands that characterise the binder.

The analysis of the black spray paint was effective in characterizing the binder, which was identified as an alkyd resin modified with styrene and nitrocellulose. The spectrum exhibited the typical absorption of the alkyd binder, including O–H stretching at ca. 3450 cm⁻¹, C–H stretching of aliphatic chains at 2953, 2924, and 2854 cm⁻¹, C=O stretching at 1722 cm⁻¹, and C–O/C–C stretching at 1260,

1176, and 1114 cm^{-1} . Aromatic C–H stretching at 3070 cm^{-1} and aromatic skeletal ring vibrations at 1599, 1580, 1489, and 1452 cm^{-1} confirmed the presence of styrene units, while the N–O stretching at 1649 cm^{-1} was consistent with nitrocellulose incorporation. Additional C–H bending (1383 cm^{-1}) and C–H out-of-plane bending (740, 708 cm^{-1}) further supported the identification of the styrene-modified alkyd resin.

Bond Type Assigned	Band (cm^{-1})	References
O–H stretching – intramolecular bonded	ca. 3450 m	
Aliphatic C–H stretching	3070 w (Styrene)	
C–H stretching	2953 sh, 2924 m, 2854 m (Alkyd)	
C=O stretching	1722 s (Alkyd)	
N–O stretching	1649 w (Nitrocellulose)	[18,22,45];
Aromatic skeletal ring vibrations	1599 m, 1580 m, 1489 w, 1452 m (Alkyd-Styrene)	[212]: IMP00113
C–H bending	1383 m	
C–O and C–C stretching	1260 s, 1176 m, 1114 s (Alkyd); 1068 s (Alkyd, Nitrocellulose), 1038 sh, 972 sh (Alkyd)	
C–H out-of-plane bending	740 m, 708 m (Styrene)	

Table 10 ATR–FTIR signals of the major binder of all spray paints investigated (s: strong, m: medium, w: weak, sh: shoulder).

In addition to the binder, diagnostic peaks attributable to talc (PW26) were observed at 1012 and 667 cm^{-1} , added to the formulation as a filler. A weak signal at 771 cm^{-1} may correspond to trace amounts of calcium carbonate (PW18, CaCO_3), a hypothesis supported by EDX analysis, which detected calcium (par. 7.3.2). Other signals at 1068, 1038, and 972 cm^{-1} likely reflect contributions from

both the alkyd binder and nitrocellulose. In general, the combined IR and elemental data indicate a complex mixture of organic binder and inorganic fillers.

7.3.2. Pigments and organic dyes

In this section, the multi-analytical characterization of the 13 spray paint colours is presented, focusing on the identification of organic dyes, synthetic pigments, and inorganic extenders. All samples share the same binding medium, previously described in section 7.3.1. ATR–FTIR, Raman spectroscopy, EDX, and FORS were employed within a complementary analytical framework. Vibrational techniques were primarily used for molecular identification of organic pigments and mineral phases. EDX provided elemental confirmation and enabled the detection of inorganic components not clearly resolved by vibrational techniques. Finally, FORS measurements supported pigment identification through the analysis of electronic transitions and reflectance features, highlighting the potential of this technique for in-situ investigations.

In general, inorganic pigments and fillers, such as talc (PW26), kaolin (PW19), calcium carbonate (PW18), and sulphates (PW25) were identified in several samples. However, in some cases their presence could only be confirmed by EDX due to low spectral intensity or band overlapping. Raman spectroscopy was particularly effective in identifying the main chromophores. Synthetic organic pigments, including PR170 (Naphthol AS), PY74 (Monoazo Yellow), PV23 (Dioxazine Violet), PO34 (Disazo Pyrazolone), and phthalocyanine derivatives (PB15:3, PB15:6, PG36, PG7), were identified by their characteristic Raman signals. Inorganic pigments such as titanium dioxide (PW6, rutile) and iron oxide-based pigments (e.g., PY42, PY43, PBr6, PBr7) were also detected. Nevertheless, in the case of darker paints, fluorescence and local heating effects limited the applicability of Raman spectroscopy, even though carbon black (PBk7) was detected by Raman spectroscopy in brown paints. EDX analysis

complemented the spectroscopic data by providing elemental compositions consistent with the identified pigments and extenders, including TiO₂, iron oxides, calcium compounds, Al-silicates, and Cu-based phthalocyanines. EDX was particularly valuable for confirming the presence of elements such as Mg, Al, and Cu, which are not always easily distinguished through vibrational spectroscopy. FORS spectra further supported pigment identification by enabling the analysis of electronic transitions. Characteristic S-shaped reflectance curves with diagnostic inflection points and absorption bands allowed the assignment of valence charge (VC), molecular orbital (MO), and ligand field/charge transfer (LF/CT) transitions, particularly for titanium white and polycyclic pigments. Additional near-infrared bands indicated the presence of non-structured water and alkyd binders. The integrated analytical results are summarized in Table 11. The assignments of pigments and dyes identified by FTIR and Raman spectroscopy are summarized in Table 12, the results of the EDX analyses are presented in Table 13, and a summary of the FORS spectra is provided in Table 14.

Component	ATR- FTIR	Raman	EDX	FORS	Diagnostic contribution
Alkyd binder	✓	–	–	✓ (NIR bands)	FTIR primary, FORS confirmatory
PR170 (Naphthol AS)	✓	✓	–	–	Raman primary
PY74 (Monoazo Yellow)	✓	✓	–	✓ (MO $n \rightarrow \sigma^*$)	Raman primary, FORS supportive
PV23 (Dioxazine Violet)	✓	✓	–	✓ (MO)	Raman primary
PO34 (Disazo Pyrazolone)	✓	✓	–	–	Raman primary
PB15:3 / PB15:6 (Phthalocyanine blue)	–	✓	✓ (Cu)	✓ ($\pi-\pi^*$)	Raman + EDX confirmatory
PG7 / PG36 (Phthalocyanine green)	✓	✓	✓ (Cu, Cl)	✓ ($\pi-\pi^*$)	Multi-technique
PW6 (TiO ₂ , rutile)	–	✓	✓ (Ti)	✓ (VC, inflection ~400–405 nm)	Multi-technique
Iron oxides (PY42, PY43, PBr6, PBr7)	✓	✓	✓ (Fe)	✓ (CT, LF)	Multi-technique
PBk7 (Carbon black)	–	✓ (limited)	–	–	Raman limited (fluorescence issues)
PW18 (CaCO ₃)	–	–	✓ (Ca)	–	EDX primary
PW19 (Kaolin)	✓	–	✓ (Al, Si)	–	FTIR + EDX
PW26 (Talc)	✓	–	✓ (Mg, Si)	–	FTIR + EDX
PW25 (Sulphates)	–	–	✓ (S)	–	EDX primary

Table 11 Integrated multi-analytical identification of pigments, dyes and extenders in the 13 spray paints.

Pigment	IR signals (cm ⁻¹)	References	Raman signals (cm ⁻¹)	References
PB15:3	1653, 1647, 1605, 1584, 1508, 1495, 1465, 1456, 1418, 1334, 1118, 1090, 1073, 900, 878, 800, 779, 731	[18,35,212,213] IRUG IOD00255, IOD00436	138, 173, 233, 256, 289, 414, 483, 592, 643, 680, 719, 746, 779, 833, 849, 953, 1007, 1038, 1107,1142, 1193, 1206, 1214, 1305, 1340, 1428, 1451, 1528, 1610	[212,214,215] IRUG ROD00657, ROD00414
PB15:6			173, 233, 256, 592, 680, 746, 779, 833, 953, 1007, 1038, 1107, 1142, 1305, 1340, 1411 , 1451, 1482 , 1528, 1593 , 2667 , 2872 , 3058	[214,215]
PBk	Not detected		1304, 1598	[212] IRUG RMP00202
PBr6		[212,216] IRUG	229, 298, 386, 610, 649	[212] IRUG RMP00112
PBr7	796, 3299	IMP00518		
PBr25	1599, 1385, 1254, 1163, 1113, 1066, 1042, 978, 908, 740, 710	[212] IRUG IOD00446	335, 426, 565, 780, 1040, 1108, 1129, 1157, 1226, 1245, 1289, 1359, 1418, 1449, 1482, 1553, 1582, 1621	[214,215]
PG7	1489, 1463, 1452, 138, 1163, 740	[18,212,217] IRUG IOD00493	346, 685, 740, 777, 818, 1212, 1283 1338, 1538	[215,217]
PG36	1560, 1489, 1172, 919, 800, 775-745	[212,217]	184, 214, 260, 311, 321, 328, 449, 661, 747, 770,	[212,214,215,217] IRUG ROD00293

		IRUG IOD00450	963, 1168, 1176, 1193, 1271, 1286, 1323, 1531	
PO34	1659, 1601, 1568, 1551, 1512, 1452, 1387, 1340, 1252, 1155, 1007, 912, 862, 777	[35,212] IRUG IOD00547	173, 256, 286, 366, 533, 599, 661, 767, 846, 914, 1046, 1157, 1235, 1255, 1272, 1340, 1418, 1450, 1477, 1534, 1596	[35,212,214,215] IRUG ROD00060
PR170	Ca. 3400, 3296, 3176, 1674, 1659, 1599, 1552, 1518, 1495, 1485, 1450, 1385, 1362, 1336, 1286, 1261, 1225, 1203, 1176, 1165, 1043, 1012, 910, 860, 847, 800, 779, 741	[35,45,212] IRUG IOD00271	185, 210, 238, 264, 300, 421, 495, 540, 574, 613, 664, 728, 802, 863, 964, 1013, 1044, 1117, 1141, 1165, 1206, 1244, 1288, 1333, 1362, 1390, 1424, 1453, 1489, 1511, 1550, 1603	[35,212,214,215] IRUG ROD00048
PV23	1636, 1560, 1541, 1176, 1090, 740, 731	[212] IRUG IOD00405, IOD00305	314, 484, 526, 590, 617, 670, 922, 952, 1165, 1207, 1255, 1345, 1390, 1430, 1590, 1611, 2553, 2598, 2641, 2735, 2778, 2821	[30,212,214,215] IRUG ROD00042
PW6	Out of range		141, 222, 318, 445, 610	[18,212,218,219] IRUG RMP00146
PW18	Not detected		1087	[18,218]
PW19	1025, 919	[18,212] IRUG IMP00314.	746, 931	[18]
PW25	Not detected		1002	[18,212,219] IRUG RMP0011

PW26	1012, 667	[18,45,212] IRUG IMP00113.	233, 680	[18]
PY42	3299, 3116, 910, 796, 671	[212] IRUG IMP00541	241, 299, 388, 480, 549, 610, 660	[212,220] IRUG RMP00141
PY43	3299, 1636, 1042, 908	[212] IRUG IMP00032.		
PY74	1674, 1552, 1516, 1459, 1404, 1362, 1336, 1286, 1252, 1223, 1201, 1178, 1025, 953, 916, 860, 822, 802, 779, 756	[18,212] IRUG IOD00510	109, 184, 223, 256, 315, 357, 401, 437, 462, 495, 523, 574, 600, 623, 644, 654, 733, 780, 802, 844, 915, 1044, 1066, 1087, 1117, 1159, 1169, 1244, 1263, 1298, 1325, 1352, 1403, 1422, 1438, 1489, 1506, 1550, 1593, 1668	[18,212,214,215] IRUG ROD00018

Table 12 Assignments of pigments, dyes, and inorganic fillers identified in the 13 spray paint colours through ATR–FTIR and Raman spectroscopy.

Sample	EDX elemental analysis
White – W	Al, Si, Ca, Ti
Black – Bk	Mg, Si, Ca,
Yellow – Y	Mg, Al, Si, Ca, Ti
Orange – O	Mg, Al, Si, Ca, Ti, Fe
Red – R	Mg, Al, Si, Ca, Ti, Fe,
Pink – P	Al, Si, Ca, Ti, Fe,
Light Violet – LV	Al, Si, Ca, Ti
Dark Violet – dv	Al, Si, Ca, Ti
Light Blue – LV	Mg, Al, Si, Ca, Ti, Fe, Cu
Dark Blue – DV	Mg, Al, Si, Ca, Ti, Cu
Green – G	Al, Si, Cl, Ca, Ti, Cu, Br
Light Brown – LBr	Al, Si, Ca, Ti, Fe
Dark Brown – DBr	Al, Si, Ca, Ti, Fe

Table 13 Elemental composition of spray paint samples as determined by EDX analysis.

Pigment	FORS signals (nm)	Electronic transition	References
Titanium white, Rutile form	Inflection point: ~ 400- 405	VC	[221]
Monoazo yellow	370, 420, 455 Inflection point: ~ 510	MO n(azo) - π - π^*	[24,222]
Iron oxides- hydroxides	430, 480, 650-680, 920	CT and LF	[24,223]
Polycyclic pigment (dioxazine)	535, 565, 630	MO	[24,224,225]
Phtalocyanine blue	420, 430, 625, 710	MO (π - π^*)	[24,223,226]
Phtalocyanine green	650, 730, 775	MO (π - π^*)	[24,226,227]

Table 14 Assignments of pigments, dyes, and inorganic fillers identified in the 13 spray paint colours through FORS analysis. Abbreviations: VC = valence-conduction band transition; MO = molecular orbital transition (π - π^*); CT = charge transfer transition; LF = ligand field transition.

The following section provides a detailed account of the characterization results for each colour, with specific reference to the identified pigments, organic dyes, and extenders.

7.3.3. White alkyd spray paint

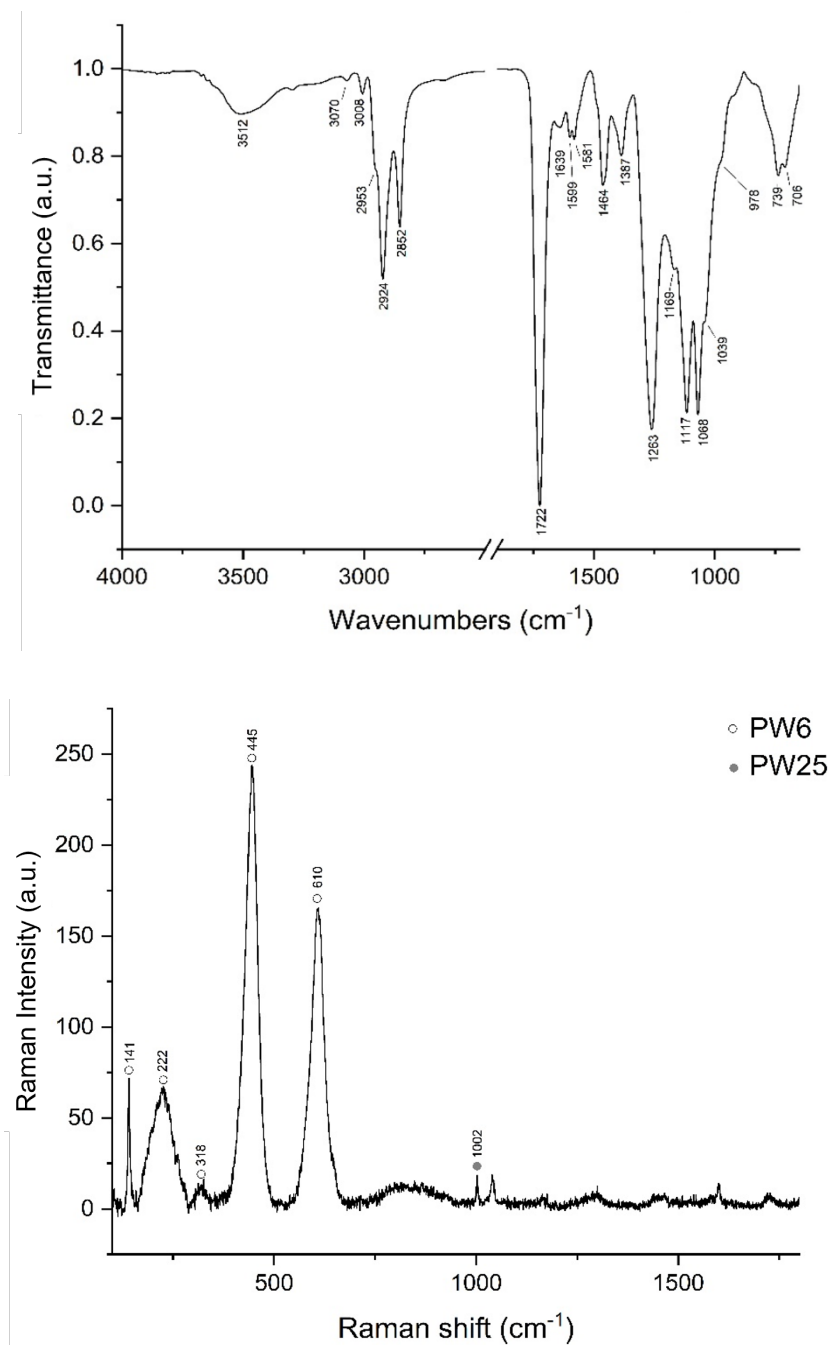


Fig. 14 ATR-FTIR and Raman spectra of white spray paint (W).

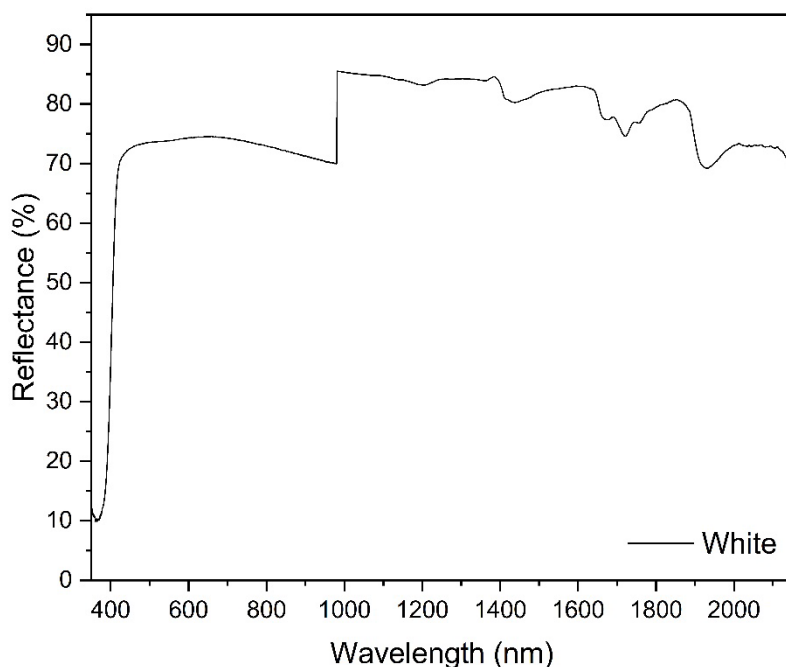


Fig. 15 FORS spectrum of the white spray paint (W).

FTIR analysis of the white spray paint (Fig. 14) revealed only vibrational signals attributable to the organic binder. The presence of rutile (TiO_2) could not be confirmed via FTIR, as its characteristic Ti–O and Ti–O–Ti stretching vibrations predominantly fall within the mid- to far-infrared region, often beyond the spectral range ATR–FTIR instrument ($4000\text{--}650\text{ cm}^{-1}$). Similarly, although CaSO_4 was detected by both Raman spectroscopy and EDX analysis, no corresponding diagnostic bands were observed in the FTIR spectrum. This absence can likely be attributed to the inherently lower sensitivity of ATR–FTIR compared to Raman spectroscopy for minor inorganic phases dispersed within an organic matrix. In heterogeneous paint systems, the practical detection limit of ATR–FTIR for mineral components may lie in the order of a few weight percent, depending on sample homogeneity, penetration depth, and band overlap with the organic binder. Therefore, CaSO_4 may be present below the FTIR detection

threshold, while still being detectable by Raman spectroscopy and EDX, which are more sensitive to crystalline and elemental signatures, respectively. Instead, Raman analysis allowed the identification of both titanium white (PW6) and calcium sulphate (PW25). Moreover, EDX data further indicated the presence of aluminum, which is consistent with minor amounts of kaolin (PW19). FORS measurements conducted on the white mock-up displayed S-shaped reflectance spectra, typical of semiconducting materials and indicative of a valence charge (VC) electronic transition (Fig. 15). All spectra exhibited a strong absorption edge at the UV–visible boundary, a well-known feature of white pigments. The inflection point of the S-shaped curve, determined as the maximum in the first derivative of the reflectance spectra, was located at 404 nm. This value is consistent with the rutile polymorph of titanium white (TiO_2), thereby supporting its identification despite the limitations of FTIR [221]. In addition, the FORS spectra showed broad and poorly resolved absorption bands centered around 1200 nm and 1935 nm, assigned to unstructured water [24]. Three additional absorption bands in the 1670–1770 nm region matched the spectral signature of an alkyd resin binder, further confirming the results of FTIR analysis [24].

Although FTIR spectroscopy already provided clear evidence of the alkyd binder, FORS analysis was retained for complementary reasons. While FTIR identifies functional groups through vibrational transitions in the mid-infrared region, FORS operates in the UV–Vis–NIR range and provides information on electronic transitions, pigment reflectance behaviour, and absorption edge features. In particular, the S-shaped reflectance curve and the position of the absorption edge at 404 nm allowed confirmation of the rutile form of TiO_2 , which could not be directly detected by FTIR within the available spectral range. The combined use of FTIR and FORS therefore ensured a more robust characterization of both organic and inorganic components, especially in complex commercial spray paint systems.

7.3.4. Black alkyd spray paint

The analysis carried out on the black spray paint were effective in characterizing the binder, as described in the previous section (par. 7.3.1). In addition to the typical spectral signals of the binder, diagnostic IR bands attributable to talc (PW26) were observed at 1012 cm^{-1} and 667 cm^{-1} . A further weak band at 771 cm^{-1} may correspond to trace amounts of calcium carbonate (PW18, CaCO_3), a hypothesis supported by EDX analysis, which detected calcium.

As in the case of the white spray paint, EDX also revealed the presence of aluminium (Al), and in this case magnesium (Mg) as well, likely indicating minor quantities of kaolin (PW19) and talc (PW26), respectively. Attempts to acquire Raman spectra were unsuccessful, as laser excitation caused thermal degradation of the sample. As previously reported by Marazioti et al., the identification of inorganic pigments commonly employed in black and silver spray paints is often hindered under standard Raman conditions due to strong fluorescence [18].

In contrast to other samples, titanium dioxide (TiO_2) was not detected in this case. Based on the collected evidence, the black coloration of the paint can be attributed to the presence of carbon black (PBK7). This interpretation is consistent with the absence of distinctive signals in the FTIR spectrum. Carbon black is generally characterised by a predominantly amorphous structure, which results in weak or non-specific IR features, making its identification by FTIR challenging. Therefore, the attribution to PBK7 is based on the combined analytical evidence rather than on a single diagnostic spectroscopic signal.

7.3.5. Yellow alkyd spray paint

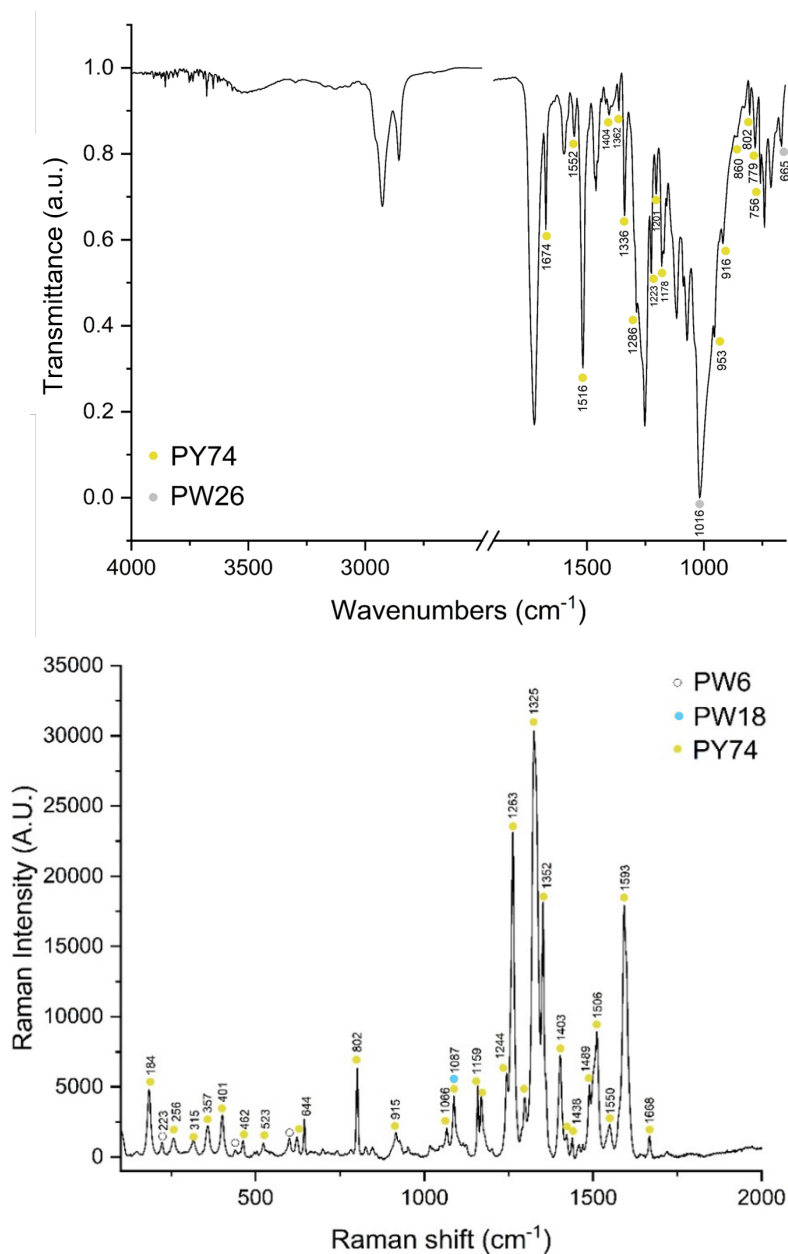


Fig. 16 ATR-FTIR and Raman spectra of yellow spray paint (Y).

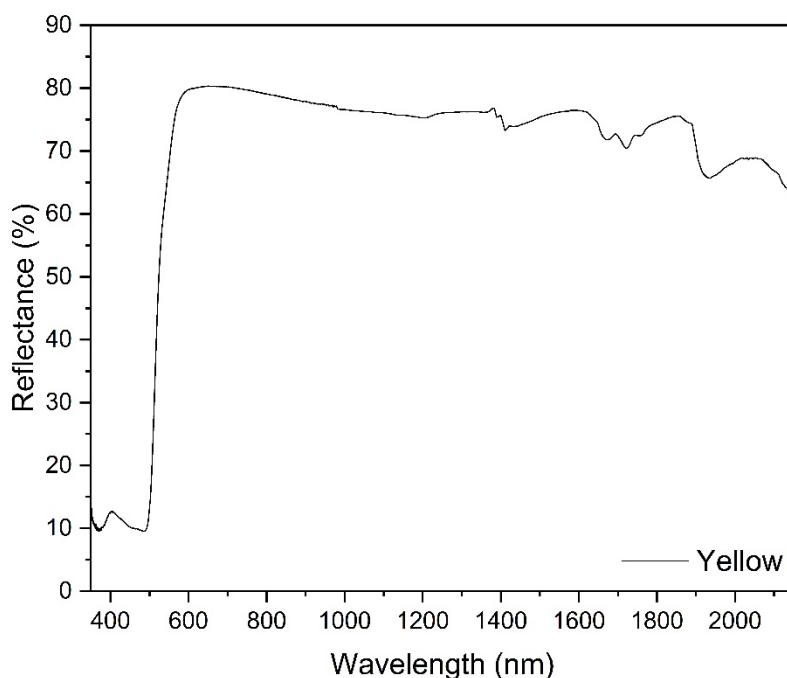


Fig. 17 FORS spectrum of the yellow spray paint (Y).

ATR–FTIR spectroscopy conducted on the yellow spray paint (Fig. 16) revealed the presence of the monoazo yellow pigment PY74 and talc (PW26). Raman spectroscopy confirmed PY74 and further indicated signals attributable to titanium dioxide (PW6) and calcium carbonate (PW18). EDX analysis supported the identification of these inorganic pigments and fillers by detecting Ti, Mg, Si, and Ca, and additionally revealed the presence of Al, consistent with kaolin (PW19). FORS spectra Fig. 17 exhibited intense UV–Vis absorption bands with an inflection point near 510 nm, characteristic of monoazo yellow pigments [24,222]. In addition, broad absorptions signals around 1200 nm and 1935 nm were attributed to non-structured water, while three distinct bands between 1670 and 1770 nm were assigned to the alkyd resin binder [24].

7.3.6. Orange alkyd spray paint

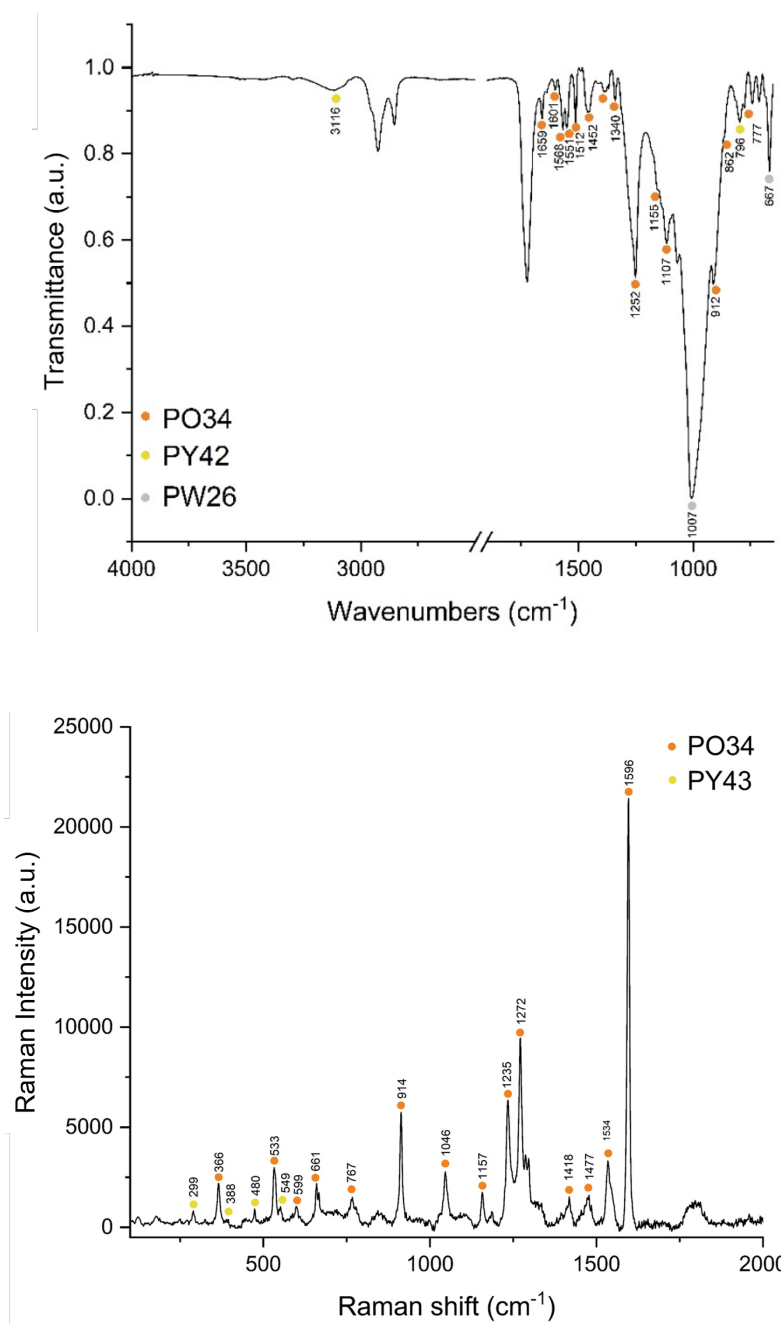


Fig. 18 ATR-FTIR and Raman spectra of orange spray paint (O).

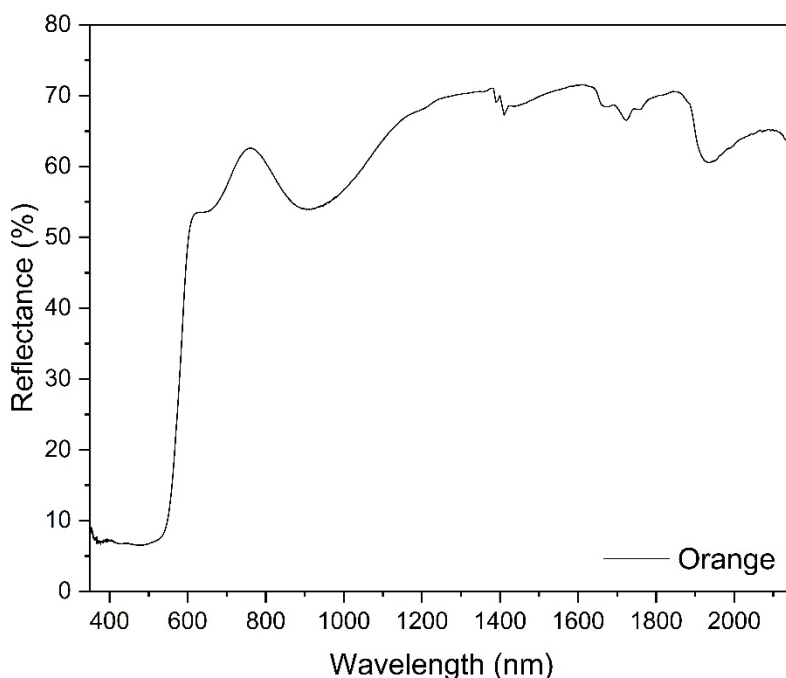


Fig. 19 FORS spectrum of the orange spray paint (O).

ATR–FTIR spectroscopy revealed the presence of the organic pigment PO34 together with iron oxides and hydroxides, consistent with PY42 and PY43. Raman spectroscopy confirmed both the iron-based pigments and PO34 (Fig. 18). Talc (PW26) was indicated by FTIR and further supported by EDX, which detected magnesium (Mg). The EDX analysis also revealed calcium (Ca), aluminium (Al), and titanium (Ti), suggesting the presence of calcium carbonate (PW18), kaolin (PW19), and titanium dioxide (PW6), most likely in the rutile form. Although TiO_2 was not observed in Raman spectra, its detection by EDX indicates either trace concentrations below the Raman sensitivity or spectral masking by strong iron pigment scattering. Similarly, kaolin and talc were not detected by Raman, likely due to low abundance or overlapping signals. The EDX detection of iron further corroborates the presence of the iron-based yellow pigments identified by FTIR and Raman analysis.

FORS spectrum (Fig. 19) exhibited strong absorption near the UV–Vis boundary, characteristic of the organic pigment PO34 [24,223]. Reflectance spectra showed absorption bands at 675 nm and 920 nm, a reflectance maximum at 760 nm, and an inflection point at 585 nm, with additional shoulders at 430 nm and 480 nm, typical of iron oxide–hydroxide pigments associated with ligand field and charge transfer electronic transitions [24,223]. Broad absorption bands around 1200 nm and 1935 nm indicated non-structured water, while bands between 1670 and 1770 nm corresponded to the alkyd binder [24].

7.3.7. Red alkyd spray paint

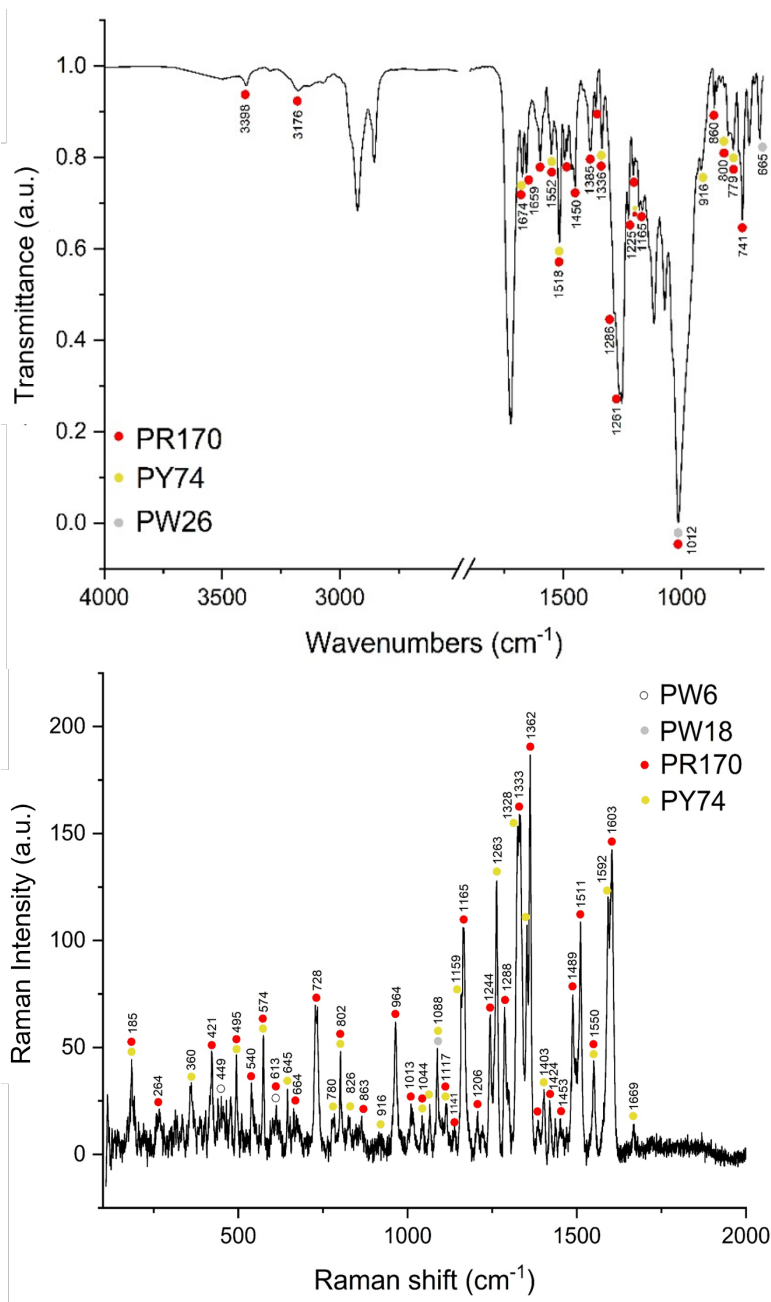


Fig. 20 ATR-FTIR and Raman spectra of red spray paint (R).

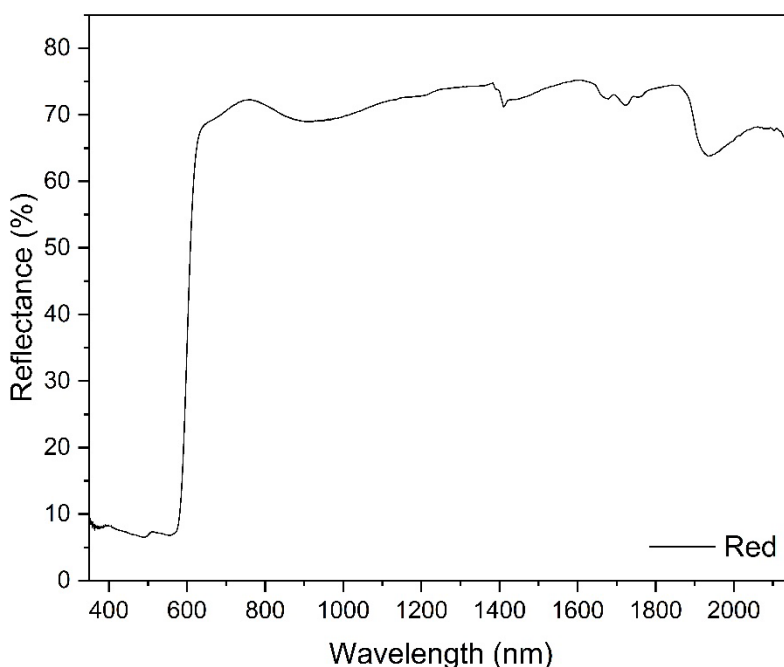


Fig. 21 FORS spectrum of the red spray paint (R).

ATR–FTIR analysis (Fig. 20) indicates the presence of the organic pigments PR170 (Naphthol AS, monoazo red) and PY74 (monoazo yellow), revealed the presence of the organic pigments PR170 (Naphthol AS, monoazo red) and PY74 (monoazo yellow), whose overlapping vibrational bands reflect their molecular structure’s similarities. Raman spectroscopy confirmed both pigments and detected rutile titanium dioxide (PW6) and calcium carbonate (PW18). Talc (PW26) was identified via FTIR and corroborated by magnesium detection in EDX analysis. Additional elements observed by EDX, such as calcium (Ca), aluminum (Al), and silicon (Si), iron (Fe), further support CaCO_3 (PW18), and kaolin (PW19) identification, and moreover suggest the presence of trace iron oxides/hydroxides (such as PY42 and PY43).

FORS spectrum (Fig. 21) displayed S-shaped curves with pronounced UV–Vis absorption characteristic of organic colorants. Notable signals include weak absorption bands at 680 nm and 920 nm, a reflectance peak at 760 nm, an

inflection point at 600 nm, and a shoulder near 480 nm, consistent with iron oxide–hydroxide pigments and ligand field/charge transfer transitions[24,223]. Additional UV absorption bands at 422 nm and 456 nm are attributed to PY74 [24,222]. Broad absorption bands near 1200 nm and 1935 nm indicate non-structured water, while bands between 1670 and 1770 nm correspond to the alkyd binder [24].

7.3.8. Pink alkyd spray paint

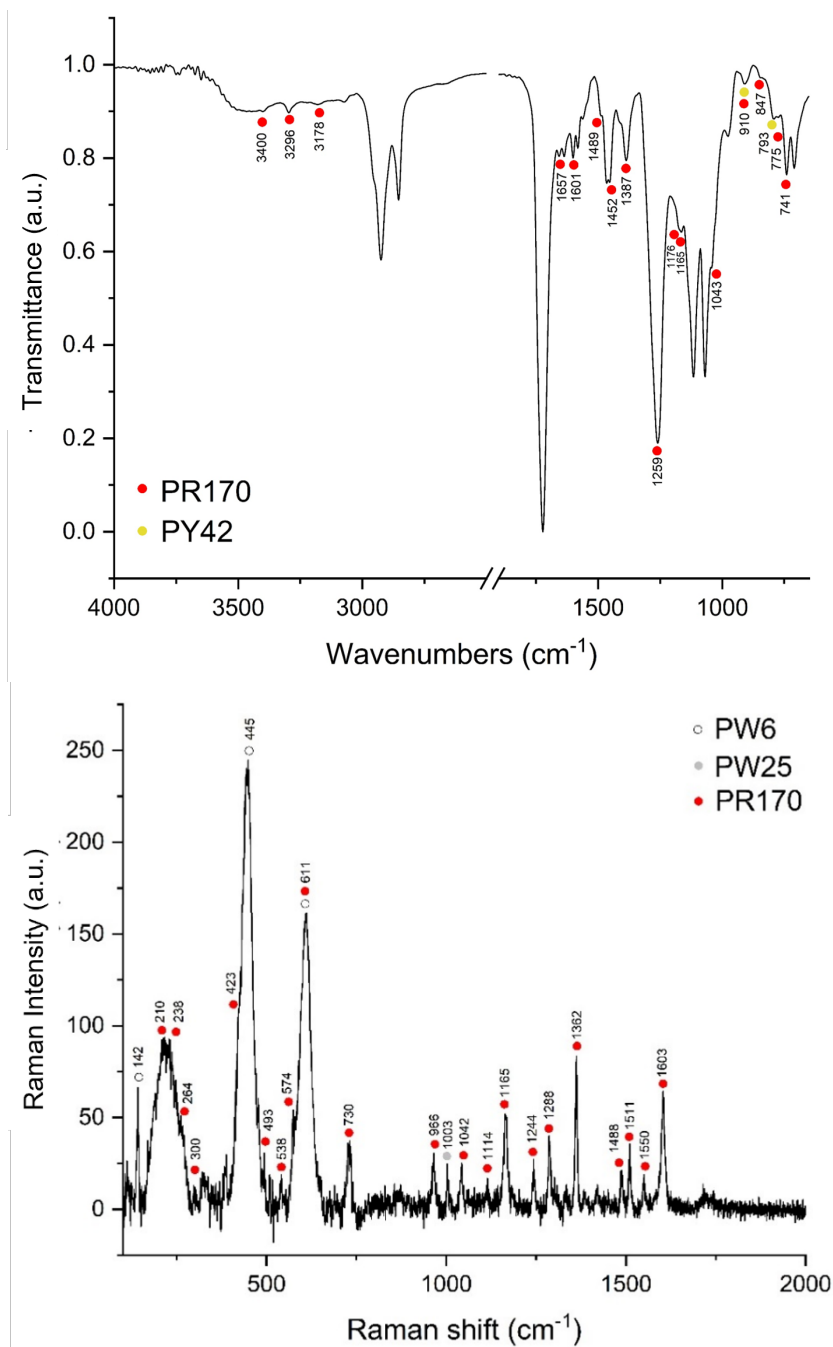


Fig. 22 ATR-FTIR and Raman spectra of pink spray paint (P).

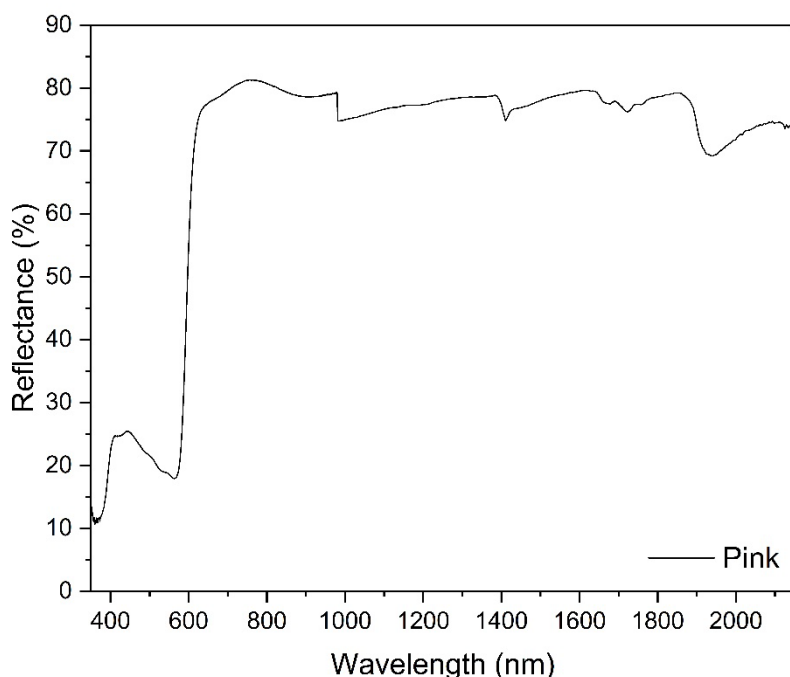


Fig. 23 FORS spectrum of the pink spray paint (P).

ATR–FTIR detected Naphtol red (PR170) along with weak signals attributable to iron oxide yellow (PY42). Raman spectroscopy confirmed the presence of the red dye and rutile TiO_2 , but PY42 was not observed, likely due to its low abundance or weak Raman scattering. EDX analysis revealed titanium (Ti), calcium (Ca), aluminium (Al), and iron (Fe), confirming the presence of gypsum (PW25), in accordance with Raman results, and suggesting the presence of kaolin (PW19), and iron oxides/hydroxides.

FORS spectrum (Fig. 23) showed characteristic UV–Vis absorption signals of organic pigments, including weak bands at 675 nm and 920 nm, a reflectance maximum at 760 nm, and an inflection point at 594 nm, with shoulders at 425 nm and 480 nm typical of iron oxide–hydroxide pigments [24,223]. A distinct inflection at 394 nm confirms the presence of rutile TiO_2 [221]. Broad absorption bands around 1200 nm and 1935 nm correspond to non-structured water, while

three bands between 1670 and 1770 nm indicate the alkyd binder [24]. These data suggest a composition similar to the red spray paint, with PR170 as the main chromophore. The pink hue is likely due to a higher proportion of white pigment (TiO_2), which dilutes the red pigment to produce a lighter shade.

7.3.9. Light and Dark Violet alkyd spray paints

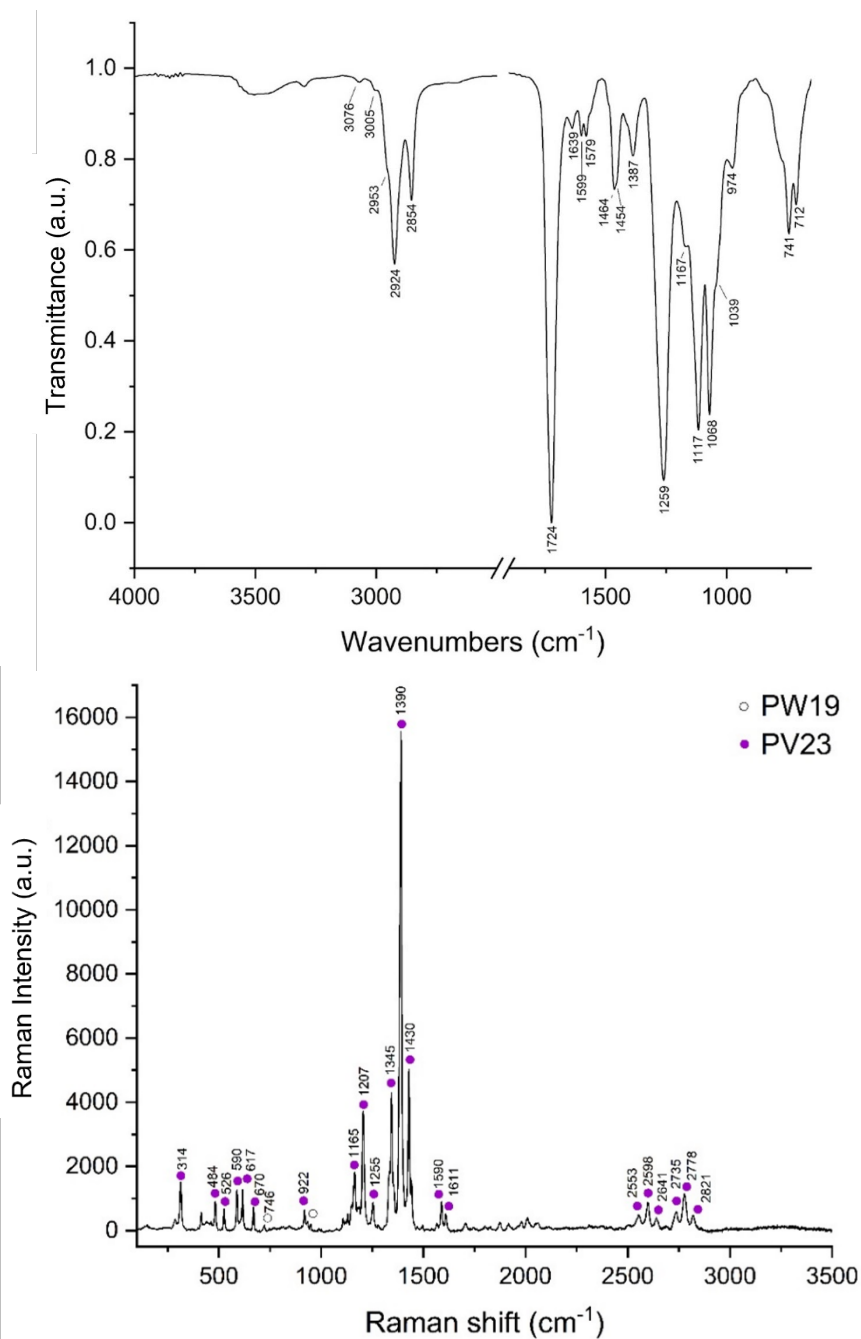


Fig. 24 ATR-FTIR and Raman spectra of Light Violet spray paint (LV).

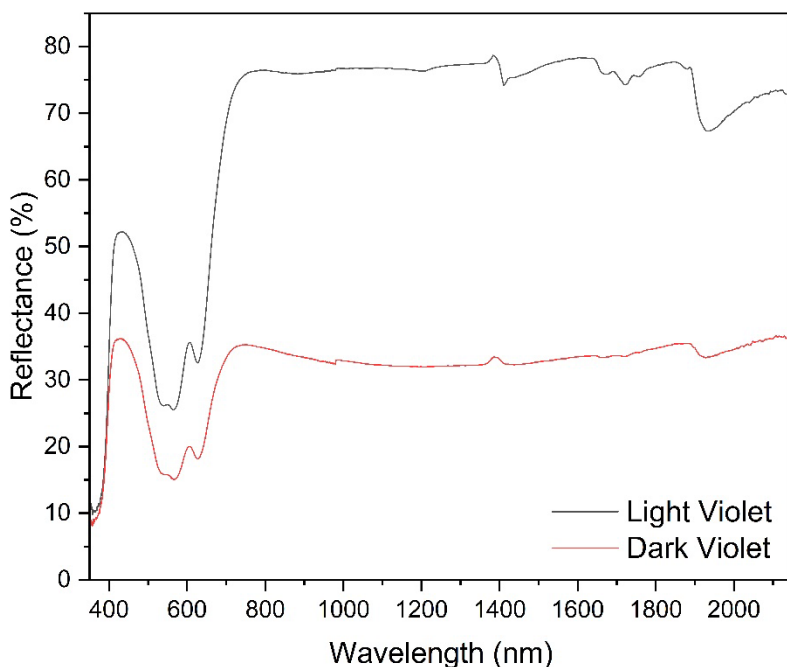


Fig. 25 FORS spectra of the light and dark violet spray paints (LV, and DV respectively).

The LV and DV spray paints produced similar results. ATR–FTIR spectroscopy (Fig. 24) confirmed the presence of an alkyd resin binder in both samples, although it was not effective for pigment identification. Raman spectroscopy played a crucial role in identifying the main chromophore, revealing diagnostic bands consistent with Dioxazine Violet (PV23) in both the light and dark violet samples. As shown in Fig. 24 the IR and Raman spectra corresponding to the light violet (LV) sample are presented for conciseness, since the spectra of the dark violet sample are essentially identical. EDX analysis further revealed titanium (Ti), aluminium (Al), silicon (Si), and calcium (Ca) in both paints, indicating the presence of titanium dioxide (TiO_2 , PW6, likely rutile), kaolin (PW19), and calcium-based fillers such as calcium carbonate (PW18) or gypsum (PW25). FORS spectra (Fig. 25) of both paints exhibited three absorption bands at approximately 535 nm, 625 nm, and 565 nm, consistent with polycyclic pigments such as PV23 [24,224,225]. The inflection point of the reflectance

curve was 400 nm in the light violet and slightly shifted to 397 nm in the dark violet, confirming the presence of rutile TiO_2 [221]. Broad absorption bands around 1200 nm and 1935 nm indicated non-structured water, while three bands between 1670 and 1770 nm were attributed to the alkyd binder [24].

In general, the analytical results demonstrate that both the light and dark violet paints share a common formulation. The difference in tone between the two samples, similar to what was observed in the red and pink paints, likely arises from variations in the relative proportions between the violet chromophore (PV23) and titanium dioxide (PW6), which acts as a white pigment contributing to lightness and opacity, as well as from minor variations in the content of colourless extenders.

7.3.10. Light Blue alkyd spray paint

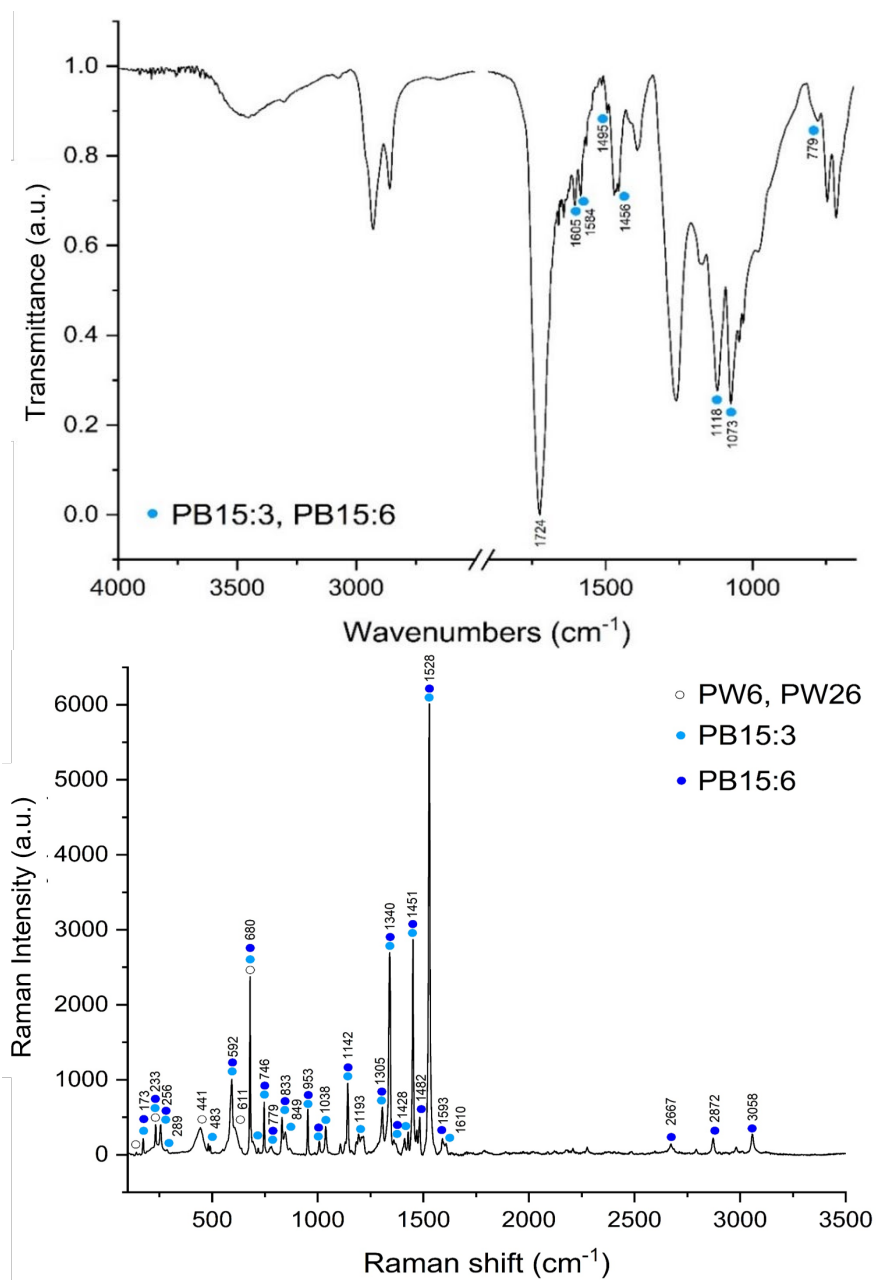


Fig. 26 ATR-FTIR and Raman spectra of light blue spray paint (LB).

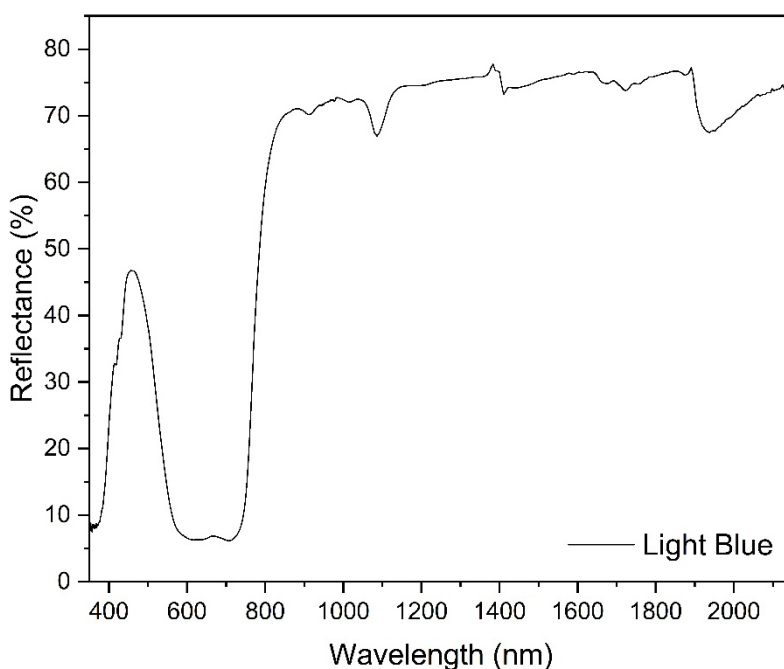


Fig. 27 FORS spectrum of the light blue spray paint (LB).

ATR–FTIR spectroscopy of the light blue spray paint primarily revealed the typical signals of the alkyd resin binder, with only few signals attributable to phthalocyanine blue (PB15:3, β -form): 1605, 1584, 1495, 1456, 1118, 1073 and 779 cm^{-1} (Fig. 26). Due to overlapping vibrational modes, the simultaneous presence of PB15:6 (ϵ -form) could not be definitively established via FTIR, as both polymorphs exhibit similar IR profiles.

Raman spectroscopy (Fig. 26) provided more conclusive evidence, clearly identifying PB15:3, and additional bands consistent with PB15:6, suggesting coexistence of both polymorphs. Titanium dioxide (TiO_2 , PW6) was also detected. EDX analysis confirmed titanium (Ti) and copper (Cu), consistent with PB15-type pigments and TiO_2 . Additional elements, including magnesium (Mg), aluminium (Al), silicon (Si), iron (Fe), and calcium (Ca), were detected. Iron was observed exclusively by EDX, suggesting minor or trace iron oxides/hydroxides (e.g., PY42 and/or PY43). Mg, Al, and Ca indicate the presence of talc (PW26),

kaolin (PW19), and calcium carbonate (PW18) or gypsum (PW25), respectively. Talc was not detected in FTIR, likely due to low concentration or overlapping signals. FORS spectrum (Fig. 27) exhibited strong absorption bands at approximately 620 nm and 710 nm, with shoulders near 418 nm and 430 nm, attributable to Molecular Orbital (MO) transitions of phthalocyanine pigments [24,223,226]. Additional bands at 910 nm and 1100 nm support the presence of phthalocyanine-based colorants [24,223]. The first derivative of the reflectance spectrum revealed an inflection point at 398 nm, characteristic of rutile TiO_2 [221]. Broad absorption bands around 1200 nm and 1935 nm correspond to non-structured water, and three bands between 1670 and 1770 nm indicate the alkyd binder [24].

7.3.11. Dark Blue alkyd spray paint

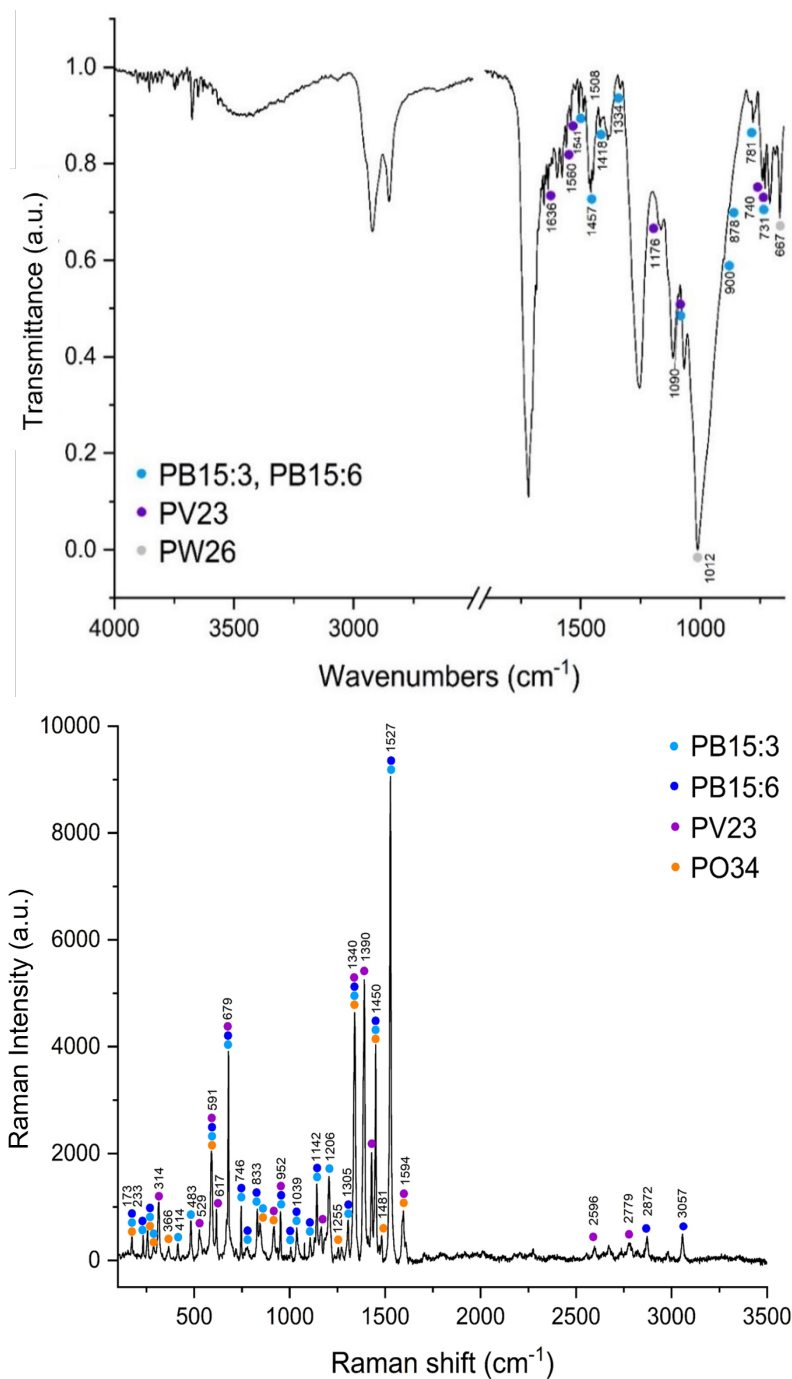


Fig. 28 ATR-FTIR and Raman spectra of dark blue spray paint (DB).

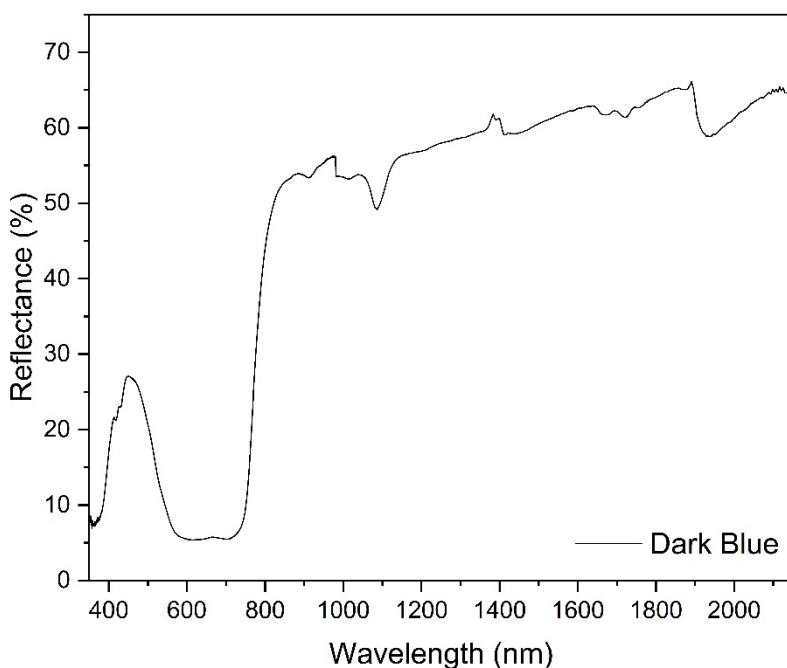


Fig. 29 FORS spectrum of the dark blue spray paint (DB).

ATR–FTIR analysis of the dark blue spray paint revealed the presence of a phthalocyanine blue pigment, likely a mixture of PB15:3 (β -form) and PB15:6 (ϵ -form), consistent with the composition of the light blue sample. The IR spectra also displayed bands attributable to carbazole Dioxazine Violet (PV23) and talc (PW26), as shown in Fig. 28.

Raman spectroscopy confirmed PB15:3, PB15:6, and PV23, and additionally detected characteristic signals of Disazo Pyrazolone Orange (PO34). Notably, three distinct Raman bands at 366 cm^{-1} , 1255 cm^{-1} , and 1481 cm^{-1} , which do not correspond to the phthalocyanine or dioxazine pigments, were tentatively attributed to PO34, although overlapping signals from the dominant chromophores complicated unequivocal identification.

EDX analysis confirmed copper (Cu), consistent with phthalocyanine pigments, and detected silicon (Si), aluminium (Al), and magnesium (Mg), supporting the presence of kaolin and talc as inorganic fillers. EDX analysis revealed the

presence of titanium (Ti), suggesting the presence of titanium dioxide (TiO_2 , PW6), as a white pigment. However, TiO_2 was not observed in the Raman spectra, likely due to low concentration or spectral masking by the signals of the organic pigments. FORS spectrum (Fig. 29) acquired on the dark blue mock-up exhibited two intense absorption bands at ~ 620 nm and ~ 710 nm, with shoulders near 418 nm and 430 nm, consistent with Molecular Orbital (MO) transitions of phthalocyanine pigments [24,223]. Additional bands at ~ 910 nm and ~ 1100 nm were observed, the latter likely corresponding to C–H overtone vibrations. Compared to the light blue sample, the main 620 nm band showed a broader onset, starting around 568 nm, and a weak shoulder at ~ 530 nm suggested the presence of PV23 [24,223,225]. The inflection point at 398 nm, derived from the first derivative of the reflectance spectrum, confirms rutile-phase TiO_2 (PW6) [221]. Broad absorption bands around 1200 nm and 1935 nm correspond to non-structured water, while three bands between 1670 nm and 1770 nm are consistent with the alkyd binder [24].

Green alkyd spray paint

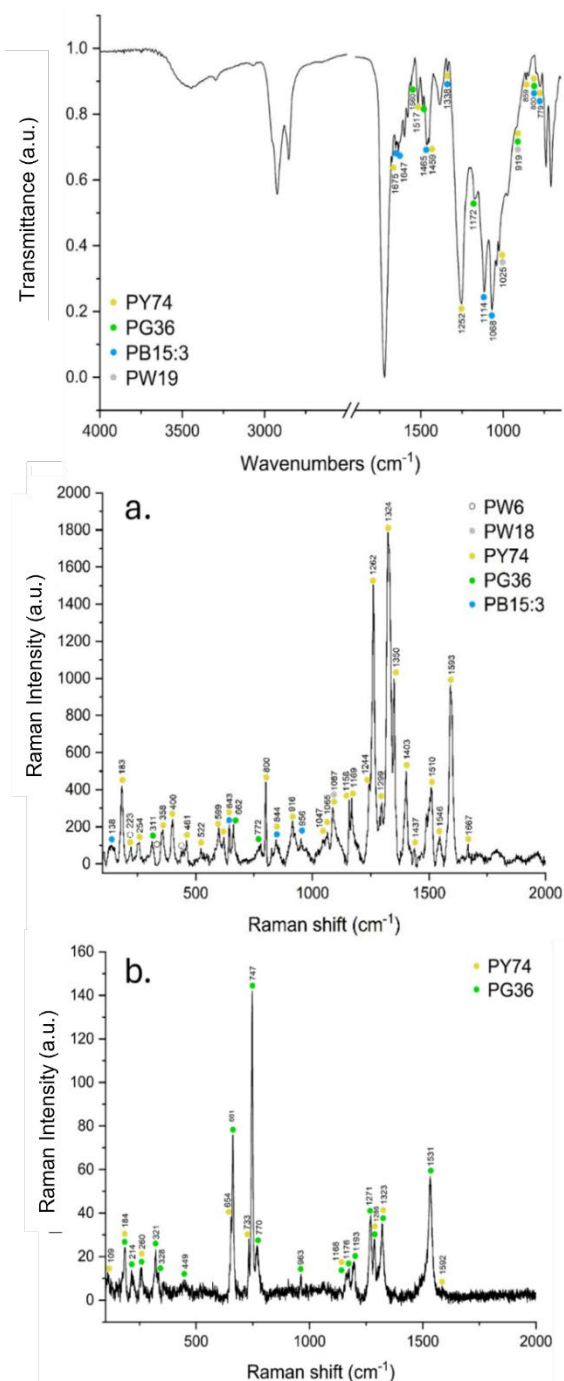


Fig. 30 ATR-FTIR and Raman spectra a: laser source 532 nm; b: 785 nm laser source) of green spray paint (G).

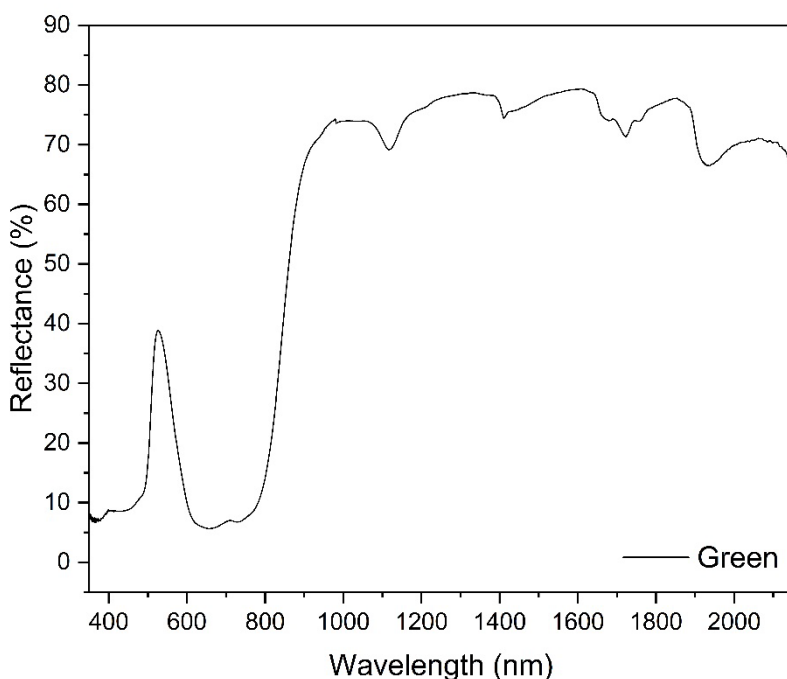


Fig. 31 FORS spectrum of the green spray paint (G).

The green spray paint (Fig. 30) is characterized by a mixture of brominated and chlorinated copper phthalocyanine (PG36), monoazo yellow (PY74), and phthalocyanine blue (PB15:3), as revealed by ATR–FTIR spectroscopy. The IR spectra also showed signals attributable to kaolin (PW19). Raman spectroscopy with a 532 nm laser primarily highlighted PY74, together with weaker signals from PB15:3 and PG36. In contrast, Raman analysis with a 785 nm laser proved more effective in detecting additional signals of PG36, thereby confirming its presence alongside PY74. The 532 nm Raman spectrum also indicated the presence of titanium dioxide (TiO₂, PW6) and calcium carbonate (PW18), both of which were corroborated by EDX through the detection of Ti and Ca. Kaolin (PW19) was further supported by ATR–FTIR and by EDX, the latter showing aluminium (Al) as a confirming elemental marker. EDX also detected copper

(Cu), chlorine (Cl), and bromine (Br), providing strong evidence for PG36, whose molecular structure incorporates these elements.

The FORS spectrum (Fig. 31) of the green mock-up exhibited three prominent absorption bands centered at approximately 650 nm, 730 nm, and 780 nm, consistent with Molecular Orbital (MO) electronic transitions typical of phthalocyanine green pigments [24,226,227]. An additional absorption band at ~1100 nm is likely attributable to the second overtone of C–H stretching vibrations. In the visible region, absorption bands at around 420 nm and 453 nm, together with an inflection point near 510 nm, align with the spectral characteristics of monoazo yellow pigments [24,222]. Furthermore, broad and poorly resolved absorption bands centered near 1200 nm and 1935 nm were observed, indicative of non-structured (physically adsorbed) water, while three absorption bands between 1670 nm and 1770 nm are attributed to the alkyd binder [24].

7.3.13. Light Brown alkyd spray paint

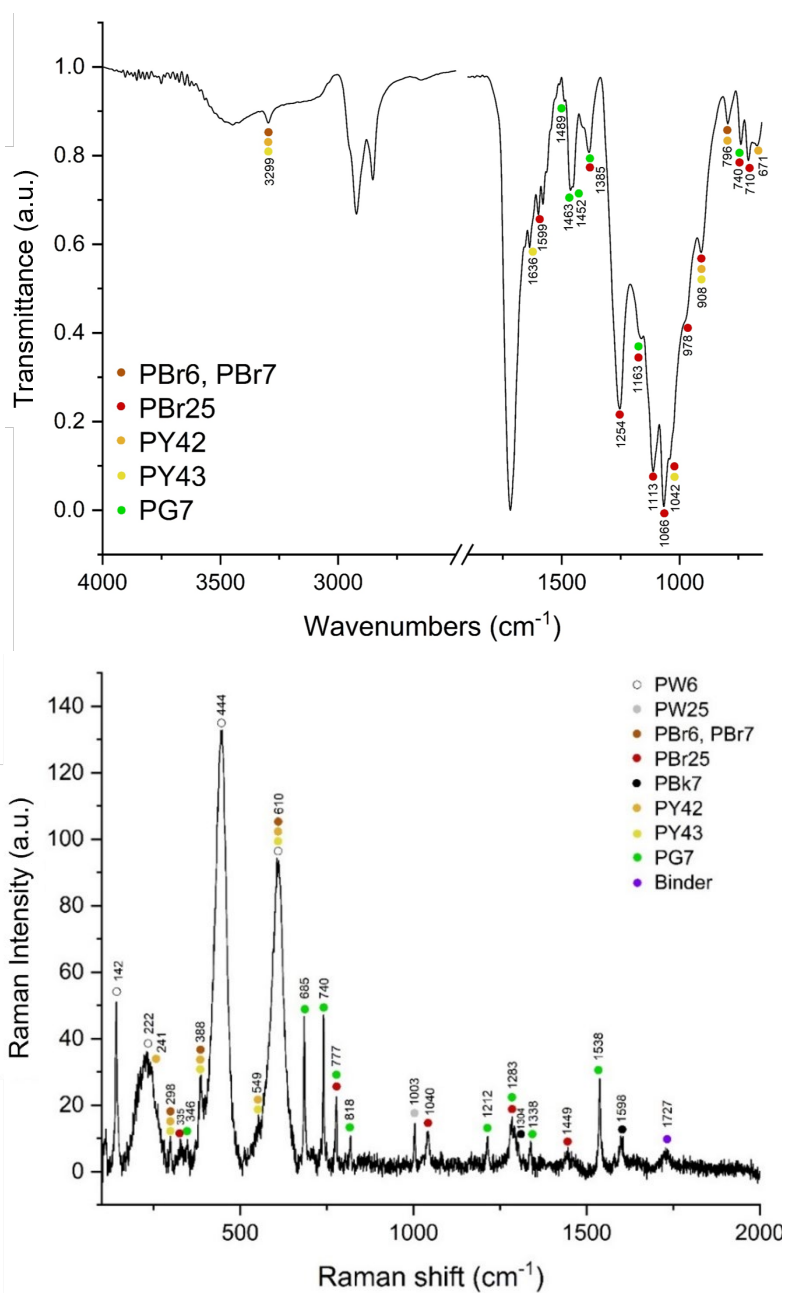


Fig. 32 ATR-FTIR and Raman spectra of light brown spray paint (LBr).

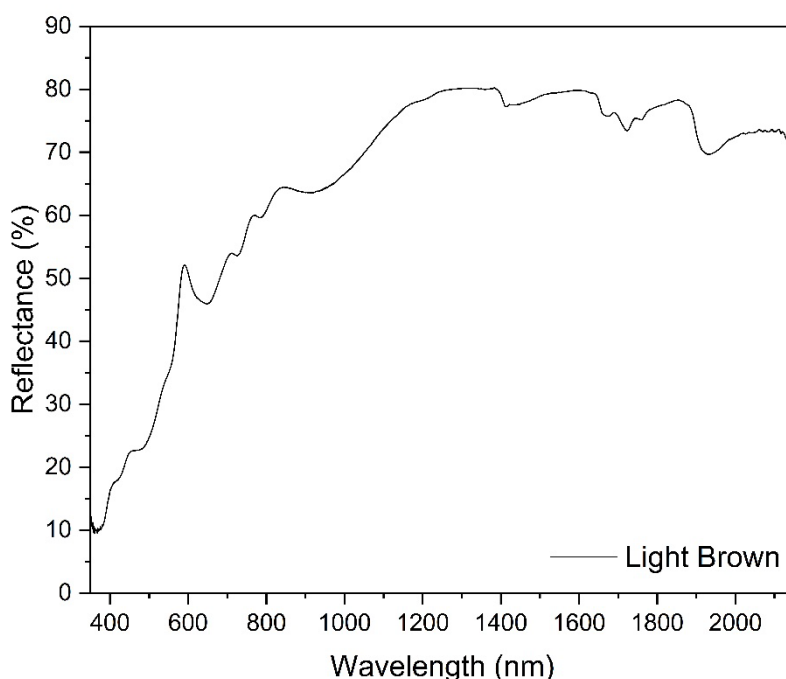


Fig. 33 FORS spectrum of the light brown spray paint (LBr).

ATR–FTIR analysis of the light brown spray paint revealed the presence of multiple brown pigments, including inorganic iron oxides and hydroxides such as PBr6 and PBr7, together with the organic pigment Benzimidazolone Brown (PBr25). Iron-based yellow pigments were also identified, namely Iron Oxide Yellow (PY42) and Mars Yellow of the goethite type (PY43). In agreement with Pellis et al., the near-beige hue of the paint appears to be achieved through the inclusion of Phthalocyanine Green (PG7), whose diagnostic Raman peaks are clearly visible in the spectrum [228]. Raman spectroscopy corroborated the pigments and colorants detected by FTIR and further identified titanium dioxide (PW6) and calcium sulphate (gypsum, PW25) (Fig. 32). EDX analysis supported these findings by detecting titanium (Ti), silicon (Si), iron (Fe), aluminium (Al), and calcium (Ca), consistent with the presence of titanium white, iron oxides, kaolin, and either gypsum or calcium carbonate. However, copper (Cu) and

chlorine (Cl), which would be expected as elemental markers of PG7, were not detected.

The FORS spectrum (Fig. 33) collected from the light brown mock-up exhibited distinctive bands, including two prominent absorption bands at approximately 650 nm and 920 nm, accompanied by shoulders near 430 nm and 480 nm. These bands are attributable to iron oxide-hydroxide species, most likely goethite and correspond to Ligand Field (LF) and Charge Transfer (CT) electronic transitions [24,223]. Additional, less-defined absorption bands could suggest the coexistence of organic colorants such as PBr25.

The reflectance curve showed an initial inflection point at 394 nm, characteristic of rutile-phase titanium dioxide (TiO_2) [221]. As observed across all mock-up samples, broad and poorly defined absorption bands centered near 1200 nm and 1935 nm were attributed to non-structured (physically adsorbed) water, while three absorption bands between 1670 nm and 1770 nm correspond to the alkyd resin binder [24].

7.3.14. Dark Brown alkyd spray paint

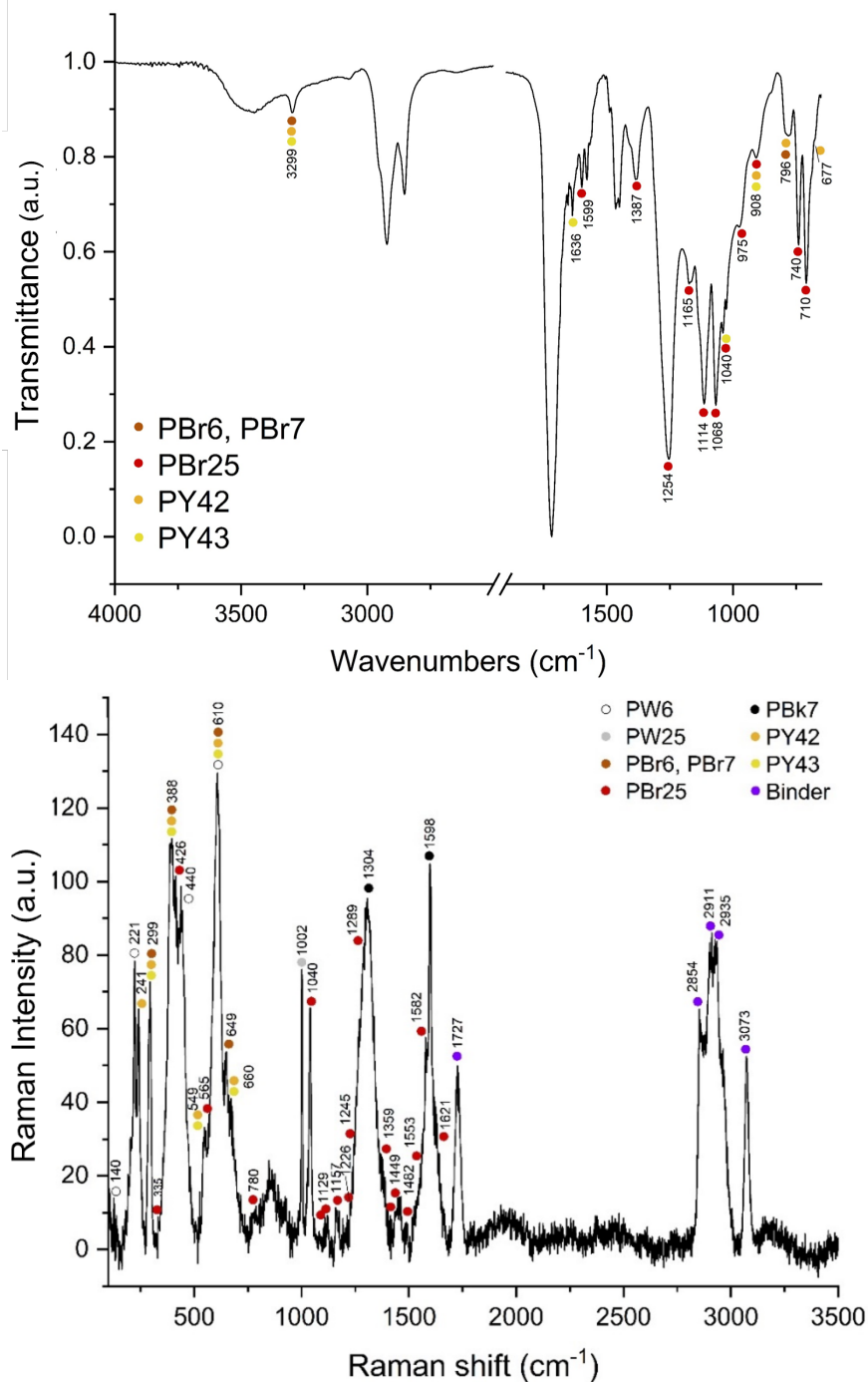


Fig. 34 ATR-FTIR and Raman spectra of dark brown spray paint (DBr).

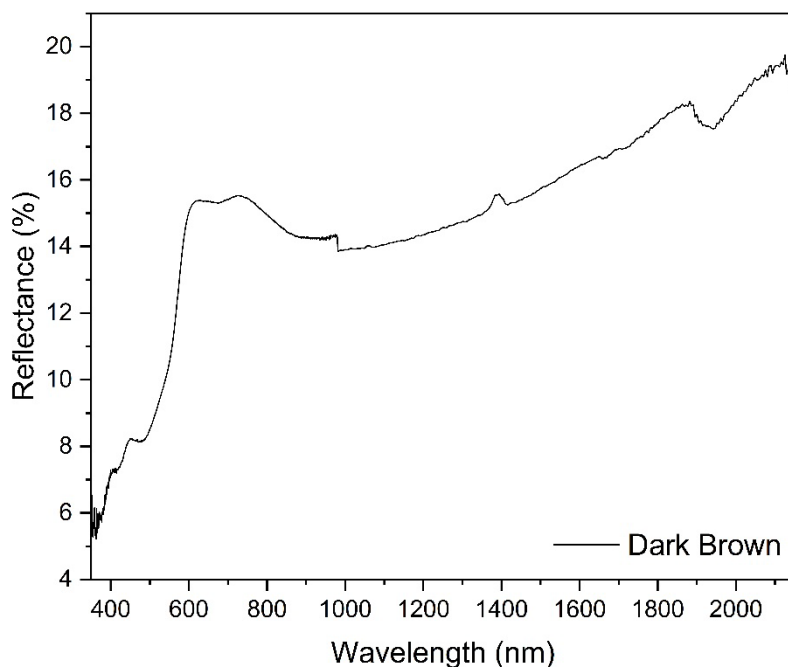


Fig. 35 FORS spectrum of the dark brown spray paint (DBr)

The composition of the dark brown spray paint is overall similar to that of the light brown sample, with the main difference being the absence of Phthalocyanine Green (PG7). ATR–FTIR spectra (Fig. 34) revealed signals attributable to PBr6, PBr7, and Benzimidazolone Brown (PBr25), together with iron-based yellow pigments such as PY42 and Mars Yellow (PY43). Raman spectroscopy corroborated these findings, confirming the presence of the three brown pigments (PBr6, PBr7, PBr25) and the two iron-based yellows (PY42, PY43), and further identified titanium dioxide (PW6), calcium sulphate (PW25), carbon black, and bands associated with the alkyd binder (1727, 2854, 2911, 2935, 3073 cm^{-1}), according to the literature [229]. Interestingly, the Raman signals of the binder appeared more clearly in the dark brown sample than in other colours, likely due to the lower relative concentration of pigments with respect to the medium. EDX analysis detected iron (Fe), silicon (Si), calcium (Ca), titanium (Ti), and aluminium (Al), supporting the identification of iron

oxides/hydroxides, kaolin (PW19), gypsum or calcium carbonate (PW25), and titanium white (PW6), respectively.

The FORS spectrum (Fig. 35) of the dark brown mock-up displayed two absorption bands centered at ~680 nm and ~920 nm, with additional shoulders at ~430 nm and ~480 nm, consistent with iron oxide-hydroxide species and attributable to Ligand Field (LF) and Charge Transfer (CT) transitions [24,223]. Less-defined absorptions suggest the coexistence of organic colorants. As in all samples, broad bands centered near 1200 nm and 1935 nm were assigned to non-structured water, while three absorption bands between 1670 nm and 1770 nm are consistent with the alkyd binder [24].

In conclusion, the composition in terms of organic dyes, inorganic pigments, and/or fillers can be summarized in Table 15.

Table 15 Summary of the composition of the spray paints, listing identified organic dyes, inorganic pigments, and fillers.

Sample	Organic dyes	Inorganic Pigments	Extenders / Fillers
White <i>W</i>	—	PW6 – TiO ₂	PW19 – Al ₂ Si ₂ O ₅ (OH) ₄ PW25 – CaSO ₄
Black <i>Bk</i>	—	(PBk7 – Carbon Black)	PW18 – CaCO ₃ PW19 – Al ₂ Si ₂ O ₅ (OH) ₄ PW26 – Mg ₃ Si ₄ O ₁₀ (OH) ₂
Yellow <i>Y</i>	PY74 – Monoazo Yellow	PW6 – TiO ₂ PY42 (FeOOH)	PW18 – CaCO ₃ PW19 – Al ₂ Si ₂ O ₅ (OH) ₄ PW26 – Mg ₃ Si ₄ O ₁₀ (OH) ₂
Orange <i>O</i>	PO34 – Disazopyrazolone	PY42 – FeO(OH) PY43 – Fe ₂ O ₃ • H ₂ O PW6 – TiO ₂	PW18 – CaCO ₃ PW19 – Al ₂ Si ₂ O ₅ (OH) ₄ PW26 – Mg ₃ Si ₄ O ₁₀ (OH) ₂
Red <i>R</i>	PR170 – Monoazopigment, Naphthol AS PY74 – Monoazo Yellow	PY42 – FeO(OH) PY43 – Fe ₂ O ₃ • H ₂ O PW6 – TiO ₂	PW18 – CaCO ₃ PW19 – Al ₂ Si ₂ O ₅ (OH) ₄ PW26 – Mg ₃ Si ₄ O ₁₀ (OH) ₂
Pink <i>P</i>	PR170 – Monoazopigment, Naphthol AS	PY42 – FeO(OH) PW6 – TiO ₂	PW19 – Al ₂ Si ₂ O ₅ (OH) ₄ PW25 – CaSO ₄
Light Violet <i>LV</i>	PV23 – Dioxazine	PW6 – TiO ₂	PW18 – CaCO ₃ PW19 – Al ₂ Si ₂ O ₅ (OH) ₄ PW25 – CaSO ₄
Dark Violet <i>DV</i>	PV23 – Dioxazine	PW6 – TiO ₂	PW18 – CaCO ₃ PW19 – Al ₂ Si ₂ O ₅ (OH) ₄ PW25 – CaSO ₄
Light Blue <i>LB</i>	PB15:3 – Cu- Phtalocyanine Blue, β form	PY42 – FeO(OH) PY43 – Fe ₂ O ₃ • H ₂ O PW6 – TiO ₂	PW18 – CaCO ₃ PW19 – Al ₂ Si ₂ O ₅ (OH) ₄

	PB15:6 – Cu-Phtalocyanine Blue, ϵ form		PW25 – CaSO_4 PW26 – $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
Dark Blue DB	PB15:3 – Cu-Phtalocyanine Blue, β form PB15:6 – Cu-Phtalocyanine Blue, ϵ form PO34 – Disazopyrazolone PV23 – Dioxazine	PW6 – TiO_2	PW19 – $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ PW25 – CaSO_4 PW26 – $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
Green G	PB15:3 – Cu-Phtalocyanine Blue, β form PG36 – Cu-Phtalocyanine Green YS PY74 – Monoazo Yellow	PW6 – TiO_2	PW18 – CaCO_3 PW19 – $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Light Brown LBr	PBr25 – Benzimidazolone Brown PG7 – Phthalocyanine Green BS	PBk7 – Carbon Black PBr6 – Fe_2O_3 PBr7 – $\alpha\text{-FeOOH}$ PY42 – $\text{FeO}(\text{OH})$ PY43 – $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ PW6 – TiO_2	PW19 – $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ PW25 – CaSO_4
Dark Brown DBr	PBr25 – Benzimidazolone Brown	PBk7 – Carbon Black PBr6 – Fe_2O_3 PBr7 – $\alpha\text{-FeOOH}$ PY42 – $\text{FeO}(\text{OH})$ PY43 – $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ PW6 – TiO_2	PW19 – $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ PW25 – CaSO_4

7.3.15. Quantification of the inorganic fraction

Considering the results, the multi-analytical approach demonstrated its effectiveness for the comprehensive characterization of spray paints, enabling the identification of organic pigments, inorganic pigments, and fillers, as well as the binder. Raman spectroscopy was particularly valuable for detecting organic pigments, ATR–FTIR for the binder and certain fillers, EDX for elemental confirmation and detection of trace elements. Furthermore, FORS turned out to be a useful technique for non-destructive analysis, even for possible in-situ spray paint characterization. Limitations include fluorescence and local heating effects in Raman, restricted detection of some pigments due to the measurement range (e.g., TiO_2), overlapping signals in complex mixtures, and the limited specificity of FORS for pigment combinations. To sum up, this integrated methodology provides a robust and complementary understanding of paint composition.

Finally, thermogravimetric analyses (TGA) were performed on selected spray paints in order to estimate the relative amounts of organic components (e.g., binder, stabilizers, organic dyes) and inorganic components (e.g., fillers, inorganic pigments), considering the higher thermal stability of the inorganic fraction. For each measurement, small paint flakes (approximately 2–3 mm in size), corresponding to a few milligrams of material, were carefully detached from the mock-ups and analysed without further chemical treatment. The results are summarized in the Table 16.

Sample	Weight loss (%) Organic Fraction	Inorganic residues weight (%)
White – <i>W</i>	46.81	53.19
Yellow – <i>Y</i>	61.23	38.77
Orange – <i>O</i>	42.90	57.10
Red – <i>R</i>	62.44	37.56
Pink – <i>P</i>	60.23	39.77
Light Violet – <i>Lv</i>	71.07	28.93
Dark Violet – <i>Dv</i>	69.28	30.72
Light Blue – <i>Lb</i>	58.56	41.44
Dark Blue – <i>Db</i>	65.76	34.24
Green – <i>G</i>	79.21	20.79
Light Brown – <i>LBr</i>	55.52	44.48
Dark Brown – <i>DBr</i>	76.13	23.87
Black – <i>Bk</i>	66.55	33.45

Table 16 Thermogravimetric analysis (TGA) of selected spray paints, providing an approximate estimation of the relative amounts of organic (binder, stabilizers, organic dyes) and inorganic (fillers, inorganic pigments) components.

These results indicate that the concentration of the inorganic fraction varies substantially depending on the colour and, consequently, on the paint formulation. Among the selected colours, the orange sample exhibits the highest content of inorganic pigments and fillers (57.1%), followed by white (53.19%). Conversely, the lowest concentrations of inorganic components were found in the green (20.79%) and dark brown (23.87%) samples, while the remaining colours display intermediate values (Table 16).

Further considerations can be drawn from these results, particularly when viewed in light of the characterization analyses (FTIR, Raman, EDX and FORSE reported in the previous sections). The red and pink spray samples, both

containing the same pigment (PR170), display comparable inorganic fractions, although the pink sample shows a slightly higher value (30.71%) compared to the red (28.93%). This observation is consistent with the hypothesis that the pink formulation incorporates a higher proportion of white fillers than the red one, in order to lighten the shade in accordance with the principles of subtractive colour mixing.

A similar trend is observed when comparing the Light Blue (41.44%) and Dark Blue (34.24%) samples, where the lighter shade again corresponds to a higher content of inorganic fillers. Moreover, the results obtained for the Dark Brown sample align with the Raman spectroscopic data, as its spectrum even revealed signals from the alkyd binder, an indication that this component is relatively more concentrated in the dark brown formulation than in the other paints. Such binder-related signals were generally absent in the corresponding analyses of the other colours.

7.4. Conclusions

The chemical characterization of the MTN94 alkyd spray paints provided numerous insights into the composition of the materials used in the mural under investigation. The multi-analytical approach adopted – combining ATR–FTIR, micro-Raman spectroscopy, SEM–EDX, FORS, and TGA – proved to be effective in identifying both organic and inorganic components.

All samples exhibited a common alkyd-styrene–nitrocellulose binder system, consistent with modern formulations of fast-drying synthetic paints. The identification of this resin type is particularly relevant for conservation purposes, as its high reactivity towards oxidation and hydrolysis processes may play a key role in the degradation phenomena observed on the mural surface.

In terms of chromophoric systems, the analysis revealed the use of both inorganic pigments – such as titanium white (rutile TiO_2), iron oxides and hydroxides, talc, kaolin, and calcium carbonate – and a wide range of synthetic organic colorants, including monoazo, disazo, Naphthol AS, dioxazine violet, and phthalocyanine pigments.

These chromophores are characterized by distinct electronic transition mechanisms, such as ligand field and charge transfer transitions in metal-based pigments and π – π^* or n – π^* transitions in conjugated organic systems. Similar pigment combinations and chromophoric behaviours have been reported in previous studies on modern synthetic paints and contemporary mural materials, confirming the widespread use of mixed organic–inorganic systems to balance chromatic intensity, opacity, and durability [230].

This combination reflects a typical strategy in modern spray paint formulations, where mixtures of inorganic and organic pigments are used to achieve desired chromatic intensity, opacity, and stability.

The integration of elemental and spectroscopic data allowed not only to identify the pigments, but also the detection of fillers and extenders that modulate the

paints' optical and mechanical properties. FORS analyses confirmed the spectral assignments and demonstrated the technique's potential for non-invasive, in-situ identification of spray paint colours on large mural surfaces.

In conclusion, the analytical results define a coherent compositional framework for the MTN94 spray paints used in the case study. The obtained data will serve as a basis for the further study of the ageing behaviour and degradation mechanisms of the paints, and for assessing their stability under accelerated artificial ageing, which will be discussed in Chapter 9. These findings also provide information for future conservation strategies involving similar contemporary artworks, since, although MTN94 paints are among the most widely used spray products in contemporary muralism and have been previously investigated in the literature, their formulations are subject to frequent industrial modifications over time. Therefore, the detailed characterization presented here contributes to updating the current knowledge on their composition and to supporting conservation efforts for materials that, while ubiquitous in Street Art, remain intrinsically variable and industrially dynamic.

8. Monitoring and Validation through a Case Study: Degradation of the “Anna Maria” Mural

8.1. Introduction

The increasing number of large-scale outdoor murals in contemporary urban environments has drawn growing attention to the need for long-term monitoring within a preventive conservation framework. Outdoor artworks are continuously exposed to a complex set of environmental risk factors, including solar radiation, temperature fluctuations, relative humidity variations, wind-driven rain, airborne microparticles, and pollutant gases (e.g., NO_x, SO₂, and ozone), which may act synergistically in accelerating degradation processes. In addition, mechanical stresses induced by wind exposure, thermal expansion–contraction cycles, and moisture migration through the substrate further contribute to material instability. In this context, systematic monitoring represents a fundamental tool of preventive conservation, allowing early detection of chromatic alterations, surface cohesion loss, cracking, efflorescence, and other weathering-related phenomena before irreversible damage occurs.

This chapter presents the monitoring study of “Anna Maria”, a large-scale mural (approximately 290m²) executed by the artist SKIM in May 2023 on the south façade of the “A.M. Agnoletti” High School in Sesto Fiorentino (Italy). The work, painted on an ETICS (External Thermal Insulation Composite System) substrate, offered a unique opportunity to investigate the in-situ behaviour of contemporary spray paints under real environmental exposure, characterised by seasonal climatic variability and urban atmospheric conditions.

A systematic two-year monitoring campaign was conducted, combining photographic documentation, non-invasive colorimetric and gloss measurements, and thermographic analyses. The objectives were not only to evaluate the chromatic and morphological changes occurring on the mural over time, but also to relate observed degradation patterns to environmental stressors such as solar

exposure orientation, rainfall events, temperature and humidity fluctuations, and atmospheric pollutants. Particular attention was given to the interaction between the ETICS substrate and the painted layer, as moisture dynamics and salt migration can significantly influence surface deterioration. The results were further supported by analytical investigations on micro-samples collected from the wall and compared with data obtained from laboratory mock-ups and accelerated ageing experiments discussed in chapter 9.

Through this integrated approach, the chapter aims to contribute to the broader understanding of the degradation dynamics affecting contemporary murals executed with spray paints on ETICS façades and reinforces the role of structured monitoring programs as a preventive conservation strategy for managing environmental risk in outdoor contemporary heritage.

8.2. Materials and methods

8.2.1. Photographic Documentation

Photographic acquisitions of the mural painting were carried out using a Nikon D3400 digital camera equipped with an 18–105 mm lens and a Hoya HMC UV(C) 67 mm filter. Images were taken under natural daylight conditions, aiming to maintain comparable solar illumination, weather, and time of day across the monitoring campaigns. The camera was mounted on a tripod to ensure stability and reproducibility of the recordings. All photographs were acquired with the same settings (focal length 25 mm, aperture $f/25$, exposure time $1/25$ – $1/$ s, ISO 100, exposure compensation 0). Both wide-angle shots of the entire façade and close-up images of selected details were collected to document the conservation state of the mural and monitor chromatic and morphological alterations over time.

Minimal post-processing was performed using Adobe Lightroom Classic 2022,

limited to optical lens distortion correction and geometric adjustment of the images to ensure proper alignment.

8.2.2. Colour measurements

Colour measurements were carried out on both the real mural and the mock-ups. Data were collected periodically, starting from the first acquisition one week after the mural's completion, and subsequently after 1, 7, 12, 14, 20, and 24 months. Different areas were mapped across the painted mural's surface. The mapped points corresponded to 26 different colours (Fig. 36). The measurement areas were selected at a height of approximately 1.5-2 meters from the ground, and each measurement was set as the average of five taken in each mapped area. The colourimeter and the setup used are the same described in section 5.2.3

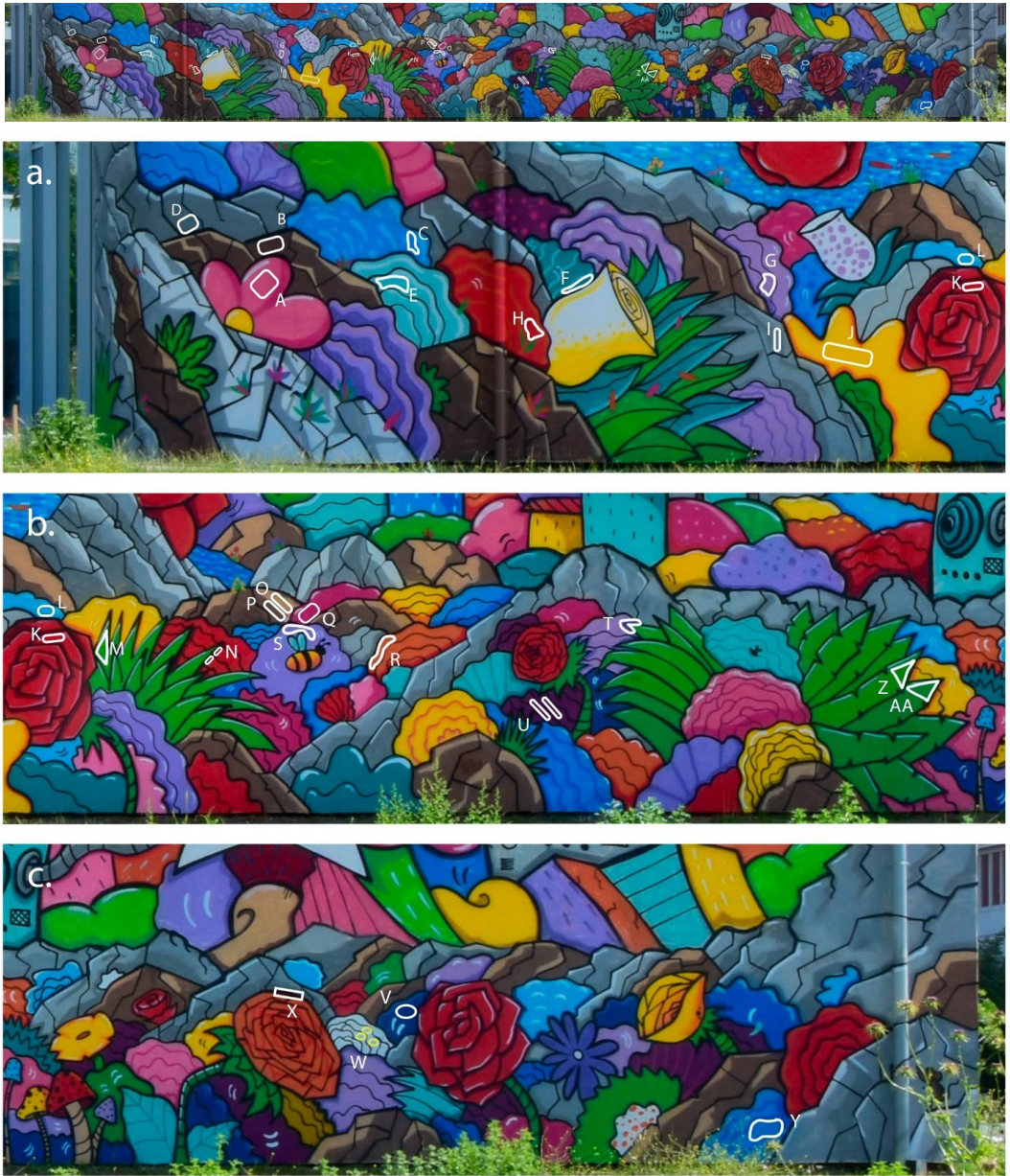


Fig. 36 Overview of the lower register of the mural, with mapping of the colour and gloss measurement areas from 0 to 24 months after the artwork's completion (May 2023 – May 2025) - white lines. Detail of the mapping on the left (a), central (b), and right (c).

To determine the colour changes, CIELAB coordinates (L, a, b), colour variations ΔE , chroma variations $\Delta C'$, and the other values were evaluated following the indications of the Commission Internationale de l'Éclairage (CIE 2000) [231].

ΔE_{00} accounts for differences in lightness (L), chroma (C), and hue (H), while applying weighting and scaling corrections to compensate for the non-uniformity of human visual perception across different regions of the colour space.

These values were obtained using the equations below, respectively:

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{K_L S_L}\right)^2 + \left(\frac{\Delta C'}{K_C S_C}\right)^2 + \left(\frac{\Delta H'}{K_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{K_C S_C}\right) \left(\frac{\Delta H'}{K_H S_H}\right)} \quad (\text{equation 1})$$

$$C'_n = \sqrt{a_n^2 + b_n^2} \quad (\text{equation 3})$$

$$\Delta C' = C'_n - C'_{n-1} \quad (\text{equation 3})$$

Where $\Delta L'$ represents the corrected lightness difference, $\Delta C'$ the corrected chroma difference, and $\Delta H'$ the corrected hue difference; S_L , S_C , and S_H are weighting functions for lightness, chroma, and hue, respectively; and K_L , K_C , K_H are parametric correction factors. R_T is the rotation term accounting for the interaction between chroma and hue. The parameters a and b correspond to the CIELAB colour coordinates along the red–green and yellow–blue axes, respectively.

In the present research, the adoption of the CIEDE2000 colour-difference formula (ΔE_{00}) for the in-situ monitoring campaign reflects its improved perceptual uniformity compared to the original ΔE^*_{ab} (1976) metric. The CIEDE2000 formulation incorporates corrections for lightness, chroma, and hue non-uniformities within the CIELAB colour space and has been demonstrated to correlate more closely with human visual assessment (Luo et al., 2001; Sharma et al., 2005). Given the heterogeneous chromatic range of the mural and the complex outdoor viewing conditions, ΔE_{00} was considered more appropriate for

evaluating visually perceptible changes in real environmental exposure [231,232].

In heritage science, it is generally assumed that ΔE values greater than 3 CIELAB units correspond to chromatic differences that are perceptible to the naked eye [13,191,233].

8.2.3. Gloss measurements

Gloss measurements were conducted on the mural concurrently with the colorimetric measurement campaigns. The gloss values were recorded in the same areas mapped for the colorimetric analyses. Gloss values were measured using the same glossmeter and setup described in section 5.2.4.. Measurements were conducted 3 times on each mural mapped area.

8.2.4. Thermographic analysis

Thermographic analysis was conducted on the mural in April 2025 in both the Mid-Wave Infrared (MWIR, 3–5 μm) and Long-Wave Infrared (LWIR, 8–14 μm) ranges, using two thermal cameras.

The former was a FLIR A6751 MWIR thermal camera (3–5 μm , operational range: -40 °C to 50 °C) with an indium antimonide (InSb) detector (640 × 512 pixels, 15 μm pitch, Noise Equivalent Temperature Difference, NETD < 20 mK, ± 2 °C accuracy from -20 °C to 350 °C), operating up to 480 fps (ResearchIR MAX software). The latter was a TESTO 890 thermal camera (8–14 μm , operational range: -30 °C to 60 °C) with an uncooled microbolometer detector (1280 × 960 pixels, NETD < 40 mK, ± 2 °C accuracy from -30 °C to 100 °C). Active and passive thermography were performed, using two 1 kW halogen lamps and solar heating, respectively. The thermograms acquired in active mode were processed by subtracting, on a pixel-by-pixel basis, the reference frame was captured immediately before heating.

8.3. Results and discussion

8.3.1. Colour changes

In parallel with the characterization of the spray paints and the study of their degradation (Chapters 7 and 9, respectively) a monitoring campaign was conducted to assess the conservation state of the large-scale mural painting (approximately 290 m²) executed by SKIM in May 2023 on the south façade of the “A.M. Agnoletti” high school in Sesto Fiorentino, Italy. The campaign commenced immediately following the completion of the artwork. Given the considerable dimensions of the façade, the monitoring strategy required a structured mapping approach. Photographs of the entire surface were acquired, along with closer images to document finer details. The mural was executed on a white plaster substrate, corresponding to the finishing layer of the external thermal insulation system (ETICS) applied to the building masonry in 2022.

The diagnostic campaign started one week after the mural’s completion, a diagnostic campaign was initiated, employing non-invasive analyses of colorimetry and gloss on the painted surface. Subsequent surveys were conducted at 1, 7, 12, 14-, 20-, 22-, and 24-months post-completion to monitor the evolution of the aesthetic characteristics of the work. As shown in Fig. 37, during the first two years, the façade underwent several transformations, most notably an evident shift in the tonality of certain colours, such as orange, pink, red, and light brown. Although photographs were taken at different times under carefully controlled conditions – attempting to maintain consistent solar illumination, weather conditions, and time of day – it was not possible to achieve perfectly identical acquisition conditions for each session. Nonetheless, the camera setup was maintained consistently across all campaigns in terms of lens choice, focal distance, focus, exposure times, and ISO settings, ensuring the comparability of

the recorded images. Additional photographs of façade details are available in the sections 8.3.2, and 8.3.4 (Fig. 40, and Fig. 42).

Gloss measurements, performed at three different angles, yielded consistently low values ranging between 0 and 0.5 gloss units (GU), which they were



Fig. 37 Mural painting Anna Maria by SKIM. The upper image was taken immediately after the completion of the work in 2023, while the lower image was taken two years later. Alterations in several colours can be observed.

considered negligible. These low gloss values are attributed to the rough texture of the wall surface, which inhibits significant light reflection. Consequently, gloss data are not reported in this work, and it is concluded that the surface gloss has remained largely unaffected over time.

Colorimetric data, on the other hand, revealed measurable changes. The comparison was made between initial colour coordinates measured shortly after the mural's completion in May 2023 and those taken two years later, in May 2025. The ΔE values, which indicate perceptible colour differences when exceeding a threshold of 3 CIELAB units [13,191,233] , are presented in Fig. 38.

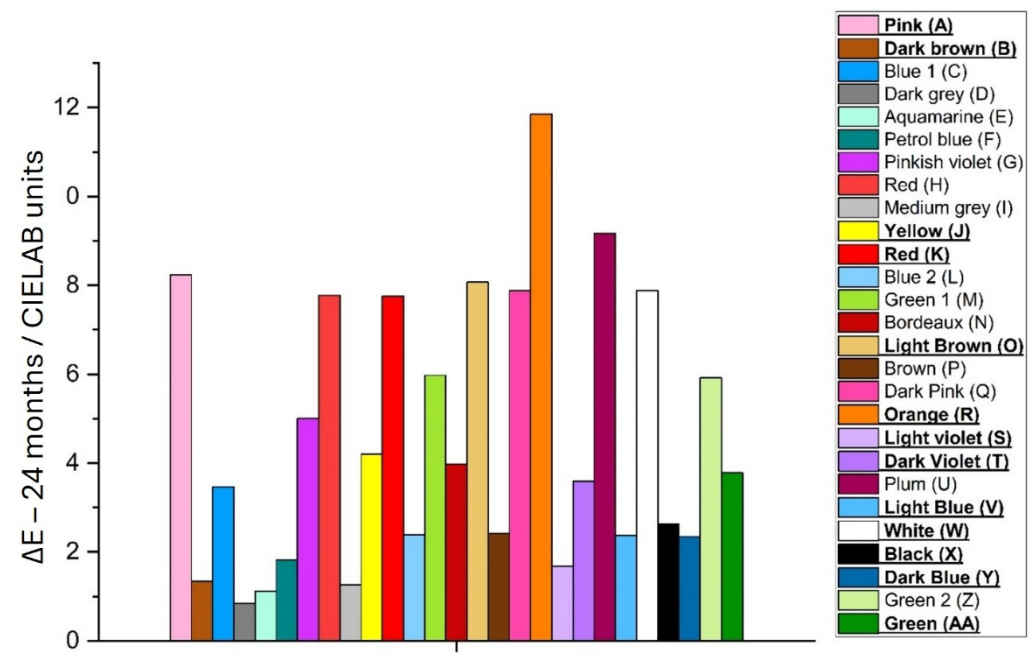


Fig. 38 Histogram showing the ΔE values calculated by comparing the colorimetric coordinates of each mapped colour between 24 and 0 months after the completion of the mural painting. The legend highlights the colours corresponding to those characterized.

Most of the colours exhibited ΔE values greater than 3 CIELAB units, meaning that the changes are likely noticeable to the human eye. Particularly affected were the orange tones; various shades of red (labelled H, K, N); pinks (A, G, Q, U); yellow (J); light brown (O); white (W); and three green hues (M, Z, AA). Only one blue (C) and a dark violet (T) slightly exceeded the threshold [13,191,233]. To verify measurement reliability, the same red colour (codes: H and K) was measured in two separate areas, yielding almost identical values (7.78, and 7.76

CIELAB units, respectively) and confirming the consistency and reproducibility of the colorimetric monitoring.

Table 17 reports the complete dataset of ΔE_{00} values for all 26 monitored colours across the entire two-year campaign, providing full numerical transparency of the collected measurements, and a detailed overview of the mural’s colour stability over the two-year period.

ΔE_{00} values recorded (CIELAB units)	Time (months)						
Mapped colours	1	7	12	14	20	22	24
Pink (A)	1.33	2.45	4.39	5.52	7.81	8.22	8.24
Dark brown (B)	0.47	0.59	0.58	0.60	0.79	1.35	1.35
Blue 1 (C)	0.20	1.39	2.02	2.81	3.06	3.19	3.47
Dark grey (D)	0.14	0.20	0.38	0.53	0.78	0.83	0.84
Aquamarine (E)	0.19	0.30	0.37	0.57	0.78	1.05	1.11
Petrol blue (F)	0.41	0.79	0.86	0.92	1.26	1.65	1.83
Pinkish violet (G)	0.37	2.77	3.45	3.82	4.29	4.70	5.01
Red (H)	1.10	3.44	3.63	4.57	5.88	6.72	7.78
Medium grey (I)	0.17	0.55	0.63	0.66	0.86	0.98	1.26
Yellow (J)	0.09	2.41	2.76	3.03	3.84	4.15	4.20
Red (K)	0.94	0.96	2.06	2.58	6.37	6.83	7.76
Blue 2 (L)	0.08	0.52	0.73	1.26	1.75	2.25	2.38
Green 1 (M)	0.25	1.28	2.27	2.96	3.89	5.18	5.98
Bordeaux (N)	0.56	0.94	1.09	1.56	3.10	3.22	3.97
Light brown (O)	1.75	4.94	5.93	6.47	7.49	7.98	8.07
Brown (P)	0.33	0.72	0.86	1.06	1.85	2.30	2.42
Dark pink (Q)	1.02	2.25	4.34	5.41	6.10	6.88	7.88
Orange (R)	0.79	5.22	7.11	8.54	10.46	11.35	11.85
Light violet (S)	0.11	0.48	1.04	1.14	1.27	1.51	1.68
Dark violet (T)	0.63	1.22	1.42	1.71	2.37	3.19	3.59
Plum (U)	0.84	3.00	4.74	5.97	8.11	8.36	9.17
Light blue (V)	0.28	1.09	1.27	1.68	2.09	2.16	2.38
White (W)	1.02	3.63	5.83	7.17	7.49	7.83	7.88
Black (X)	0.77	1.25	1.40	1.58	1.79	2.19	2.63
Dark blue (Y)	0.13	0.42	0.63	0.85	1.61	2.19	2.34
Green 2 (Z)	0.37	1.05	2.56	3.31	4.90	5.12	5.92
Green (AA)	0.46	0.81	1.86	2.17	2.62	3.02	3.78

Table 17 Summary of ΔE values for all monitored colours across the different measurement sessions, providing an overview of the mural's colour stability over the two-year monitoring period.

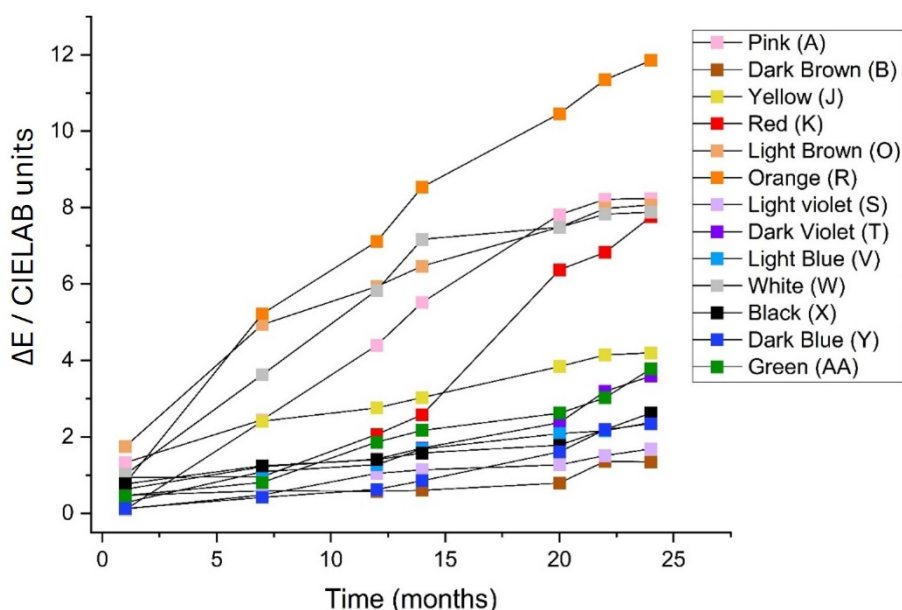


Fig. 39 Temporal evolution of ΔE values for selected spray paint colours over the two-year monitoring period of the mural painting. Colours correspond to those analysed in Section XX, highlighting the differing rates of chromatic change across the palette.

The temporal evolution of ΔE values over the two-year monitoring period of the mural painting is presented in Fig. 39. For conciseness, only the colours corresponding to those subjected to detailed multi-analytical characterization and accelerated artificial ageing test (Chapters 7, 9, 10 respectively) are shown.

This selection facilitates direct comparison between in-situ monitoring results and laboratory-based ageing data, highlighting similarities and differences in chromatic behaviour over time. In particular, orange (R), pink (A), white (W), light brown (O), and red (K) exhibited rapid and pronounced changes in ΔE , indicating a relatively high sensitivity to environmental exposure. In contrast, yellow (Y), green (AA), black (X), light and dark blue (V, Y), light and dark violet (S, T), and dark brown (B) displayed more gradual, near-linear variations in ΔE , suggesting greater stability under outdoor conditions. These observations underscore the heterogeneous response of contemporary spray paints to natural

weathering, likely reflecting differences in pigment composition, binder interactions, and surface exposure, and provide a quantitative basis for assessing colour stability in future conservation planning.

8.3.2. Cracks and efflorescences – possible degradation mechanisms

Over time, surface deterioration features became evident, affecting both the painted layer and the underlying finishing coat. . Linear discontinuities were observed propagating through the thickness of the finishing mortar layer. According to the terminology of the ICOM–ISCS Illustrated Glossary on Stone Deterioration Patterns, such features can be classified as cracking phenomena within the substrate layer [2].

In addition to substrate cracking localized areas of paint layer separation were identified. In one area, the painted film was found to be partially detached from the underlying plaster, allowing removal of fragments for analysis. In accordance with conservation terminology, this phenomenon is more accurately described as

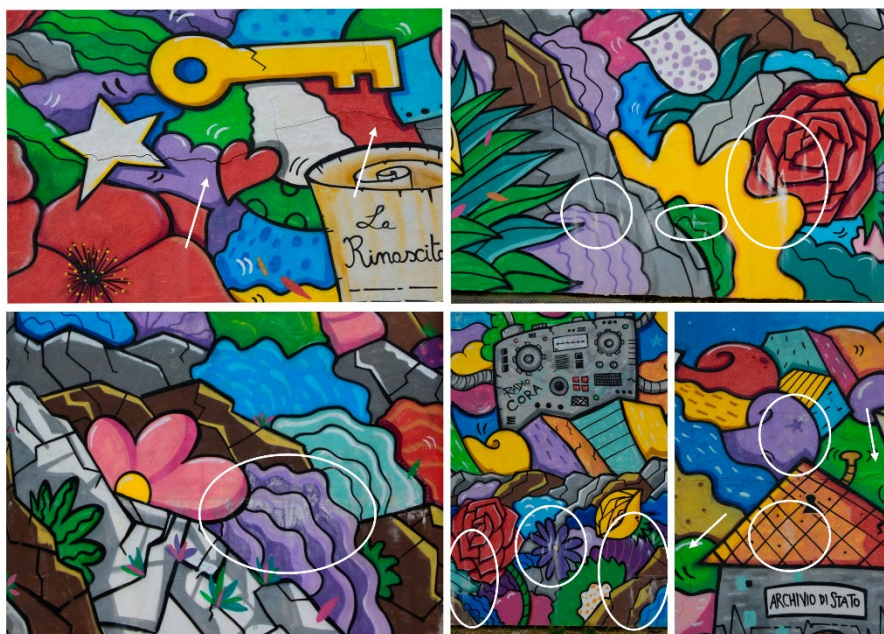


Fig. 40 Selected details of the mural painting showing efflorescences (highlighted within circles) and cracks (indicated by arrows).

detachment or *incipient delamination* rather than simple cracking, as it involves loss of adhesion between stratigraphic layers. Within less than one year after completion, whitish crystalline formations appeared on the painted surface. These formations, partially cohesive and in some cases up to 0.5 mm thick, displayed poor adhesion to the underlying painted layer. Mechanical testing with a scalpel revealed that the paint layer beneath remained intact, indicating that the material was not derived from external accumulation, but from internal migration processes. Based on their morphology, poor adhesion, sampling location (predominantly in the lower register of the façade), and chemical composition, these whitish formations are interpreted as efflorescence phenomena resulting from rising damp and repeated salt crystallization cycles within the masonry. The salts, likely including calcium carbonate and other soluble species, migrated through the porous substrate and crystallized at the surface following moisture evaporation.

Their rapid crystallization and regeneration represent a critical challenge for any preventive conservation or maintenance strategy on the façade, as efflorescence is linked to ongoing moisture dynamics rather than superficial contamination. Fig. 40 shows selected details of the painted façade, highlighting the cracking patterns affecting the substrate, localized paint detachment, and efflorescence phenomena.

To gain further insights into the degradation mechanisms affecting the mural painting, three efflorescence samples were collected from three different areas of the lower register of the façade. In addition, a site where the paint layer had completely detached from the masonry allowed the removal, using a scalpel, of small fragments of the substrate for subsequent characterization.

The photographs of the efflorescence sampling areas are shown in Fig. 42.

In this section, the results of ATR-FTIR analyses, integrated with elemental EDX characterization, for the substrate (S) beneath the spray-painted surface and the

three deposit layers (E1–E3), sampled in spring 2025, two years after the mural painting was completed, are presented.

8.3.3. Inorganic substrate - S

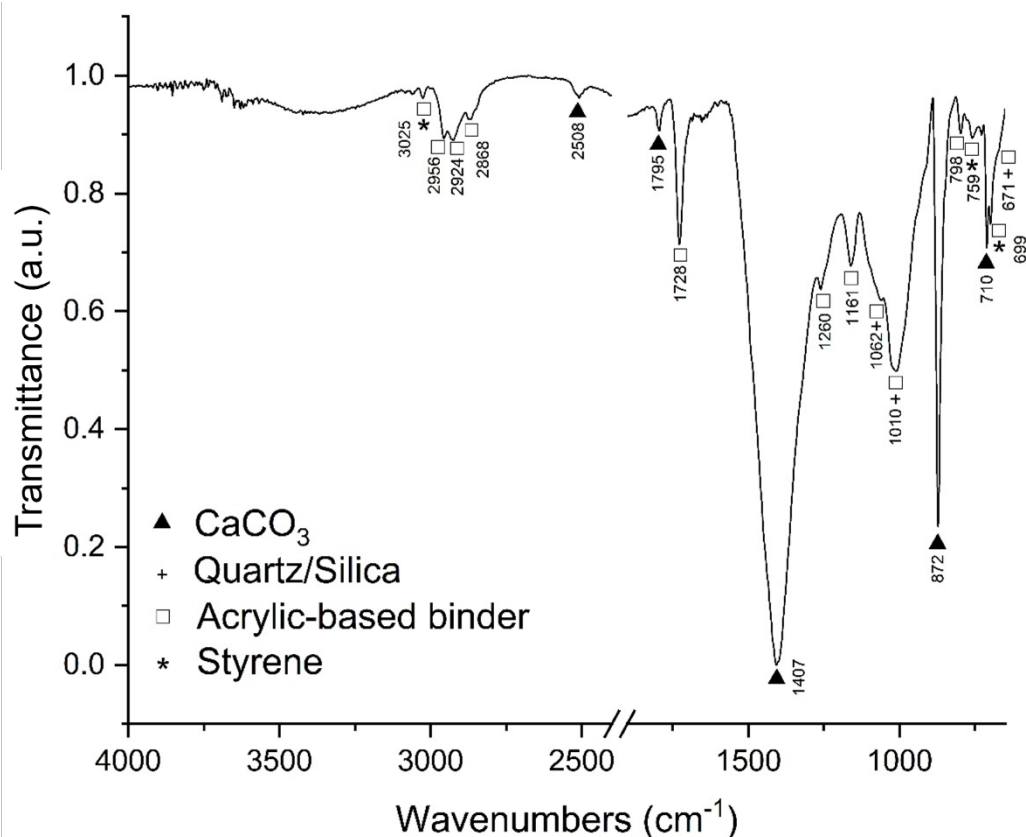


Fig. 41 ATR-FTIR spectrum of the inorganic substrate (S) beneath the mural painting.

The FTIR spectrum of the inorganic substrate, corresponding to the *finishing coating layer* (S, Fig. 41, Table 18), collected from an uncovered portion of the facade, indicates a formulation composed of mineral fillers and an organic binder. The dominant absorptions at 1407, 872 and 710 cm^{-1} are diagnostic of calcite (CaCO_3), in agreement with EDX detection of Ca, C and O. [235,236]. The presence of a styrene–acrylic copolymer binder is supported by characteristic C–H stretching vibrations in the 3000–2850 cm^{-1} region and a strong carbonyl band at 1728 cm^{-1} ($\nu\text{C=O}$), consistent with ester functionalities.

Bond Type Assigned	Band (cm⁻¹)	Reference
vC–H (aromatic)	3025 w (Sty)	[234]
vC–H (aliphatic)	2956 w, 2924 w, 2868 w	[18,35]
Overtone/combination [CO₃]²⁻	2508 w, 1795 w	[235] IRUG IMP00061
vC=O (ester)	1728 s	[18,35]
v₃ CO₃²⁻	1407 s	[235,236]; IRUG IMP00061
vC–O	1260 m	[18,35]
vC–O–C	1161 m	[18,35]
vSi–O, vC–O	1062 sh, 1010 m-s	[18,35,237]; IRUG IMP00193
v₂ CO₃²⁻	872s	Out-of-plane bending (calcite) [235,236]; IRUG IMP00061
vSi–O	798 w	[237]; IRUG IMP00193
δC–H (oop) Aromatic C–H out-of-plane	759 w, 699 s (Sty)	[238]
v₄ CO₃²⁻	710 m	[235,236]; IRUG IMP00061
vSi–O / δC–H	671 sh	[237]; IRUG IMP00193

Table 18 Signals and assignments for the inorganic substrate (S) beneath the mural painting wall.

Si–O stretching bands and elemental detection of Si and Al further indicate siliceous and aluminosilicate fillers, while Ti detected by EDX is attributed to titanium dioxide pigment.

From a conservation perspective, the identification of a styrene–acrylic matrix combined with CaCO₃ and siliceous fillers is particularly relevant. Styrene–acrylic copolymers are known to undergo photo-oxidative degradation and hydrolytic processes under prolonged UV exposure and moisture fluctuations, leading to embrittlement and microcracking. In ETICS systems, thermal

expansion–contraction cycles and moisture migration through the multilayered façade can induce mechanical stress within the finishing coat.

The high content of calcium carbonate fillers may further contribute to salt-related degradation phenomena. Moisture infiltration and evaporation cycles can promote dissolution–recrystallization processes, potentially explaining the observed efflorescence and contributing to localized detachment phenomena.

To conclude, the analytical results suggest that the observed cracking and detachment patterns are likely linked to the combined effects of polymer ageing, thermal stress, and moisture-driven salt crystallization processes typical of ETICS finishing systems exposed to outdoor environments.[239,240][237]

8.3.4. Efflorescences

Three samples of whitish efflorescences were collected from different areas of the wall to enable their analysis by ATR-FTIR and EDX. The figure indicates the specific sampling locations.



Fig. 42 Sampling areas for the efflorescences E1, E2, and E3.

The FTIR spectra of efflorescence samples E1, E2 and E3 (Fig. 38, Table 19) clearly point to a carbonate-based composition. All three deposits show the typical strong, broad asymmetric band of carbonates around 1392 cm^{-1} , followed by two sharp and intense peaks at $\sim 870\text{ cm}^{-1}$ and $\sim 710\text{ cm}^{-1}$, which are diagnostic of calcium carbonate. In addition, weaker bands at $\sim 1793\text{ cm}^{-1}$ and $\sim 2508\text{ cm}^{-1}$ can be ascribed to overtones and combination modes commonly observed in crystalline carbonates. The breadth of the ν_3 band at 1392 cm^{-1} , slightly shifted compared to well-crystallized calcite, suggests some heterogeneity in the deposits, possibly due to mixed phases, low crystallinity, or partial substitution with other cations.

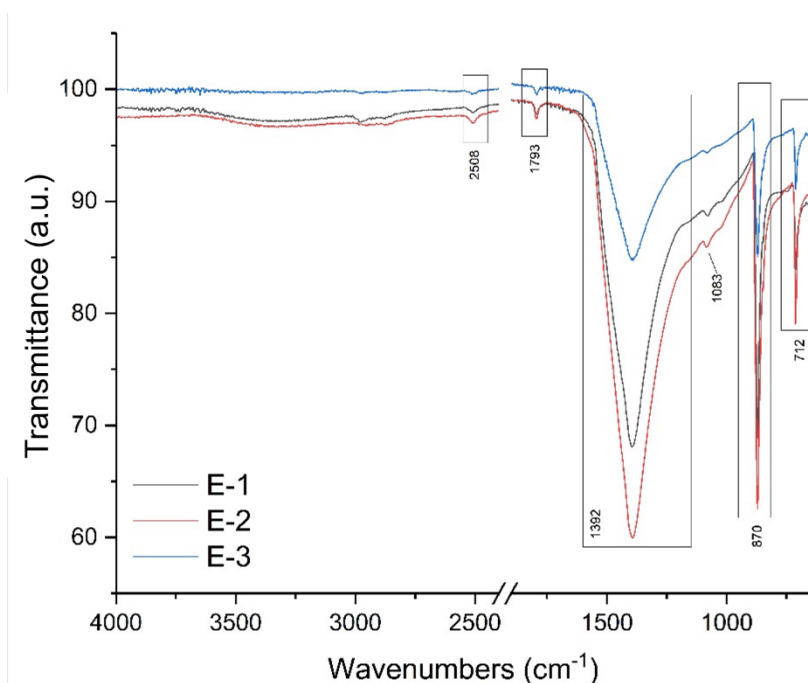


Fig. 43 ATR-FTIR spectrum of efflorescences E1-3, sampled from the mural painting.

Bond Type Assigned / Functional Group	Band (cm ⁻¹)	Reference
CO₃²⁻ overtone / combination band	2508 w	[236]
CO₃²⁻ overtone / combination band	1793 w	
v₃ asymmetric stretching of CO₃²⁻ (broadened envelope)	1392 s	
v₂ out-of-plane bending of CO₃²⁻	870 s	
v₄ in-plane bending of CO₃²⁻	710 s	
v₄ in-plane bending of CO₃²⁻	710 s	

Table 19 Signals and assignments for the efflorescences (E1-3), sampled from the mural painting.

Among the degradation phenomena documented during the two-year monitoring campaign, surface whitening and chalking were the most visually evident alterations observed in the photographic documentation and colorimetric measurements. These phenomena manifested as a progressive lightening of selected colour areas and the appearance of whitish superficial deposits, particularly in zones affected by cracking.

From a broader conservation perspective, it is important to distinguish between two potentially overlapping mechanisms contributing to whitening. The first is binder-related chalking, commonly associated with the photodegradation of polymeric matrices in modern paints. Under prolonged exposure to UV radiation and atmospheric oxygen, chain scission processes occur within the styrene–acrylic binder, leading to surface embrittlement, pigment release, and enrichment of white fillers at the outermost layer. This process results in a perceptible whitening effect and colour fading, as documented in several studies on contemporary murals [20,21,28].

The second mechanism involves salt efflorescence phenomena, linked to moisture migration and dissolution–recrystallization cycles within the substrate. The FTIR and EDX analyses performed on the sampled deposits confirm that the whitish formations are mainly composed of calcium carbonate, with minor contributions from other inorganic phases. EDX analysis revealed the presence of Ca, C, and O, together with minor amounts of K and Si, suggesting that the efflorescence is not a pure carbonate but may incorporate traces of potassium salts or silicate particles derived from the substrate.

The formation of calcium carbonate in this context is likely related to the carbonation of portlandite ($\text{Ca}(\text{OH})_2$) within the cementitious matrix, promoted by the interaction with atmospheric CO_2 and moisture. Cyclic wetting and drying conditions may have facilitated salt migration through pre-existing cracks in the ETICS finishing layer, enabling surface crystallization.

While binder degradation and salt crystallization represent distinct mechanisms, their visual manifestations may overlap, both contributing to progressive surface whitening and aesthetic alteration. Moreover, salt crystallization cycles can induce additional physical damage, including scaling, flaking, and localized detachment of the paint layer, especially under repeated dissolution–recrystallization conditions.

The combined action of polymer photo-oxidation, moisture-driven salt migration, and thermal stresses within the ETICS multilayer system provides a coherent framework for interpreting the cracking, whitening, and efflorescence phenomena observed on the mural.

8.3.5. Thermographic measurements

In light of the rapid deterioration affecting the painted wall and the results obtained from the analysis of the efflorescences, thermographic analysis was considered a suitable non-invasive approach to test the hypothesis of an uneven formation of surface deposits. This irregular distribution was presumed to be linked to inhomogeneous moisture levels within the wall substrate, namely the composite ETICS (External Thermal Insulation Composite System) structure. The measurements were carried out on 1–2 April 2025, in collaboration with Dr. Emma Vannini (PhD student in Physics and Astronomy, University of Florence)

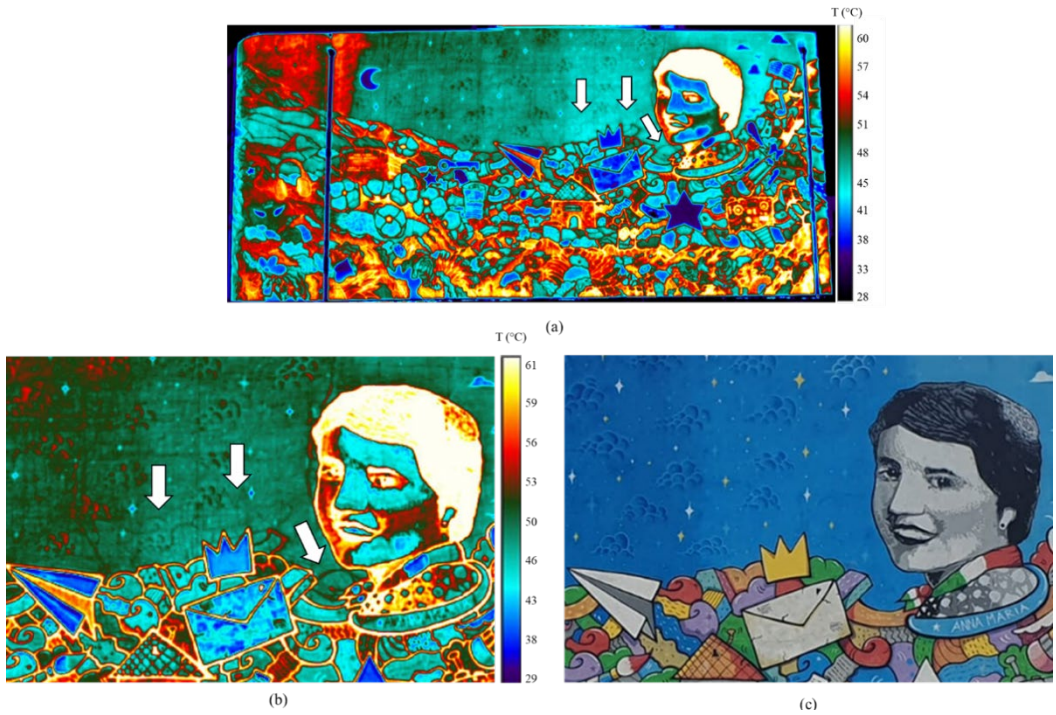


Fig. 44 a) Thermal image of the entire mural (3 – 5 μm range, passive mode with solar irradiation, $\epsilon=0.9$, camera-to-object distance=25 m, atmospheric temperature=20°C, relative humidity=50%); b) thermal image of a portion of the mural obtained by the application of the Digital Detail Enhancement (DDE) filter, that enhances high spatial frequencies, to emphasize the faint shapes beneath the blue sky, highlighted with white arrows in a) and b). c) Photograph of the region of interest.

under the supervision of Dr. Raffaella Fontana and Dr. Alice Dal Fovo (CNR-INO, Florence).

Thermographic analysis provided valuable insights into both the state of conservation of the mural and certain aspects of the artist's technique. A thermal image of the entire artwork was acquired at 5:00 p.m. on April 2nd, on a sunny day (Fig. 44). The recorded temperature values, displayed in the colour bar, indicate that the mural surface reached up to 60 °C. However, these data should be interpreted cautiously, as a generic emissivity value of 0.9 was adopted due to the unknown emissive properties of the materials composing the artwork. The overall thermal image revealed faint shapes beneath the final blue layer of the sky, particularly around the figure of the woman, which are not visible to the naked eye. These forms, highlighted by the arrows in Fig. 44 likely correspond to compositional changes or earlier versions of the design, thus providing evidence of the artist's reworking process.

Active thermography also allowed the identification of structural discontinuities within the mural, likely corresponding to the joints between consecutive polystyrene panels of the ETICS insulation and to the mechanical fixing plugs securing them (blue and yellow arrows in Fig. 46, respectively) [241]. Visible and thermal images were acquired in the lower-right portion of the mural. The regions of interest (Fig. 46b. and Fig. 46d.), marked by green and pink squares frame in Fig. 46a and Fig. 46c, were analysed in active modality and processed by subtracting a pre-heating reference frame. Focusing on another detail in the lower part of the mural, thermographic data were also collected from the area where one of the efflorescence samples (E2, see par. 8.3.4) had been taken. The thermograms of this region (Fig. 45) revealed slightly lower surface temperatures in the efflorescence compared to the surrounding painted areas, indicating the persistence of moisture below the paint layer (specifically beneath the violet flower motif). Similar anomalies were observed in other regions affected by

efflorescence, supporting the hypothesis of an uneven distribution of water within the inorganic matrix.

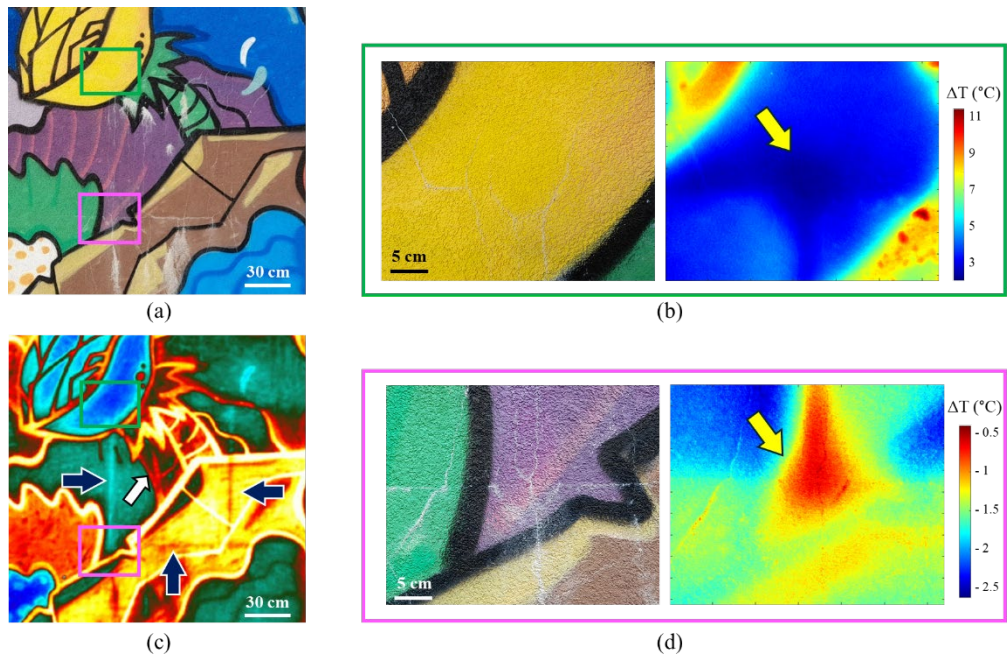


Fig. 46 (a, c) Visible and DDE MWIR thermal images from the lower right corner; (b, d) region of interest analysed in active modality and highlighted in a. and c. by green and pink squares, respectively. b. and d. were generated by subtracting a pre-heating frame. The blue, yellow and white arrows indicate thermal discontinuities that are likely to be related to panel joints, fixing plugs and a pentimento, respectively.

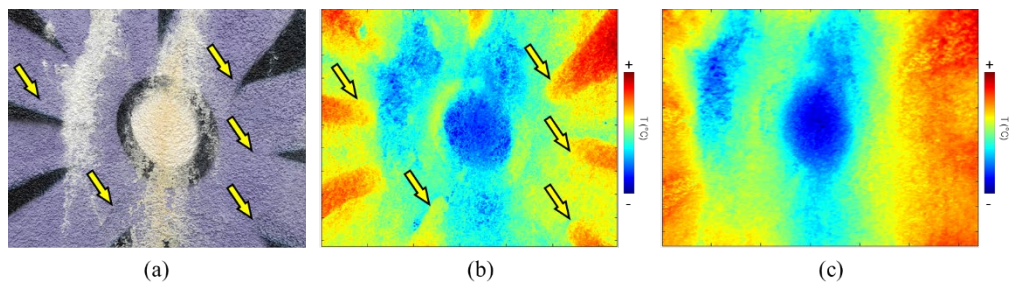


Fig. 45 Area where E2 was sampled: a) visible-light image; b) and c) thermographic outputs in the 3 – 5 μm and 8 – 14 μm ranges, respectively. The thermograms reveal colder regions associated with the efflorescences, indicating the presence of underlying moisture. Yellow arrows point to the black spray lines beneath the outer paint layer, used to outline the figures.

This moisture, probably absorbed and retained by the polystyrene insulation panels of the ETICS system, may promote the dissolution of carbonates in the outer layers of the substrate. As water migrates towards the surface and evaporates, these dissolved carbonates reprecipitate as whitish efflorescences, consistent with the results of the ATR–FTIR and EDX analyses.

From a structural perspective, despite the variable thermal response caused by the wide range of pigments used by the artist, thermography made it possible to visualize the boundaries of the ETICS panels and the pattern of the mechanical plugs joining them, as mentioned before. Moreover, in several areas of the lower register, these features are even visible to the naked eye due to the advanced degradation of the paint film. Interestingly, the thermal discontinuities related to the plugs indicate the presence of a material with different thermal properties, possibly polypropylene (PP) or polyamide (PA6), commonly used in commercial fixing systems.

From an artistic standpoint, thermography also proved capable of revealing hidden features related to the creative process. The thermal image in Fig. 45 enabled the reconstruction of the artist's layering process: initial black outlines with square edges were applied first, later overlaid with coloured paint to achieve pointed contours that can be seen in the visible-light image (yellow arrows in the figure). Moreover, the spray paint lines corresponding to the preparatory grid traced by the artist to define the perspective and proportions of the composition were highlighted by thermography (see horizontal and vertical lines in Fig. 44a and Fig. 44b). Furthermore, faint shapes detected beneath the final pictorial layers (white arrows in Fig. 44 and Fig. 46) were initially interpreted as *pentimenti*: earlier design elements later modified or concealed by the artist, during the creation of the mural. This interpretation was subsequently confirmed through an

interview with the artist (see Chapter 11), who also verified the use of spray paint for the construction of the underlying grid.

In conclusion, the thermographic survey not only contributed to a better understanding of the structural behaviour and moisture dynamics of the ETICS-based wall system but also provided significant clues about the painting technique and creative process, offering a multi-level reading of the artwork that integrates material, environmental, and artistic information.

8.4. Conclusions

The monitoring of the “Anna Maria” mural over a two-year period revealed significant insights into the weathering behaviour of contemporary spray-painted artworks on ETICS façades. The combination of photographic documentation, colorimetric analysis, and thermography proved to be effective for assessing both chromatic variations and structural alterations through non-invasive methodologies.

The results showed perceptible colour changes in most of the analysed hues, particularly in pink, red, orange, and light brown tones, which exhibited ΔE values exceeding the visibility threshold after prolonged exposure [13,191]. These findings confirm the susceptibility of certain spray paint formulations to environmental degradation, in line with laboratory ageing studies. Gloss measurements, on the other hand, remained negligible throughout the monitoring period, reflecting the inherently matte and textured character of the surface.

Infrared thermography provided complementary information, revealing subsurface discontinuities corresponding to the ETICS structure and highlighting areas with higher moisture content. These observations, together with the identification of calcium carbonate efflorescences and cracking, suggest that the mural’s deterioration results from combined physical and chemical mechanisms

involving moisture migration, salt crystallization cycles, and binder photodegradation.

Beyond the diagnostic findings, the thermographic survey also offered valuable insights into the artist's creative process, disclosing hidden compositional features such as preparatory grids and pentimenti.

In conclusion, the case study illustrates how long-term, multi-technique monitoring can elucidate the complex interactions between materials, environment, and artistic practice in contemporary muralism. The results underscore the importance of preventive conservation strategies that take into account both the intrinsic properties of modern paint materials and the specific vulnerabilities of ETICS-based substrates. Future work should expand on these results through the integration of microclimatic monitoring and further comparative studies, contributing to the development of sustainable methodologies for the conservation of outdoor contemporary murals.

9. Study on the degradation of the alkyd sprays

9.1. Introduction

This chapter investigates the molecular degradation pathways of alkyd-based spray paints through Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR–FTIR), following accelerated artificial ageing. Building upon the chemical characterisation presented in Chapter 7, and the ageing protocol established in Chapter 5, this study aims to elucidate how the molecular structure of the alkyd–styrene–nitrocellulose binder system evolves under simulated environmental stress. The 13 colours analysed correspond to those selected from the artist’s palette for the “Anna Maria” mural painting, thus providing a representative overview of the materials used in contemporary outdoor spray-paint artworks. The accelerated ageing procedure, conducted under controlled cycles of UV radiation, temperature, and humidity, reproduces the principal degradation agents acting on open-air murals. By comparing the infrared spectra of unaged and aged paints, the study allowed to identify the main chemical transformations such as oxidation, hydrolysis, and to evaluate how pigment composition, optical properties, and binder-to-pigment ratios influence these degradation mechanisms. This molecular-level investigation contributes to a broader understanding of the durability and stability of modern spray paints, informing both conservation strategies and future material selection for outdoor mural practices.

9.2. Materials and methods

9.2.1. Spray paints

The colours subjected to accelerated ageing and subsequent analysis correspond to those described in Section 7.2.1, namely thirteen spray paints selected from the palette of the artist who created the mural Anna Maria, whose characterization is reported in Chapter 7. Each paint was applied onto a glass slide and left to dry at room temperature for ten days prior to undergoing accelerated ageing tests.

9.2.2. Accelerated artificial aging tests

The accelerated artificial ageing protocol applied to the spray paint samples corresponds to the combined procedure described in Section 5.2.2 and summarized in Table 7 for ease of reference.

The accelerated ageing tests for the alkyd-painted mock-ups were carried out using an Atlas SUNTEST XXL+ chamber equipped with xenon lamps filtered through daylight filters covering a wavelength range starting from 298 nm. The selected irradiation range was intended to reproduce the photo-oxidative stress induced by solar UV radiation, which is recognized as one of the primary drivers of polymer degradation in outdoor spray paints. Deionized water was used to regulate relative humidity and to simulate rainfall events. The artificial ageing parameters were defined according to the methodology proposed by Lamuraglia et al. [190], and the sequence of steps reported in Table 7. In this case, the exposure duration was extended to 650 hours in order to investigate longer-term degradation trends and enable comparison with natural ageing observed on the original mural.

9.2.3. Aged original spray paints ATR–FTIR spectroscopy – Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR–FTIR) analyses were carried out on the spray paints after 650 hours of accelerated

artificial ageing. Measurements were performed using the same instrument and setup described in section 4.1.4. The analyses aimed to characterize the chemical composition of the materials and to identify molecular variations by comparing the spectra with those of the corresponding unaged paints, whose results are reported in section 7.3.

9.3. Results and discussion

9.3.1. Molecular changes

9.3.1.1. White (W)

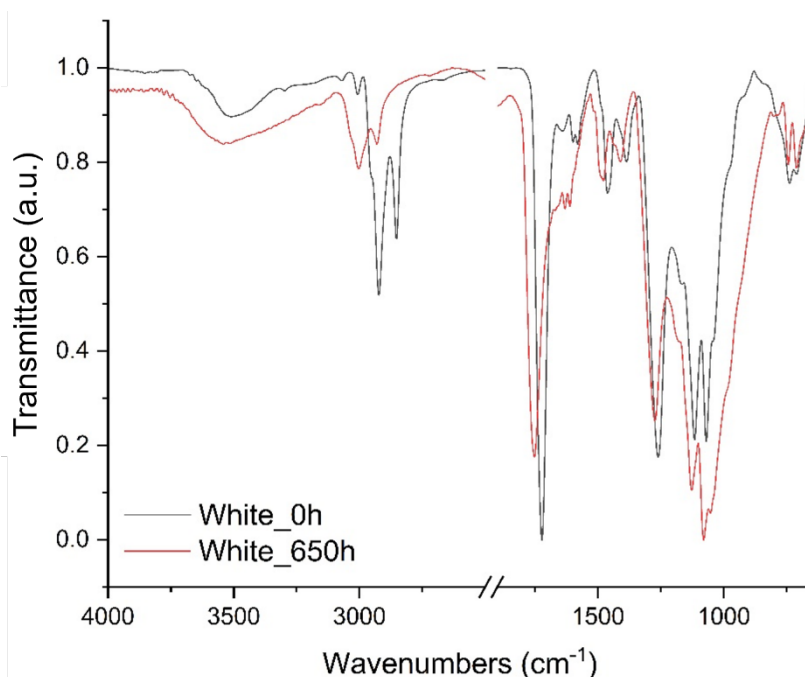


Fig. 47 Comparison of ATR-FTIR spectra of the white (W) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations

The white mock-up displayed pronounced spectral modifications after 650 hours of artificial ageing, indicative of an extensive photo-oxidative transformation within the alkyd-styrene-nitrocellulose matrix (Fig. 47). A marked increase in the broad O-H stretching band around 3500 cm⁻¹ suggests the formation of hydroxylated species such as alcohols, hydroperoxides, and carboxylic acids,

typical products of oxidative chain scission reactions triggered by UV exposure [31,46,242].

This hydroxylation process is characteristic of the advanced stages of photo-oxidation in long-oil alkyds, where radical-mediated reactions (notably Norrish type I and II) lead to an accumulation of O–H functionalities [13,228].

In the aliphatic C–H stretching region, the asymmetric band at 2924 cm^{-1} increased in intensity, whereas the symmetric band at 2852 cm^{-1} decreased. This opposite trend reflects chain scission and hydrogen abstraction processes, resulting in the volatilisation of aliphatic fragments and oxidative modification of methylene groups, as previously reported for UV-aged alkyd and acrylic coatings [46]. In addition to volatile species, chain scission reactions can generate low-molecular-weight oxidised compounds that remain within the coating as solid degradation products. These non-volatile fragments may accumulate at the surface, contributing to embrittlement, loss of cohesion, and progressive chalking phenomena.

The carbonyl stretching band at 1722 cm^{-1} decreased in intensity, consistent with the cleavage of ester linkages and the release of volatile oxidation products such as aldehydes and carboxylic acids, together with the formation of partially oxidised low-molecular-weight residues that may remain trapped within the polymer network [22,243].

In contrast, the signal at 1639 cm^{-1} increased, suggesting the formation of β -diketone structures and/or N–O functionalities derived from partial denitration of the nitrocellulose fraction [12,13,46,244,245]. Similarly, the aromatic skeletal ring vibrations at 1599 and 1581 cm^{-1} intensified, pointing to a relative enrichment of the phthalic and styrenic aromatic domains, which are more resistant to photo-oxidation and thus persist after the preferential degradation of the aliphatic chains [13,244,245]. A concurrent decrease was observed in the C–H deformation bands at 1462 and 1387 cm^{-1} , and in the ester-related C–O–C

stretching band at 1261 cm^{-1} , confirming the erosion of the organic matrix and the scission of side-chain ester groups [31,243]. In contrast, the C–O stretching bands at 1117 and 1068 cm^{-1} increased in intensity, which may indicate the formation of new oxidised ester or ether functionalities, or the spectral manifestation of secondary oxidation products [12,246]. The out-of-plane C–H aromatic bending bands at 739 and 710 cm^{-1} remained essentially unchanged, suggesting that the aromatic backbone of the binder polymer retained its structural integrity. This selective stability, accompanied by the loss of aliphatic and ester components, reflects a typical surface oxidation pattern where more stable aromatic and carbonyl-containing domains become predominant.

It is noteworthy that the white formulation, unlike the coloured paints, likely contained titanium dioxide (TiO_2) as a major pigment. TiO_2 is known to act as a photoactive degradation promoter under UV exposure, facilitating radical formation and accelerating binder oxidation and hydroxylation [46,245]. The observed pattern of hydroxylation, carbonyl loss, and redistribution of C–O and aromatic vibrations align with the photo-induced degradation typically reported for TiO_2 -rich coatings [31].

In summary, the white paint exhibited the most pronounced chemical and structural alterations among the tested colours, characterised by extensive hydroxylation, cleavage of ester and aliphatic groups, and relative enrichment of oxidised and aromatic species. These results confirm the strong photo-oxidative reactivity of light-coloured TiO_2 -containing alkyd systems under accelerated ageing conditions, leading to significant molecular reorganisation within the binder matrix [13,31,46,243].

9.3.1.2. Black

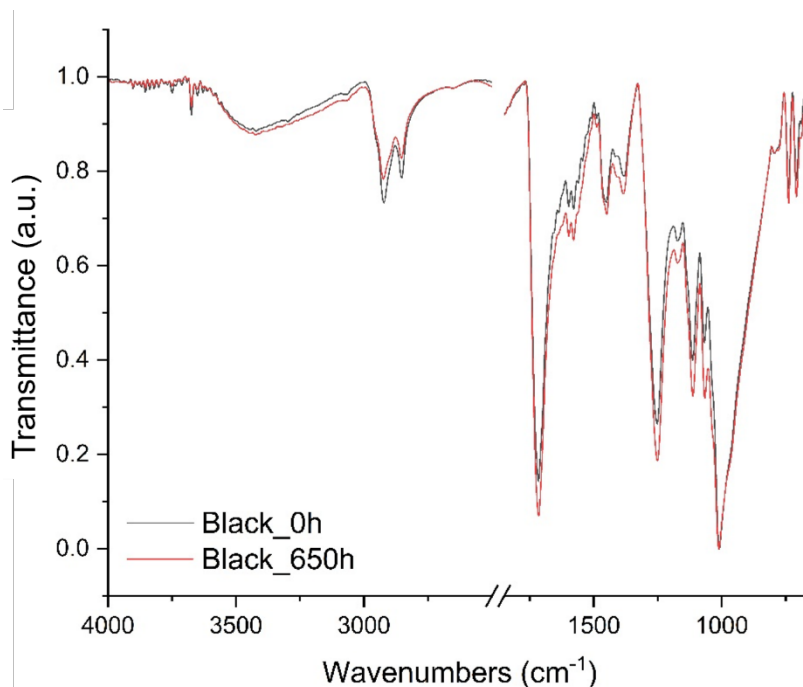


Fig. 48 Comparison of ATR-FTIR spectra of the black (Bk) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The black paint did not exhibit any significant shifts in wavenumber but displayed moderate variations in the relative intensities of several diagnostic bands (Fig. 48). A slight increase was observed in the broad O–H stretching band around 3400 cm⁻¹, suggesting limited hydroxylation processes and the formation of oxidised species such as alcohols and hydroperoxides [46,242]. In contrast, the aliphatic C–H stretching bands at 2922 and 2853 cm⁻¹ decreased in intensity, indicating minor chain scission and hydrogen abstraction reactions, consistent with the early stages of photo-oxidative degradation typically observed in alkyd-based paints under UV exposure [13,31,46].

Increases in intensity were recorded for the aromatic skeletal vibrations at 1597 and 1579 cm⁻¹, and for the C–H deformation and ester-related bands at 1450, 1385, 1263, and 1113 cm⁻¹. The enhancement of these signals likely reflects a

relative enrichment of the more rigid and aromatic polymer fractions, particularly phthalic and styrenic moieties, resulting from the selective loss of aliphatic segments [22,243]. The out-of-plane C–H aromatic bending modes at 738 and 708 cm^{-1} also increased slightly, suggesting that the aromatic backbone of the polymer remained structurally intact and relatively concentrated in the outermost layer after the degradation of more labile components [12,245]. In contrast to other colours, the talc-related Si–O stretching band at 1012 cm^{-1} and the low-wavenumber band at 667 cm^{-1} (remnant of Ti–O or mono-substituted aromatic vibrations) remained unchanged, confirming the chemical stability of the inorganic fillers during accelerated ageing. The absence of any visible chalking or filler enrichment corroborates the limited erosion of the organic binder and highlights the stabilising effect of the pigment phase [31,46]. The restrained extent of chemical change in the black paint aligns with findings from previous studies reporting enhanced UV resistance in black alkyd coatings. This stability is primarily attributed to the presence of carbon black, which acts as an efficient UV stabiliser by absorbing and scattering ultraviolet radiation, thereby mitigating the photochemical reactions that typically promote binder oxidation [242,243]. As a result, only mild oxidation of the aliphatic fraction occurred, while the more stable aromatic and ester components became relatively more prominent in the surface-sensitive ATR–FTIR spectra.

In summary, the black paint underwent limited oxidative ageing, primarily affecting the most labile aliphatic chains of the alkyd binder. The effective UV-screening action of the carbon black pigment inhibited severe photo-oxidative and erosive processes, preventing filler exposure and leading instead to a superficial enrichment of stable ester and aromatic functionalities. These results confirm the crucial role of pigment composition in modulating the photo-stability and degradation pathways of modern spray paints [13,31,46,243].

9.3.1.3. Yellow (Y)

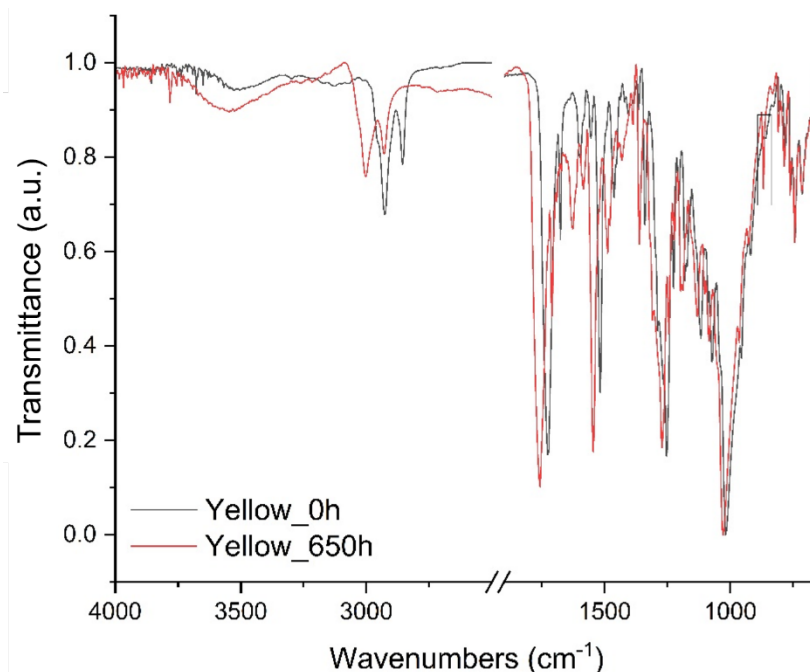


Fig. 49 Comparison of ATR-FTIR spectra of the yellow (Y) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The ATR-FTIR spectrum of the yellow paint after 650 h of accelerated ageing exhibited a general leftward shift (toward higher wavenumbers) for all bands above 860 cm⁻¹, indicating widespread structural rearrangements within the polymeric matrix (Fig. 49). The aliphatic C-H stretching bands at 2926 and 2856 cm⁻¹ decreased in intensity, suggesting minor chain scission and hydrogen abstraction processes, in line with typical photo-oxidative degradation mechanisms reported for alkyd binders [31,46,242].

Conversely, the carbonyl stretching band at 1726 cm⁻¹ and the C=C or conjugated unsaturation band at 1674 cm⁻¹ both increased in intensity, reflecting oxidative processes and the formation of new conjugated or β -diketone structures [12,242,243,246,247]. The enhancement of the carbonyl signal contrasts with the decrease observed in lighter-coloured samples (e.g., white paint), suggesting that

the formation of new carbonyl and carboxylic acid groups compensated for, or exceeded, the loss of original ester functionalities during ageing.

Aromatic skeletal vibrations at 1601, 1554, and 1518 cm^{-1} , as well as C–H deformation bands at 1462 and 1387 cm^{-1} and the C–O stretching band at 1336 cm^{-1} , also showed increased intensities, indicating ongoing oxidative modification and relative surface enrichment of the more rigid aromatic components of the alkyd resin [22,243]. In contrast, the ester- and ether-related C–O bands at 1252, 1117, and 1072 cm^{-1} decreased, consistent with cleavage of labile ester linkages and volatilization of low-molecular-weight oxidation products [13,22,31,46,243]. The talc-related Si–O stretching band showed a slight shift from 1016 to 1030 cm^{-1} without any significant change in intensity, confirming the stability of the inorganic filler. Similarly, the out-of-plane vibration at 669 cm^{-1} remained entirely stable, suggesting no filler exposure or chalking phenomena. However, new or intensified bands at 802 and 779 cm^{-1} were detected, while those at 756, 742, and 714 cm^{-1} remained unchanged. These variations correspond to characteristic vibrational modes of Pigment Yellow 74 (PY74), indicating that pigment-specific signals contributed to the overall spectral modifications [46,245,247]. The overall left shift of multiple bands above 860 cm^{-1} likely reflects subtle alterations in the bonding environment and increased polarity within the oxidised binder. Such shifts are consistent with the formation of more compact and oxygen-rich molecular structures, including lactones, ketones, or conjugated unsaturations, which modify the bond force constants within the alkyd matrix [12,242].

In summary, the yellow paint exhibited a complex and highly active photo-oxidative degradation profile, characterised by chain scission, formation of oxidised conjugated species, and selective loss of ester linkages. These processes led to an enrichment of rigid aromatic domains (phthalic units) and pigment-related species at the surface, while the inorganic fillers remained chemically

stable. The pigment PY74 appears to have played an active role in modulating the degradation dynamics — potentially catalysing oxidation through light absorption in the UV-B range — resulting in a distinctly different molecular evolution compared to other tested colours [46,243,245,247].

9.3.1.4. Orange (O)

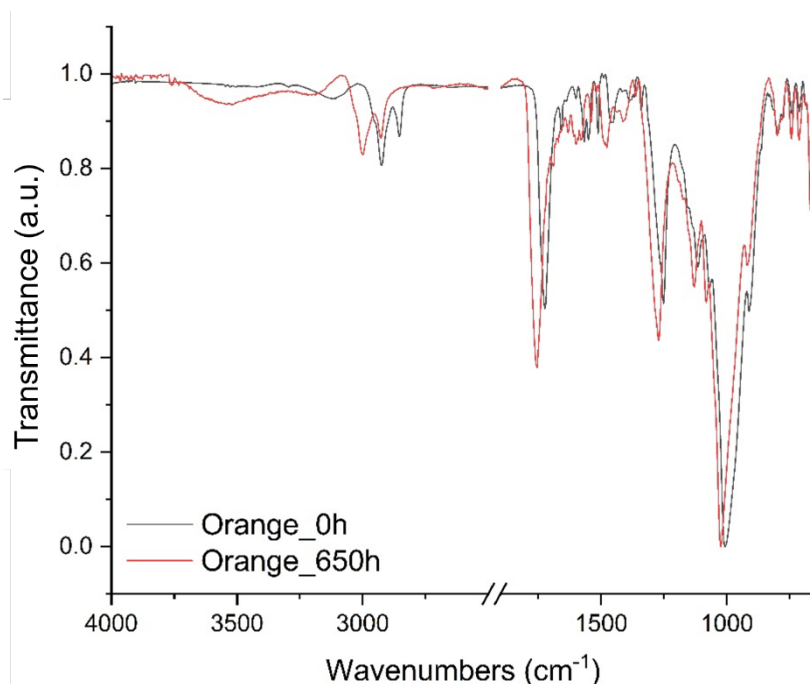


Fig. 50 Comparison of ATR–FTIR spectra of the Orange (O) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The ATR–FTIR spectrum of the orange paint after 650 h of artificial ageing exhibited a general leftward shift (toward higher wavenumbers) across all major signals in the 4000–790 cm⁻¹ range, indicating broad molecular rearrangements within the binder matrix (Fig. 50). The aliphatic C–H stretching bands at 2926 and 2854 cm⁻¹ decreased in intensity, suggesting chain scission and hydrogen abstraction processes, in agreement with typical photo-oxidative mechanisms observed in alkyd-based paints [13,31,46,242,246,247].

Conversely, the carbonyl stretching band at 1722 cm^{-1} and the C=C or conjugated unsaturation band at 1659 cm^{-1} both increased in intensity, revealing oxidative modification and the formation of conjugated or β -diketone structures within the polymer network [12,13,31,242,246]. These increases indicate that oxidation-driven formation of new carbonyl-containing species (ketones, carboxylic acids) outweighed the loss of original ester linkages, a trend consistent with progressive photo-oxidation of the alkyd resin. Several fingerprint-region bands exhibited mixed behaviour, reflecting the simultaneous degradation and rearrangement processes affecting different molecular domains of the binder. The bands at 1387 and 1068 cm^{-1} increased in intensity, while that at 1340 cm^{-1} decreased; minor increases were also observed for the ester-related signals at 1252 and 1115 cm^{-1} [12,13,31,46,244].

The increase at 1387 cm^{-1} may indicate relative surface enrichment of less volatile structural fragments or cross-linked units, whereas the enhancement at 1068 cm^{-1} suggests stabilization of C–O stretching vibrations associated with the more resilient polyester or ether moieties of the alkyd resin. In contrast, the decreased intensity at 1340 cm^{-1} likely reflects the loss of labile additives or polyethylene oxide-based surfactants, which are known to degrade under prolonged UV exposure. The talc-related Si–O stretching signal shifted slightly from 1007 to 1024 cm^{-1} , while the out-of-plane vibration at 667 cm^{-1} remained stable, confirming the chemical stability of the inorganic filler and the absence of significant chalking phenomena.

The lack of macroscopic chalking, despite clear spectroscopic evidence of binder oxidation, may be explained by a combination of formulation- and mechanism-related factors. (i) Lower contribution of photocatalytic inorganic pigments: unlike light-coloured formulations, the orange paint does not rely on TiO_2 as a dominant pigment; therefore, the photo-induced radical generation at the surface may be less intense, reducing binder erosion and pigment/filler release typically

associated with chalking. (ii) Pigment–binder interactions and optical screening: the strong absorption of the orange chromophore may partially screen UV penetration and shift the degradation profile toward chemical modification within the binder (oxidation, formation of conjugated carbonyl species) rather than surface powdering. (iii) Crosslinking versus chain scission balance: the concurrent increase in carbonyl and fingerprint bands may indicate oxidation-driven crosslinking and formation of more cohesive oxidised domains, which can stabilise the surface and delay the loss of cohesion required for chalking. (iv) Extender content and morphology: chalking is favoured when the degradation of the organic matrix leads to the release/exposure of fine inorganic extenders; if the orange formulation contains a lower fraction or different morphology of extenders/fillers, surface whitening and powdering may be less apparent within the investigated ageing timescale.

Overall, the orange formulation may undergo significant chemical ageing without reaching the critical cohesion loss threshold necessary for visible chalking under the applied accelerated ageing conditions.

Nevertheless, pigment-associated bands displayed noticeable variations, suggesting that the organic pigment PO34 (Pigment Orange 34) underwent structural modifications contributing to the overall spectral evolution. Azo pigments such as PO34 are known for their moderate light sensitivity and their potential to influence photo-oxidative processes in the surrounding polymer matrix [46,243,247].

The general left shift of all signals above 790 cm^{-1} points to subtle but consistent changes in the local bonding environment and the overall polarity of the polymer network, associated with the formation of oxidised, conjugated, and more polar species [12,242]. In summary, the orange paint displayed marked molecular modifications during artificial ageing, primarily affecting the alkyd binder through oxidation and chain scission, as indicated by decreased aliphatic C–H

signals and increased carbonyl and C=C intensities. However, despite this clear chemical ageing, no significant macroscopic chalking was observed within the investigated timescale. This suggests that oxidation-driven transformations in the orange formulation may not have reached the critical threshold of surface cohesion loss typically required for visible powdering, possibly due to formulation-specific factors such as pigment–binder interactions, UV screening effects, or the balance between chain scission and oxidative crosslinking within the polymer network.

9.3.1.5. Red (R)

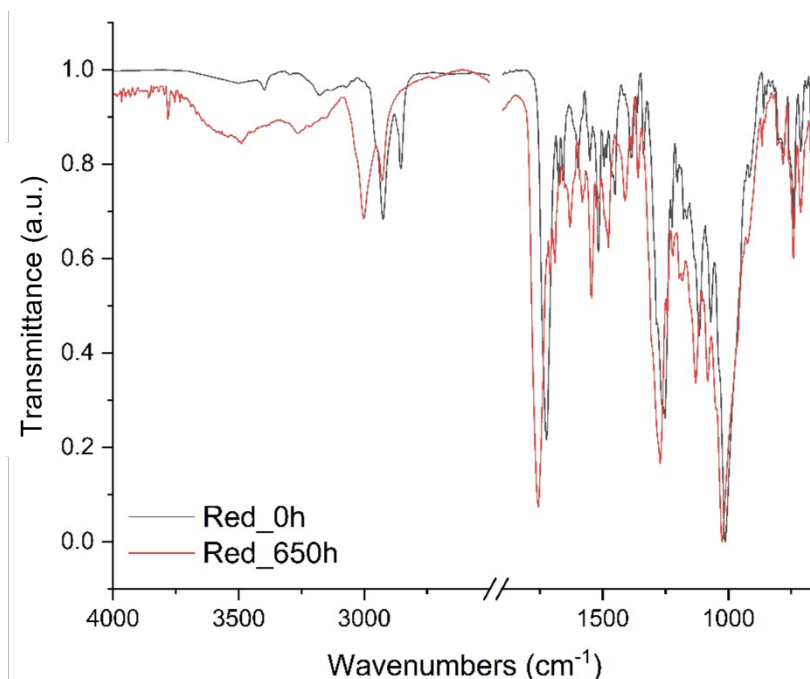


Fig. 51 Comparison of ATR-FTIR spectra of the Red (R) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The ATR-FTIR spectrum of the red paint after 650 h of artificial ageing exhibited a general leftward shift (toward higher wavenumbers) across all major signals in the 4000–916 cm⁻¹ region (Fig. 51), indicating subtle structural rearrangements in the alkyd polymer network. The broad O–H stretching bands at 3398 and 3176 cm⁻¹ and the aliphatic C–H stretching bands at 2926 and 2854 cm⁻¹ remained largely unchanged, suggesting that hydroxylation and chain scission processes were limited under the applied ageing conditions [31,242,243]. This behaviour contrasts with the more pronounced aliphatic degradation observed in lighter-coloured paints such as white and yellow. The carbonyl stretching band at 1722 cm⁻¹ increased in intensity, consistent with oxidative processes leading to the formation of new carbonyl-containing species such as ketones, aldehydes, and

carboxylic acids—typical products of β -scission and Norrish-type reactions [31,242,243].

Meanwhile, the aromatic and conjugated regions (1674, 1659, 1599, 1552, 1518, and 1450 cm^{-1}) exhibited negligible variations, suggesting that the rigid phthalic–styrenic backbone of the alkyd binder remained chemically stable during ageing. In the fingerprint region, the bands at 1385 and 1336 cm^{-1} decreased in intensity, indicating minor loss of aliphatic components or cleavage of side-chain ester functionalities [13,46,242,244]. Conversely, the ester-related bands at 1252, 1117, and 1070 cm^{-1} increased in intensity, while those at 1225, 1203, and 1178 cm^{-1} remained stable [12,13,31,46,244]. These increases likely reflect a relative surface enrichment of the more stable polyester fraction of the alkyd resin following the volatilization of low-molecular-weight fragments. The apparent intensification of C–O stretching bands may therefore correspond to residual high-molecular-weight species or crosslinked structures that accumulated on the surface during oxidation. The inorganic components showed remarkable stability: the talc-related signals at 1012 and 667 cm^{-1} remained unaffected, confirming the absence of chalking phenomena and the chemical inertness of the silicate filler. Likewise, aromatic and out-of-plane bending bands at 860, 800, 779, 741, and 712 cm^{-1} were unchanged, suggesting that the aromatic domains within the alkyd matrix were not significantly disrupted. The slight increase in PY74-related bands indicates a limited contribution of the organic pigment (Pigment Yellow 74) to the observed degradation processes. PY74 is known to be moderately photo-unstable, yet in this formulation, it appears to have remained relatively stable, possibly due to partial protection by the surrounding binder or by synergistic stabilisation from other pigment components [46,243].

To conclude, the FTIR results indicate that the red paint underwent moderate oxidative ageing, characterised by selective carbonyl enrichment and minor redistribution of ester functionalities, but limited chain scission and volatilization

of aliphatic groups. The inorganic filler and aromatic backbone remained stable, supporting the interpretation of a controlled oxidative mechanism leading to partial stabilization rather than extensive polymer degradation.

9.3.1.6. Pink (P)

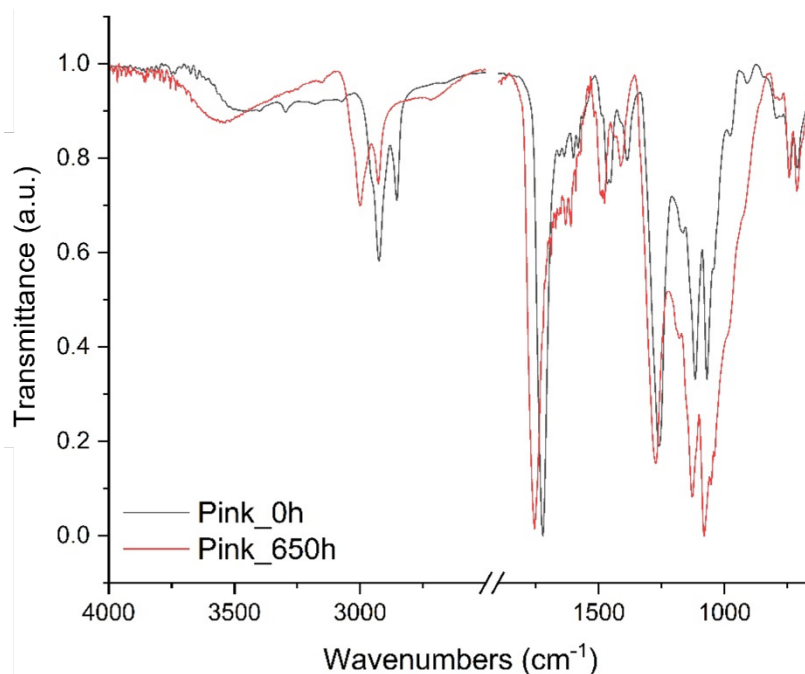


Fig. 52 Comparison of ATR-FTIR spectra of the Pink (P) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Despite sharing the same colorants as the red paint, the pink sample exhibited more pronounced molecular modifications, primarily involving the alkyd binder rather than the pigment-related bands (Fig. 52). This difference can be attributed to the lower concentration of coloured pigments in the pink formulation, resulting in a relatively higher proportion of white pigments or inorganic fillers, which tend to be chemically stable but can catalyse photo-oxidation of the organic matrix under light exposure [13,31,242,243].

A general leftward shift toward higher wavenumbers was observed between 4000 and 1068 cm^{-1} , indicating structural rearrangements and molecular oxidation within the alkyd binder. The aliphatic C–H stretching bands at 2926 and 2854 cm^{-1} decreased in intensity, consistent with chain scission and hydrogen abstraction processes typical of alkyd photo-oxidation [31,46,242]. In contrast, the carbonyl stretching band at 1722 cm^{-1} remained unchanged, suggesting that the loss of original ester carbonyls due to bond cleavage was compensated by the concurrent formation of new oxidised species, such as ketones or carboxylic acids, absorbing in the same spectral region [22,46,243].

In the fingerprint region, several bands showed increased intensity, notably those at 1601, 1581, 1466, 1385, 1255, 1117, and 1068 cm^{-1} . The enhancement of the aromatic skeletal bands at 1601 and 1581 cm^{-1} indicates a relative surface enrichment in the phthalic and aromatic domains of the alkyd resin, which are structurally more rigid and less prone to volatilisation. Similarly, the increase of the C–H deformation bands (1466 and 1385 cm^{-1}) and ester-related C–O stretching (1255 cm^{-1}) suggests that the more stable ester and aromatic components became relatively concentrated at the surface following the selective loss of aliphatic moieties. The C–O stretching bands at 1117 and 1068 cm^{-1} also intensified, reflecting either the enrichment of unreacted ester bonds or the formation of new oxidised ester/ether functionalities.

Conversely, the out-of-plane aromatic C–H bending bands at 742 and 710 cm^{-1} remained largely stable, confirming the preservation of the rigid aromatic backbone.

From a compositional standpoint, the more severe degradation of the alkyd binder in the pink paint compared to the red sample can be related to pigment concentration. The lower pigment load reduces the UV-shielding capacity of the film, leaving the polymeric matrix more exposed to photo-oxidation. Additionally, the higher proportion of white fillers, such as TiO_2 , may have

accelerated binder degradation through photocatalytic reactions, promoting hydroxylation and oxidation phenomena at the polymer surface.

To summarize, these results confirm that the alkyd binder represents the primary locus of molecular alteration in the pink paint, undergoing chain scission, oxidation, and selective surface enrichment of the more rigid polyester and aromatic fractions. The inorganic fillers remained stable, while pigment-related signals played only a secondary role in the observed spectral changes.

9.3.1.7. Light Violet (LV)

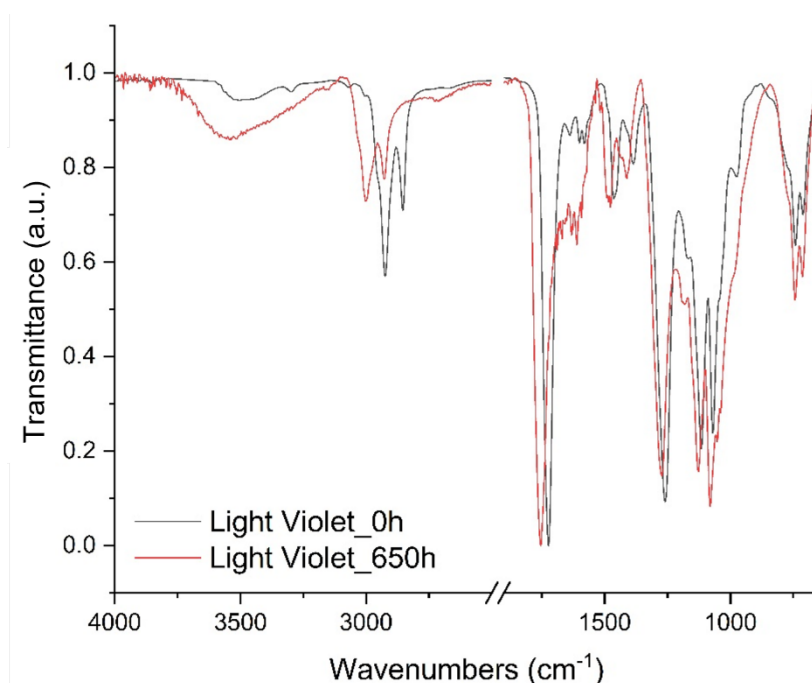


Fig. 53 Comparison of ATR-FTIR spectra of the Light Violet (LV) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The light violet sample exhibited a general shift toward higher wavenumbers (“left shift”) across the 4000–1000 cm^{-1} range (Fig. 53), indicating structural and chemical modifications within the polymeric network of the alkyd binder. The decrease in aliphatic C–H stretching bands and the disappearance of the O–H

band suggest chain scission and hydrogen abstraction processes typical of photo-oxidative ageing.

[13,31,46,242,244,246]. While the main carbonyl stretching band at 1724 cm^{-1} remained unchanged, several fingerprint-region signals increased, reflecting oxidation-driven rearrangements and the relative enrichment of more stable aromatic and carbonyl-containing structures within the degraded surface layer.

Of particular relevance is the behaviour of the band around 1115 cm^{-1} , which may overlap with polyethylene oxide (PEO)-based surfactants commonly used as additives in spray paint formulations. The increase in this signal suggests possible migration and surface accumulation of PEO-type compounds during ageing. Such migration phenomena are well documented in polymeric coatings and can precede additive degradation, leading to changes in surface polarity, gloss, and cohesion.

The observed spectral evolution therefore indicates not only binder oxidation but also additive redistribution within the paint film. This migration may contribute to surface instability and influence subsequent degradation pathways, even in the absence of pronounced inorganic filler alteration.

To summarise, the degradation of the light violet formulation appears to involve selective oxidation of aliphatic segments, surface enrichment of more stable aromatic domains, and migration of low-molecular-weight additives, while the inorganic fillers remain largely unaffected.

9.3.1.8. Dark Violet (DV)

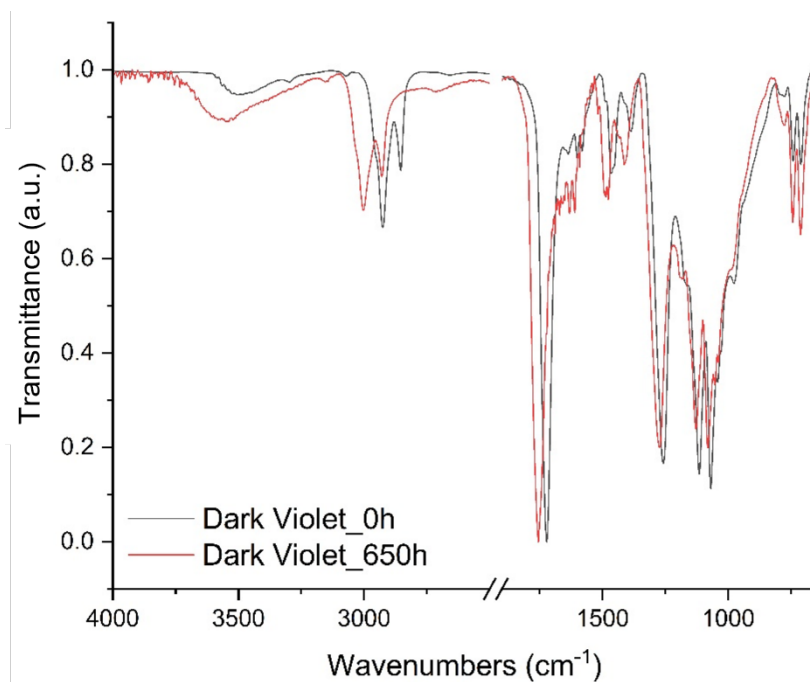


Fig. 54 Comparison of ATR-FTIR spectra of the Dark Violet (DV) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The dark violet sample exhibited a general shift toward higher wavenumbers (“left shift”) across the 4000–1000 cm⁻¹ range (Fig. 54), indicating molecular and structural rearrangements within the alkyd matrix. The O–H stretching band at 3498 cm⁻¹ increased in intensity, suggesting limited hydroxylation processes and the formation of oxidized species such as alcohols and/or hydroperoxides [13,31,46,242]. The aromatic C–H stretching band at 3070 cm⁻¹ remained unchanged, confirming the relative stability of the aromatic fraction under artificial aging. The aliphatic C–H stretching bands at 2926 and 2854 cm⁻¹ decreased in intensity, indicating chain scission and hydrogen abstraction phenomena that typically result in the loss of volatile low-molecular-weight fragments, such as aldehydes and carboxylic acids. Conversely, the carbonyl

stretching at 1722 cm^{-1} remained stable, suggesting a compensatory mechanism between ester bond cleavage and the concurrent formation of new oxidized carbonyl species [46,244,246].

In the fingerprint region, several diagnostic variations were observed. The ester-related bands at 1257 , 1115 , and 1068 cm^{-1} decreased in intensity, reflecting cleavage of C–O bonds and partial depolymerization of the alkyd matrix. The signal at 976 cm^{-1} also decreased, potentially indicating the degradation of unsaturated components ($=\text{CH}_2$ wagging) or the loss of minor organic additives. Conversely, increases were detected in the aromatic skeletal vibrations at 1601 and 1581 cm^{-1} , and in the C–H deformation bands at 1466 and 1389 cm^{-1} . These changes indicate a relative enrichment of structurally rigid aromatic and phthalic domains at the surface, resulting from the preferential volatilization of labile aliphatic segments. Slight increases were also noted in the out-of-plane aromatic C–H deformation bands at 742 and 712 cm^{-1} , further supporting the interpretation that aromatic components became more concentrated and stable at the surface during aging.

To conclude, these spectral variations confirm that the dark violet paint underwent oxidative and structural modifications within the alkyd binder. The predominant mechanisms include:

Initial oxidation, evidenced by the increase in the O–H band (3498 cm^{-1}), indicating hydroxylation and early-stage oxidation processes:

- Binder degradation, marked by the loss of aliphatic C–H signals (2926 and 2854 cm^{-1}) and the cleavage of ester linkages (1257 – 1068 cm^{-1}).
- Surface enrichment and stabilization, resulting from the relative accumulation of rigid aromatic and phthalic structures (1601 and 1581 cm^{-1}) after volatilization of labile aliphatic fragments.

These findings may suggest a selective oxidative degradation pathway, in which the aromatic backbone of the alkyd resin remains relatively stable while the aliphatic and ester fractions undergo partial decomposition and redistribution.

9.3.1.9. Light Blue (LB)

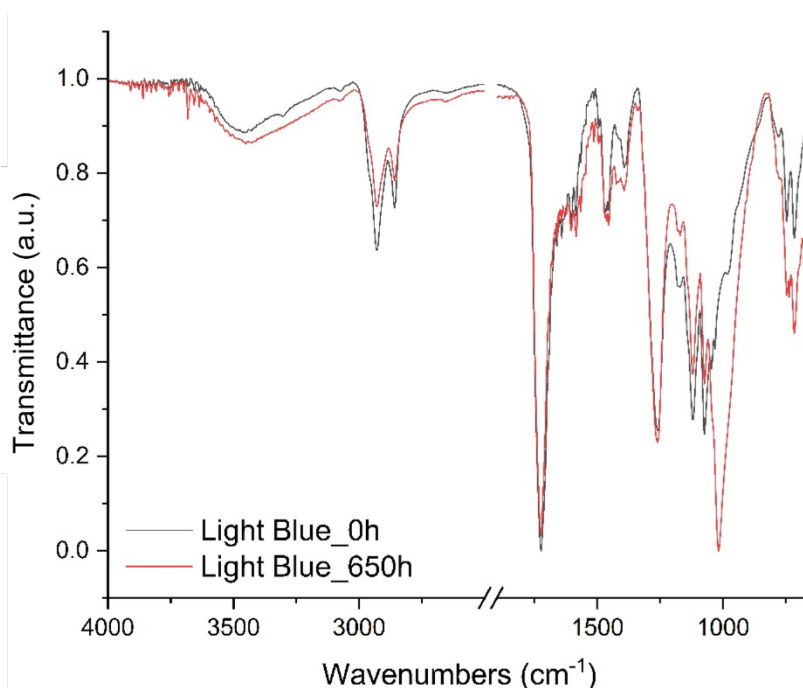


Fig. 55 Comparison of ATR-FTIR spectra of the Light Blue (LB) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The ATR-FTIR spectrum of the light blue spray paint after 650 hours of artificial ageing revealed subtle yet significant molecular modifications within the alkyd-styrene-nitrocellulose matrix (Fig. 55). The aliphatic C-H stretching bands at 2928 and 2859 cm⁻¹ slightly decreased in intensity, indicating a loss of aliphatic chain segments and partial depolymerisation of the binder. These changes are typically associated with UV-induced photo-oxidation and chain scission in alkyd systems, leading to the formation of low-molecular-weight (LMW) degradation products. In this context, LMW species refer to polymer fragments generated by

chain scission with molecular weights typically below a few thousand $\text{g}\cdot\text{mol}^{-1}$. A fraction of these products corresponds to volatile organic compounds (VOCs), generally below approximately $300\text{ g}\cdot\text{mol}^{-1}$ (e.g., aldehydes and short-chain carboxylic acids), which can evaporate from the coating. Other LMW oxidised fragments, although reduced in chain length (approximately $300\text{--}2000\text{ g}\cdot\text{mol}^{-1}$), are non-volatile and remain within the polymer matrix, where they may contribute to surface embrittlement, polarity changes, and chalking phenomena[12,13,46,247]. By contrast, the original alkyd resin typically exhibits molecular weights in the order of $10^4\text{--}10^5\text{ g}\cdot\text{mol}^{-1}$, highlighting the substantial reduction in chain length associated with photo-oxidative degradation [248–251]. Conversely, the characteristic carbonyl stretching band at 1724 cm^{-1} , together with the aromatic C=C vibrations at 1605 and 1584 cm^{-1} and the C–H bending band at 1454 cm^{-1} , remained unchanged in both position and intensity. This spectral stability suggests that the rigid polyester–aromatic backbone of the alkyd resin was preserved despite surface oxidation. Similar behaviour has been reported for long-oil alkyds subjected to moderate photo-oxidative ageing, where ester cleavage and formation of new oxidised species (ketones, γ -lactones) compensate each other within the same vibrational range [31,243,246].

A noticeable increase was observed at 1394 cm^{-1} , corresponding to C–H bending of methyl groups or, alternatively, to the enrichment of inorganic fillers such as talc at the surface. The stability of the band at 1260 cm^{-1} (C–O asymmetric stretching of ester groups) further confirms the preservation of the core polymer structure. In contrast, the progressive decrease in the 1170 , 1120 , and 1073 cm^{-1} bands reflects the degradation of lateral ester chains, surfactants, and possibly nitrocellulose fragments, all of which are highly susceptible to UV-induced oxidation and volatilisation [22,46,244].

A new, intense absorption band emerged around 1018 cm^{-1} , diagnostic of Si–O stretching in silicate-based fillers such as talc, maybe indicating a chalking

phenomenon - i.e., the exposure of inorganic pigments and fillers due to the erosion of the organic binder layer [12,22,252].

Additionally, the bands at 777, 747, and 716 cm^{-1} increased in intensity, consistent with enhanced aromatic out-of-plane C–H bending typical of styrene and phthalic moieties. The appearance of a new band at approximately 675 cm^{-1} may also be linked to either aromatic deformation in styrenic residues or Ti–O vibrations of exposed TiO_2 particles, a photoactive pigment that can catalyse further oxidation at the paint surface [46,245].

In conclusion, these spectral variations indicate that ageing predominantly affected the aliphatic fractions of the binder through photo-oxidation and hydrolytic cleavage, whereas the main aromatic and ester frameworks remained comparatively stable. The release of volatile low-molecular-weight compounds (VOCs), together with the accumulation of non-volatile oxidised LMW residues within the surface layer, contributed to progressive binder depletion and surface erosion. This process ultimately led to an increased exposure of inorganic fillers and more rigid polymer domains – features characteristic of early-stage chalking and oxidative hardening in alkyd-based coatings [13,31,46,245,247].

9.3.1.10. Dark Blue (DB)

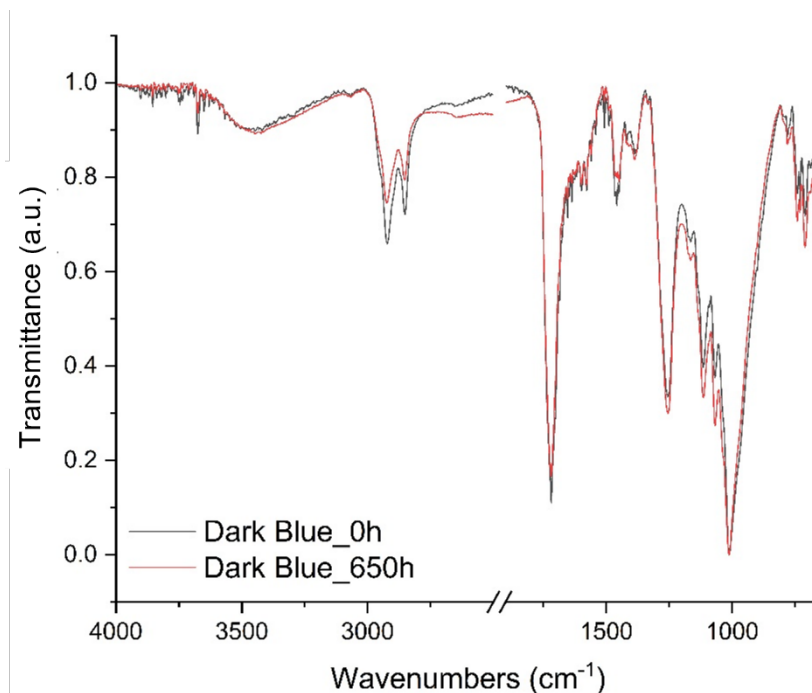


Fig. 56 Comparison of ATR-FTIR spectra of the Dark Blue (DB) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The ATR-FTIR spectrum of the dark blue spray paint after 650 hours of artificial ageing revealed moderate molecular and structural modifications within the alkyd-styrene-nitrocellulose matrix (Fig. 56). No significant wavenumber shifts were observed. The aliphatic C-H stretching bands at 2924 and 2851 cm⁻¹ exhibited decreased intensity, indicating the oxidation and volatilisation of low-molecular-weight aliphatic fragments, mainly derived from the fatty acid side chains of the alkyd resin. This is consistent with the onset of β -scission and photo-oxidative chain cleavage induced by UV exposure, as typically observed in long-oil alkyds [12,13,46,247]

A slight reduction was also detected in the carbonyl stretching band at 1718 cm⁻¹ and the C-H bending band at 1457 cm⁻¹. These changes point to partial loss of

ester groups, accompanied by mild oxidation leading to the formation of compensating carbonyl functionalities such as ketones and carboxylic acids. In contrast, several other features increased in intensity, notably those at 1254, 1114, 1068, 740, and 710 cm^{-1} .

The increase in the 1254 cm^{-1} and 1114 cm^{-1} bands, corresponding to C–O stretching of ester and ether groups, suggests an enrichment of relatively stable ester or ether functionalities, possibly due to the loss of more labile aliphatic components and partial surface cross-linking. The rise in the 1068 cm^{-1} band, within the typical range of C–O stretching for both alkyd resins and nitrocellulose, may reflect a higher relative abundance of the alkyd component after the volatilisation of other organics, or reduced denitration of nitrocellulose compared to other coloured samples.

Enhanced intensities of the 740 cm^{-1} and 710 cm^{-1} bands correspond to out-of-plane C–H bending in aromatic and styrenic structures. This enrichment of aromatic signatures indicates that the rigid phthalic and styrenic domains of the binder were less affected by UV degradation and became relatively more concentrated at the surface after the loss of the aliphatic fraction [22,31,243]

Importantly, the talc-related Si–O stretching band at 1012 cm^{-1} remained unchanged, confirming that the inorganic filler was not significantly affected and that no pronounced chalking occurred. This spectral stability contrasts with the light blue sample, in which a strong silicate enrichment was detected after ageing. The absence of chalking in the dark blue paint could be related to the UV-screening effect of the pigment itself (likely a phthalocyanine or carbon-black-containing formulation), which effectively limited binder oxidation and filler exposure [46,245]. In summary, the dark blue sample exhibited selective oxidation of aliphatic components and mild volatilisation of low-molecular-weight species, accompanied by a relative enrichment of ester and aromatic domains at the surface. The inorganic filler remained structurally stable, and no

significant surface erosion was detected. This behaviour reflects a more controlled oxidative ageing process compared to the light blue paint, indicating that the pigment composition and optical properties exerted a stabilising effect on the alkyd binder [13,46,245,247].

9.3.1.11. Green (G)

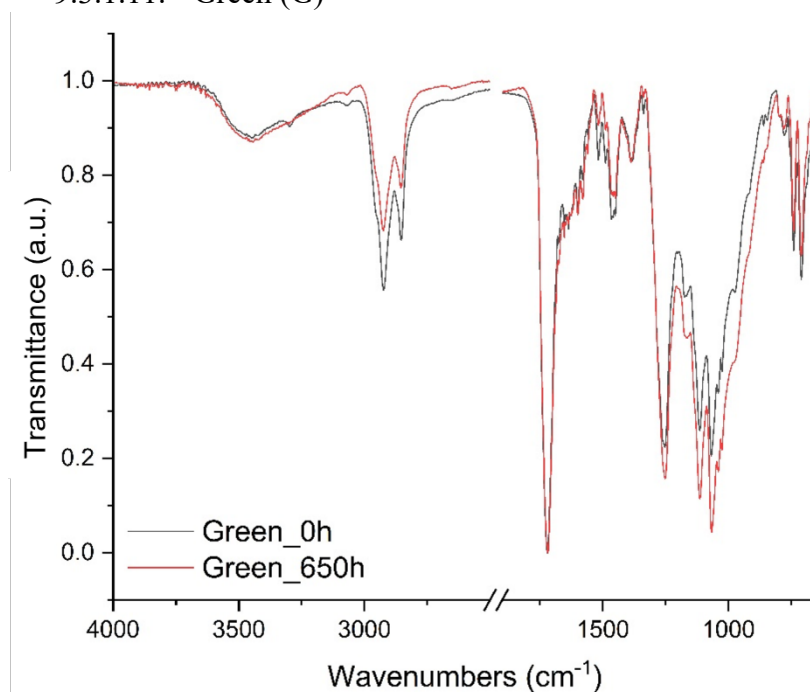


Fig. 57 Comparison of ATR-FTIR spectra of the Green (G) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The green paint exhibited no detectable wavenumber shifts across the 4000–700 cm⁻¹ range (Fig. 57), suggesting that the polymer matrix did not undergo significant structural rearrangement or cross-linking. However, moderate intensity variations were observed in specific regions of the spectrum, indicative of selective oxidative and structural modifications within the alkyd binder.

The aliphatic C–H stretching bands at 2924 and 2853 cm⁻¹ decreased in intensity, reflecting chain scission and hydrogen abstraction processes that lead to the volatilization of low-molecular-weight aliphatic fragments [46,242,244].

Similarly, a reduction in the C–H deformation band at 1465 cm^{-1} confirmed the loss of aliphatic components. The band at 1517 cm^{-1} , attributed to the organic pigment PY74 (Pigment Yellow 74), also decreased slightly, suggesting that this pigment experienced minor molecular alteration under aging, consistent with the known light sensitivity of azo pigments [31,247]. In contrast, several characteristic alkyd bands remained stable, indicating a balanced oxidative mechanism rather than severe degradation. The carbonyl stretching band at 1720 cm^{-1} ($\nu(\text{C}=\text{O})$) showed no variation, suggesting a compensation effect between ester bond cleavage and the formation of new oxidized species (ketones, acids). Likewise, the aromatic skeletal vibrations at 1601 and 1579 cm^{-1} remained unchanged, confirming the stability of the rigid phthalic aromatic backbone of the binder. The C–H deformation at 1387 cm^{-1} was also unaffected, indicating conservation of the main polymer structure despite the loss of labile aliphatic chains.

The C–O stretching bands at 1252 , 1113 , and 1068 cm^{-1} increased in intensity. This trend is attributed to the relative surface enrichment of more stable polymeric ester structures (the polyester backbone), following the removal of volatile aliphatic material. The increase around 1113 cm^{-1} may also reflect the migration and accumulation of surfactant-like poly(ethylene oxide) (PEO) components at the surface prior to their degradation.

Minor decreases in the out-of-plane aromatic C–H deformation bands at 740 and 710 cm^{-1} were observed, potentially indicating slight structural modifications or the loss of surface additives absorbing in this region.

To conclude, FTIR data confirm that the green paint experienced moderate, selective oxidative changes primarily within the alkyd binder, while the inorganic fillers and pigment remained relatively stable. The stable carbonyl and aromatic regions, combined with the selective decrease of aliphatic signals and increase of C–O stretching bands, support a degradation pattern dominated by surface

oxidation and binder redistribution rather than extensive polymer breakdown or pigment photolysis.

9.3.1.12. Light Brown (LBr)

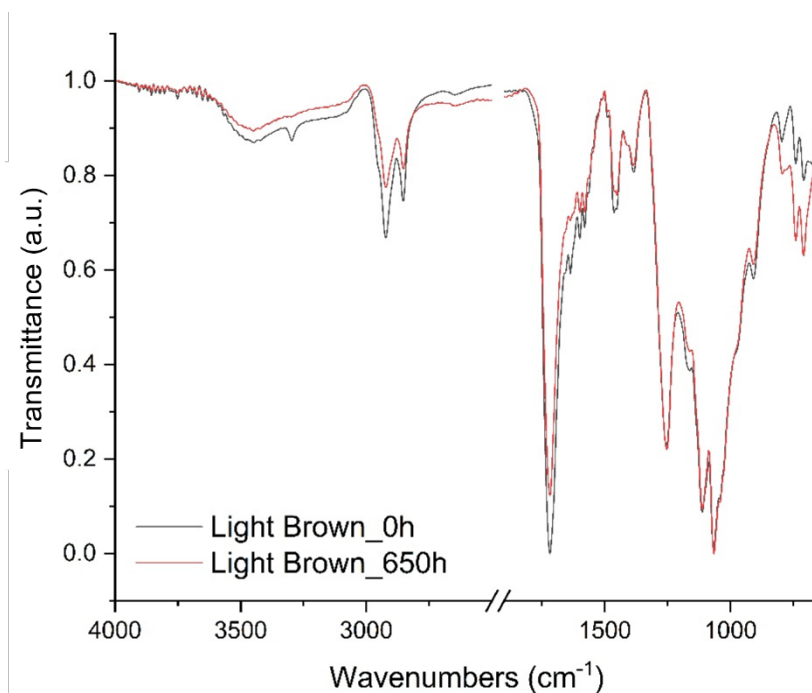


Fig. 58 Comparison of ATR-FTIR spectra of the Light Brown (LBr) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The light brown sample exhibited no significant wavenumber shifts (Fig. 58), indicating that no substantial cross-linking or structural rigidification occurred within the polymer matrix. A weak band at 3297 cm⁻¹ decreased in intensity, together with the aliphatic C-H stretching bands at 2924 and 2853 cm⁻¹, the carbonyl stretching at 1718 cm⁻¹, and the signals at 1636 cm⁻¹ (associated with PY42), 1599, 1579, and 1463 cm⁻¹ [13,22,31,46,242,246,247]. In contrast, the bands at 1385, 1254, 1113, 1066, and 908 cm⁻¹, mainly associated with C-O stretching modes of the alkyd resin and with iron oxide and hydroxide pigments, remained largely unchanged. Increases in intensity were observed at 740 and 708

cm⁻¹ [13,46,243,247]. In general, the spectral variations point to selective oxidation and surface erosion processes affecting the alkyd binder, while the inorganic components remained chemically stable.

The attenuation of the O–H stretching at 3297 cm⁻¹ and of the aliphatic C–H signals (2924 and 2853 cm⁻¹) clearly indicates chain scission and hydrogen abstraction, leading to volatilisation of low-molecular-weight fragments from the film surface. The reduction of the carbonyl band at 1718 cm⁻¹ further supports ester bond cleavage and partial depolymerisation of the alkyd backbone, without full compensation by new oxidised species, suggesting net surface erosion rather than bulk oxidation [242,246].

The decrease at 1636 cm⁻¹, attributed to the PY42 pigment (hydrated ferric oxide), suggests minor alteration or loss of the pigment component due to binder degradation. Likewise, the reduced intensity of the aromatic skeletal vibrations at 1599 and 1579 cm⁻¹ and the C–H deformation at 1463 cm⁻¹ points to the removal of both aliphatic and aromatic fractions from the outermost layer.

The stability of the C–O stretching bands at 1385, 1254, 1113, and 1066 cm⁻¹ indicates that the rigid polyester backbone of the alkyd binder remained largely intact. The persistence of the 908 cm⁻¹ signal, characteristic of Fe–O vibrations in goethite and related iron hydroxides, further confirms the chemical stability of the inorganic pigments and fillers under the applied artificial ageing conditions.

Interestingly, the slight increases in intensity of the aromatic out-of-plane C–H bending modes at 740 and 708 cm⁻¹ suggest a relative enrichment of non-volatile aromatic fragments on the surface. This phenomenon results from the preferential loss of aliphatic moieties and volatile oxidation products, leaving behind more cross-linked or rigid aromatic structures typical of the phthalic polyester portion of the binder [46,247].

To conclude, the light brown paint underwent selective oxidative degradation primarily affecting the aliphatic and carbonyl fractions of the alkyd binder,

accompanied by surface erosion and limited pigment alteration. The polyester core and the inorganic components, particularly iron oxides and hydroxides, remained stable, leading to a moderate enrichment of the aromatic backbone at the surface. These features are fully consistent with the known photodegradation mechanisms of alkyd-based coatings, where volatilisation and oxidative scission of the flexible chains dominate over bulk cross-linking processes [22,31,246].

9.3.1.13. Dark Brown (DBr)

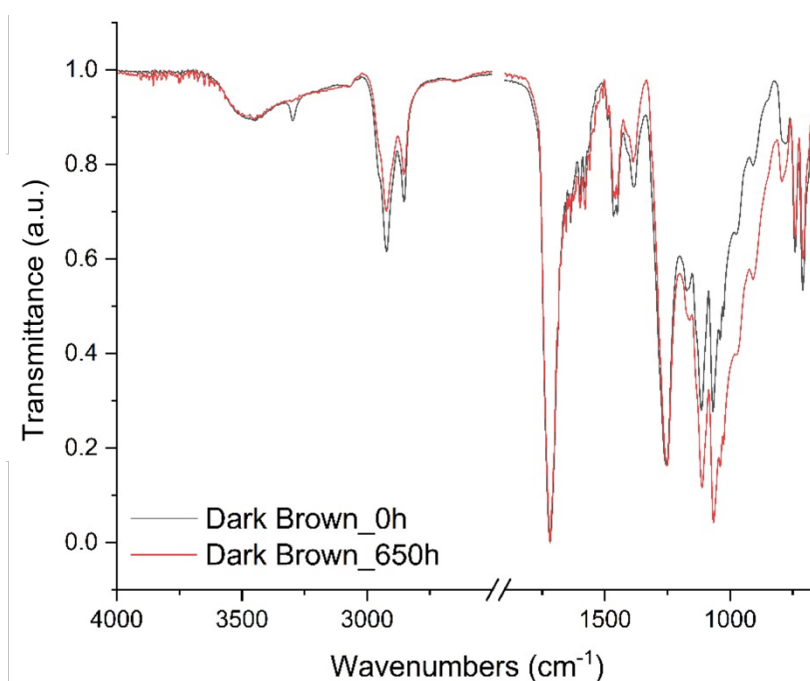


Fig. 59 Comparison of ATR-FTIR spectra of the Dark Brown (DBr) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

The dark brown sample exhibited no wavenumber shifts (Fig. 59), indicating that no macroscopic cross-linking or structural rigidification occurred within the polymer network. The weak O-H stretching band at 3299 cm⁻¹ disappeared, accompanied by decreased intensities at 2922 and 2853 cm⁻¹ (aliphatic C-H

stretching) and at 1463 and 1385 cm^{-1} (C–H bending modes) [31,46,242,244,246].

The carbonyl stretching band at 1718 cm^{-1} , together with the aromatic skeletal vibrations at 1599 and 1576 cm^{-1} and the ester-related band at 1254 cm^{-1} , remained unchanged. In contrast, increases in intensity were observed for the C–O stretching bands at 1113 and 1066 cm^{-1} , as well as for the signals at 973, 908, and 796 cm^{-1} associated with iron oxides and hydroxides. Slight decreases were recorded for the aromatic out-of-plane bending bands at 740 and 710 cm^{-1} [13,31,44,46,243,244,246,247]. These spectral variations indicate selective oxidative and structural modifications in the alkyd binder, accompanied by relative enrichment of the inorganic pigment fraction at the surface.

The disappearance of the weak O–H signal at 3299 cm^{-1} may reflect the loss of initial hydroxyl groups in the binder or the evaporation of residual moisture and solvent. The concurrent decrease of aliphatic C–H stretching bands (2922 and 2853 cm^{-1}) can be interpreted as an indication of chain scission and hydrogen abstraction, consistent with the volatilisation of low-molecular-weight aliphatic fragments from the paint surface. The diminished C–H bending bands at 1463 and 1385 cm^{-1} further confirm the depletion of aliphatic moieties, marking a progressive erosion of the more labile organic fractions [46,242,246].

The stability of the carbonyl stretching at 1718 cm^{-1} suggests a compensatory oxidative equilibrium, in which the loss of ester groups due to bond cleavage is counterbalanced by the concurrent formation of new oxidised species, such as ketones, aldehydes, and carboxylic acids, typical of alkyd photodegradation pathways [242,244]. The aromatic skeletal vibrations at 1599 and 1576 cm^{-1} remained stable, implying that the phthalic aromatic backbone of the alkyd resin retained its structural integrity. Similarly, the unaltered C–O asymmetric stretching band at 1254 cm^{-1} confirms the persistence of the polyester core of the

alkyd network, which resists oxidation and chain scission more effectively than the aliphatic side chains.

The increased intensities of the C–O stretching bands at 1113 and 1066 cm^{-1} , as well as the signal at 973 cm^{-1} , point to a relative enrichment of the more stable polymeric fractions and possible surface reorganisation of the polyester matrix following the loss of aliphatic components. The increased signals at 908 and 796 cm^{-1} , attributed to Fe–O vibrations in goethite and related iron oxides and hydroxides, further indicate an enrichment of inorganic pigments on the surface. This behaviour is consistent with the selective erosion of the organic binder, which leaves behind the more stable mineral phase [46,243,247]

In contrast, the slight decrease of the aromatic out-of-plane C–H bending bands at 740 and 710 cm^{-1} suggests minor structural rearrangements within the aromatic network, though not indicative of significant aromatic degradation, as the main aromatic framework remains spectroscopically stable.

In summary, the dark brown paint shows clear evidence of oxidative and structural degradation primarily affecting the aliphatic and hydroxyl-containing fractions of the alkyd binder. These processes were accompanied by a balanced carbonyl response, signalling partial compensation between ester loss and oxidation product formation, and by a surface enrichment of inorganic pigments and more rigid polymeric domains. The overall pattern confirms the selective erosion of volatile organic components and the chemical stability of the iron-based pigments, consistent with the typical photodegradation mechanisms of alkyd coatings under accelerated ageing.

9.4. Conclusions

The ATR–FTIR analyses of the thirteen alkyd-based spray paints after 650 hours of accelerated ageing revealed that oxidative degradation, and hydrolysis are the predominant ageing mechanisms affecting the alkyd–styrene–nitrocellulose binder system. The extent and manifestation of these processes were shown to depend strongly on pigment composition and optical characteristics. Light-coloured formulations (e.g., white, pink, and yellow) exhibited the most pronounced photo-oxidative damage, with extensive hydroxylation, ester cleavage, and volatilisation of aliphatic chains. In contrast, darker or carbon-black-rich formulations (e.g., black, dark blue, dark brown) demonstrated a more pronounced photostability, largely attributed to the UV-absorbing properties of their pigments. Intermediate colours containing organic azo or iron oxide pigments (e.g., orange, light brown, red) displayed selective oxidation and surface enrichment of aromatic or polyester domains, confirming the complex interplay between binder and pigment in dictating degradation dynamics. In conclusion, the results confirm that photo-oxidation and surface deterioration dominate over cross-linking or bulk polymerisation processes, leading to compositional gradients and exposure of inorganic fillers. These findings underscore the need for pigment-specific conservation approaches and provide a molecular basis for understanding the long-term behaviour of alkyd spray paints in outdoor mural contexts, bridging the scientific and artistic dimensions explored in the following chapters.

10. Hybrid application on ETICS mock-ups

10.1. Introduction

Considering the promising results obtained from the formulation and preliminary evaluation of the chitosan–nanosilica (Chs–NS) hybrid coating (Chapters 4, and 5), a new experimental part was designed to test its performance on a more representative substrate, namely ETICS (External Thermal Insulation Composite Systems). This choice was motivated by the need to reproduce the multilayer structure of the façade on which Skim’s mural was executed, as well as to investigate the coating’s potential in protecting contemporary wall paintings realised on thermally insulated supports.

To this end, a series of ETICS mock-ups were prepared, painted with the same alkyd-based spray paints used in the original artwork, and selectively treated with the Chs–NS hybrid coating on half of each painted surface. The specimens were subsequently subjected to the same accelerated artificial ageing protocol described in sections 5.2.2, and 9.2.2, ensuring comparability with previous tests performed on concrete-based mock-ups and isolated paint films.

This study pursued two main objectives. First, to evaluate the predictive validity of the accelerated artificial ageing protocol by comparing the colorimetric variations observed on the mock-ups with those measured on the original mural after natural weathering. In this context, “reliability” does not imply direct equivalence between artificial and natural ageing, but rather the extent to which laboratory-induced degradation trends can be meaningfully extrapolated to interpret real outdoor behaviour. Although accelerated ageing cannot fully reproduce the complexity of outdoor environmental fluctuations, it provides a controlled framework to isolate dominant degradation mechanisms and to establish comparative performance trends.

It must be emphasized that no universal conversion factor exists between accelerated artificial ageing and natural weathering. International standards for polymer durability testing (e.g., ISO 4892 series; ASTM G154, ASTM G155) explicitly caution against establishing direct time-equivalence relationships, as natural degradation depends on site-specific variables including spectral distribution, irradiance, temperature cycles, relative humidity, pollutants, and wet–dry fluctuations.

In the present study, ageing correlation was therefore approached in terms of cumulative radiant exposure (dose) rather than simple time equivalence. The accelerated artificial aging protocol was designed to deliver a controlled and reproducible stress level capable of activating the dominant degradation mechanisms (photo-oxidation, thermo-oxidative stress, moisture-related processes) observed under outdoor conditions.

While the laboratory exposure cannot replicate the full complexity of natural weathering, comparison of colorimetric trends (ΔE progression, relative stability between treated and untreated areas, and pigment-dependent behaviour) allows qualitative correlation between artificial and natural ageing responses. The objective was therefore not to define a strict acceleration factor (e.g., “x hours = y months outdoors”), but to verify whether degradation pathways and protective performance trends observed in laboratory conditions are consistent with those recorded on the original mural after natural exposure.

The limitations of this approach are acknowledged: environmental variability, pollutant interaction, biological growth, and substrate heterogeneity cannot be fully reproduced in controlled chambers. Nevertheless, accelerated ageing remains a widely accepted predictive tool in conservation science when interpreted in comparative and mechanistic terms rather than as a direct temporal simulation.

Second, to assess the protective efficiency of the Chs–NS coating in mitigating chromatic and surface alterations on alkyd-painted ETICS substrates, extending the understanding of its behaviour under prolonged environmental stress conditions beyond the 100-hours tests reported in Chapter 5.

By combining these two perspectives, this experiment aims to bridge laboratory-scale testing and real-world conservation challenges, contributing to the development of sustainable, biopolymer-based protective systems for modern and contemporary mural paintings.

10.2. Materials and methods

10.2.1. Mock-ups preparation

To simulate the artistic technique of the mural and conduct more comparable accelerated artificial ageing tests (sections 5.2.2, and 9.2.2), mock-ups were prepared to accurately replicate the complex substrate of the façade where Skim's artwork was created. An expanded polystyrene thermal insulation panel – commonly known as Styrofoam (purchased from OBI, Italy) – was used as mock-up's support. This material is widely employed to enhance the thermal insulation of buildings. The panel, measuring $100 \times 50 \times 2 \text{ cm}^3$, was cut into smaller pieces, each measuring $10 \times 15 \times 2 \text{ cm}^3$.

Each piece was scratched on one of its larger surfaces, to enhance the adherence of the mortar. Then, two layers of a cementitious mortar (Job finishing plaster, OBI, Italy), interposed by a white plaster mesh made of interwoven fibreglass filaments (75 g/m^2 , OBI, Italy), were applied. This mesh is typically applied directly to plastered surfaces to provide a stable base and prevent cracking, detachment, and other common plaster-related issues. The mock-ups were left to dry for about 4 days.

Subsequently, two coats of White Ready-Mix Mortar (Knauf, OBI, Italy) were applied as finishing. The substrate was completed using a mixture of lime and

hydraulic-setting cement, blended with water and prepared according to the manufacturer's specifications. The specimens were left to set and dry at room temperature for two weeks before the colour paints were applied.

After the mortar had set, each mock-up was coloured with one of the thirteen colours selected from the artist's "palette". The colour was applied by spraying the product directly onto the mortar's surface from approximately 20 cm. The colours were then left to dry at room temperature for 10 days.

10.2.2. Chs-NS Hybrid coating application

The chitosan–nanosilica (Chs–NS) hybrid coating, prepared according to the procedure described in section 4.1.2 applied to one half of the coloured surface of each ETICS mock-up. In this case, the coating was applied using a spray bottle to ensure a homogeneous distribution of the treatment across the selected area ($5 \times 7.5 \text{ cm}^2$). The amount of hybrid solution applied to each mock-up was measured, corresponding on average to approximately 2 g of product. This value, when related to the treated surface area (37.5 cm^2), corresponds to an application rate of about 0.05 g cm^{-2} .

After application, the treated mock-ups were left to dry under laboratory conditions for 1 week to allow solvent evaporation and coating stabilisation prior to subsequent measurements and artificial ageing tests.

10.2.3. Colorimetric measurements

Colour measurements were carried out on each mock-up, on both the untreated and Chs-NS treated parts, before and after the application and the accelerated aging test.

The colourimeter used is the same described in section 5.2.3 An uncoloured mock-up was taken as control.

Each measurement was the average of five taken at the same spot on each mock-up. To accurately identify the precise measurement spot, a plastic mask was used.

To determine the colour changes, CIELAB coordinates (L, a, b), colour variations ΔE , chroma variations ΔC^* , and the other values were evaluated following the indications of the Commission Internationale de l'Éclairage (CIE 2000), following the procedure described in section 8.2.2 [231].

10.2.4. Gloss measurements

Accordingly to the measurements carried out on the mural, gloss measurements were done also on the mock-ups, always before and after the Chs-NS application and the accelerated artificial ageing tests.

For mock-ups, gloss measurements were taken by using a silicone mask, ensuring that the same measurement area was identified each time.

Gloss values were measured by using the same glossmeter and setup described in section 5.2.4. Measurements were conducted 3 times both on each mural mapped area and on each mock-up.

10.2.5. Accelerated artificial aging tests

The accelerated artificial ageing protocol applied to the ETICS mock-ups was identical to that described in sections 5.2.2, and 9.2.2 previously employed for the concrete-based mock-ups and spray paint samples, respectively. The use of the same conditions ensured full comparability among concrete mock-ups, isolated spray paints, and ETICS-based specimens, allowing a consistent evaluation of the hybrid coating's protective performance.

10.3. Results and discussion

10.3.1. Natural vs artificial accelerated aging

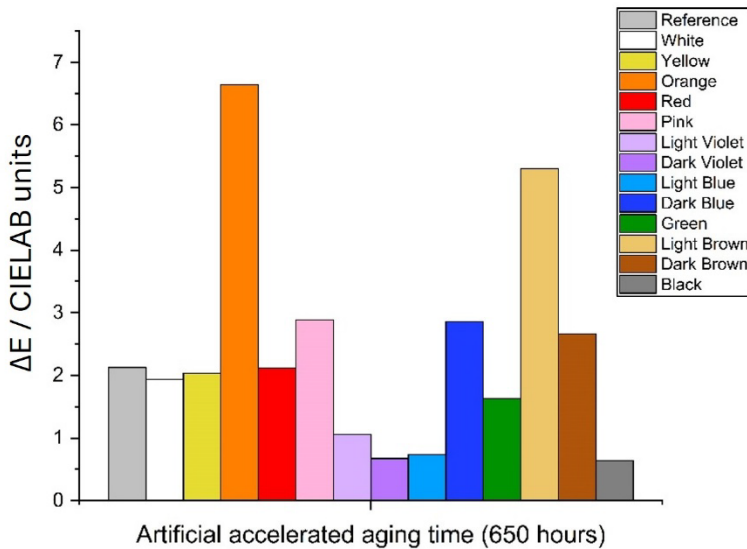


Fig. 60 ΔE_{00} values measured for the mock-ups after 650 h of accelerated artificial aging.

The comparison between natural aging (NA) of the mural painting and accelerated artificial aging (described in section 10.2.5.) performed on laboratory mock-ups was initially approached by analysing the ΔE_{00} values of homologous colours. The aim was to establish potential correlations between outdoor weathering and controlled laboratory conditions. Fig. 60 shows ΔE_{00} values measured for the mock-ups after 650 h of accelerated artificial aging. As summarized in Table 20, the most comparable ΔE values were matched for each colour. Taken together, the results reveal heterogeneous behaviour among the different hues. For instance, Dark Brown (B) and Dark Blue (Y) showed a more pronounced variation under artificial aging than in the corresponding mural areas, resulting in higher ΔE values. In contrast, colours such as Yellow (J), White (W), and Pink (A) exhibited ΔE values after 650 h of accelerated artificial aging that

Colour	ΔE_{00} – 650 h artificial (CIELAB units)	ΔE_{00} – Real case (CIELAB units)
White (W)	1.93	~ 1 month (0.30)
Yellow (J)	2.03	~ 7 months (2.41)
Orange (R)	6.64	~ 12 months (7.11)
Red (K)	2.11	~ 14 months (2.58)
Pink (A)	2.89	~ 7 months (4.39)
Light Violet (S)	1.05	~12 months (1.04)
Dark Violet (T)	0.67	~12 months (1.42)
Light Blue (V)	0.74	~7 months (1.09)
Dark Blue (Y)	2.86	> 24 months (2.34)
Green (AA)	1.63	~12 months (1.86)
Light Brown (O)	5.30	~ 12 months (5.93)
Dark Brown (B)	2.66	> 24 months (1.35)
Black (X)	0.64	< 1 month (0.77)

Table 20 Comparison of ΔE values from natural aging (NA) of the mural and accelerated artificial aging of mock-ups, showing the closest temporal correspondences between laboratory and real exposure, supporting the evaluation of the predictive validity of the accelerated ageing protocol.

closely matched the intermediate values observed on the mural after 1–7 months of exposure.

Similarly, Orange (R), Violet tones (S, T), Green (AA), and Light Brown (O) displayed ΔE values comparable to those measured on the mural after approximately 12 months of outdoor weathering. Red (K) and Light Blue (V) showed stronger responses to artificial aging, with ΔE values corresponding to

about 14 months of natural exposure. Black (X), however, behaved differently: while highly stable under

While ΔE_{00} provides a general overview of colour change, it encompasses different parameters that may vary independently, particularly lightness (dL') and chroma (dC'). For this reason, a more detailed analysis was performed by comparing dL' and dC' values of homologous colours under natural and accelerated artificial aging. The scatter plot in Fig. 61 highlights consistent trends across both aging conditions. Except for artificially aged Dark Brown, all colours exhibited an increase in lightness, appearing visually brighter.

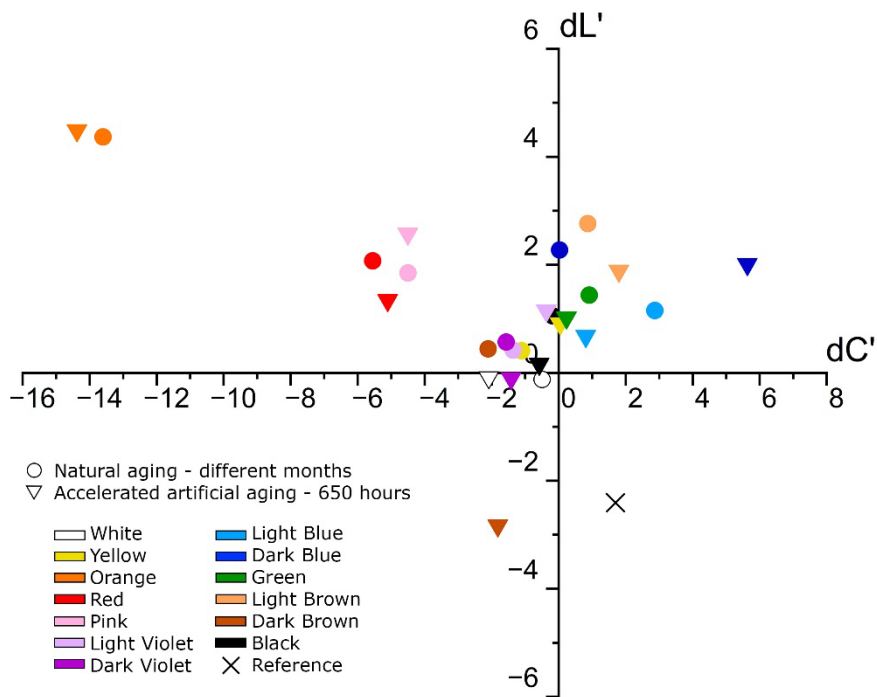


Fig. 61 Scatter plot comparing dL' (lightness) and dC' (chroma) values of homologous colours subjected to natural aging (NA) on the mural and accelerated artificial aging on mock-ups, highlighting similarities and divergences in colour variation trends.

Colour	Natural aging (NA)		Accelerated Artificial Aging 650 h	
	dL' - Lightness	dC' - Chroma	dL' - Lightness	dC' - Chroma
White (W)	-0.490	-0.124	-0.088	-2.085
Yellow (J)	0.410	-1.106	0.912	0.048
Orange (R)	4.370	-13.601	4.490	-14.375
Red (K)	2.074	-5.548	1.342	-5.100
Pink (A)	1.848	-4.495	2.574	-4.498
Light Violet (S)	0.420	-1.356	1.150	-0.365
Dark Violet (T)	0.570	-1.562	-0.100	-1.414
Light Blue (V)	1.152	2.871	0.676	0.808
Dark Blue (Y)	2.274	0.029	2.010	5.634
Green (AA)	1.438	0.915	1.022	0.233
Light Brown (O)	2.762	0.870	1.888	1.799
Dark Brown (B)	0.442	-2.104	-2.830	-1.818
Black (X)	1.054	-0.175	0.160	-0.581
Reference (Not coloured mock-up)	-	-	-2.410	1.701

Table 21 Lightness (dL') and chroma (dC') values of homologous colours subjected to natural aging (NA) on the mural and accelerated artificial aging on mock-ups.

Some hues, most notably Orange, followed by Red, Pink, and the two Violet tones, underwent a decrease in chroma, corresponding to perceptible fading. Conversely, Light Brown, Green, and Blue showed an increase in chroma, becoming more saturated under both natural and artificial aging. A notable exception was Dark Brown, which darkened under accelerated artificial aging ($dL' < 0$) while becoming slightly lighter under NA, although the two processes produced comparable chroma values.

Taken together, these observations indicate that homologous colours aged in the field and in the laboratory generally cluster closely in terms of dL' and dC', suggesting that accelerated artificial aging can reproduce certain degradation pathways with reasonable approximation. The closest matches were observed for Yellow, Orange, Red, Pink, Violet, Green, Light Blue, and Light Brown, while larger discrepancies emerged for Dark Blue, Dark Brown, and Black. This

divergence implies that some pigments are more sensitive to environmental stressors that are not fully replicated under laboratory conditions, such as airborne pollutants, wind, or biological colonization.

10.3.2. Evaluation of the hybrid coating on ETICS mock-ups

Following the application of the Chs–NS hybrid coating on half of the surface of each ETICS mock-up, painted with the same alkyd-based colours used for the SKIM mural, colorimetric measurements were carried out to assess chromatic variations occurring before and after the coating treatment. Subsequent measurements were performed after 650 hours of artificial ageing to evaluate the

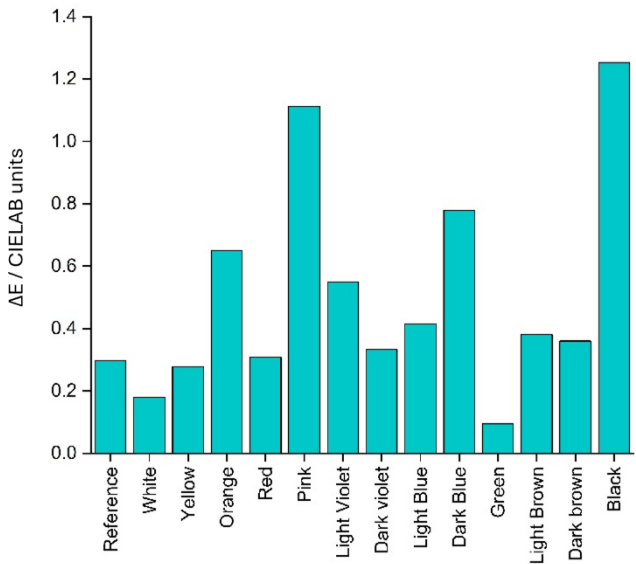


Fig. 62 ΔE_{00} values recorded for each alkyd-based colour following the application of the Chs–NS hybrid coating on the ETICS mock-ups.

colour changes induced by accelerated weathering. As demonstrated in the previous section (10.3), this artificial ageing procedure effectively reproduces the degradation trends observed in natural outdoor exposure for the specific real-case study considered here. This experimental approach, although indirect, allows for a preliminary evaluation of the potential chromatic and protective behaviour of

the hybrid coating when hypothetically applied to the original mural. By correlating colorimetric variations before and after accelerated ageing, it becomes possible to infer the coating's efficiency in limiting colour fading and surface alterations under simulated environmental stress.

Fig. 62 shows the ΔE_{00} values related to the chromatic variations measured upon coating application for each colour tested. As can be observed, all ΔE_{00} values remain below 1.4 CIELAB units, indicating that the application of the hybrid formulation did not induce perceptible colour changes on the alkyd paints selected in this study.

Colour variation measurements were also performed after the 650-hour artificial ageing test. Fig. 63 presents photographs of the mock-ups after coating application – applied to the right-hand half of each sample – and after ageing.

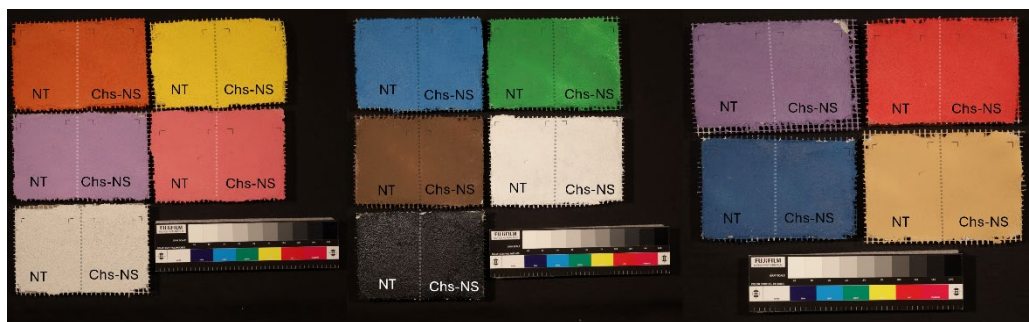


Fig. 63 Photographic documentation of the ETICS mock-ups after the application of the Chs-NS hybrid coating (applied on the right-hand half of each sample) and subsequent artificial ageing (650 h). The untreated left-hand side served as control. The boundary between treated and untreated areas is marked by a dashed line.

The untreated side (left) served as a reference, and the boundary between treated and untreated zones is indicated by a dashed line. The corresponding ΔE_{00} values are reported in Fig. 64.

When comparing the colorimetric results obtained for the treated and untreated areas, it was observed that the chitosan–nanosilica coating effectively reduced colour variation under accelerated ageing in several cases. In particular, the

hybrid protective coating demonstrated notable efficacy on the light brown, dark blue, pink, and orange samples, which exhibited lower ΔE_{00} values compared to their untreated counterparts.

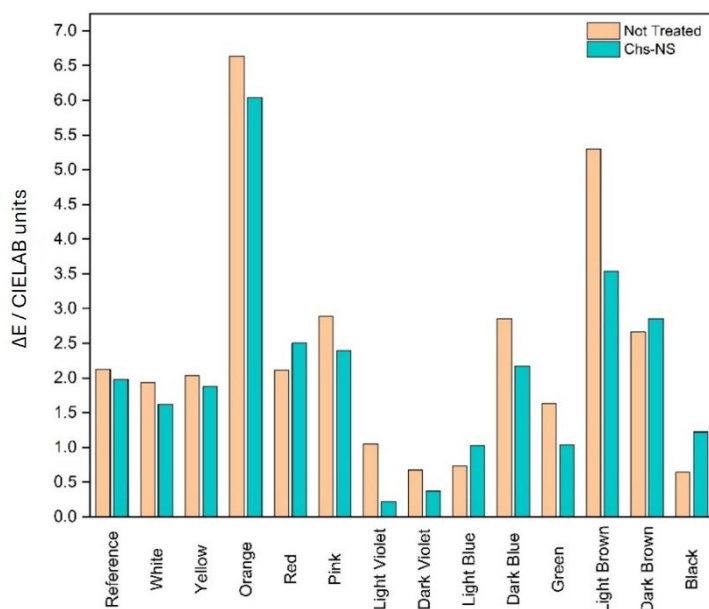


Fig. 64 Histogram comparing the ΔE_{00} values measured before and after artificial ageing (650 h) for both treated and untreated portions of the ETICS mock-ups. Lower ΔE_{00} values for the treated areas indicate the protective effect of the Chs-NS coating against colour variation under accelerated ageing conditions.

The application of the Chs-NS hybrid coating resulted in reduced colour variation for most of the mock-ups, particularly those containing pigments more susceptible to photodegradation. The results indicate that the hybrid formulation may contribute to a retardation of photo-induced oxidative degradation processes occurring in the alkyd binder. However, it is important to note that photo-oxidation is not the sole chemical phenomenon operating under the applied ageing conditions. In addition to UV-driven radical reactions, thermo-oxidative effects, moisture-assisted hydrolytic processes, and pigment-binder interfacial interactions may also contribute to the overall degradation behaviour observed in

the alkyd systems. The combined action of these mechanisms can influence both chemical modification and physical surface changes.

Nevertheless, the protective performance was less pronounced in certain cases, especially for the red, black, and light blue paints, possibly due to substrate-related interactions and the intrinsic photo-instability of some pigment–binder systems. This behaviour aligns with previous observations on the original on the “Anna Maria” mural (Chapter 8), where the substrate itself influenced colour stability and accelerated surface degradation. These findings suggest that, while the Chs–NS coating provides a measurable protective effect in some colour systems, further optimisation is needed to enhance its resistance to photo-oxidative stress while also improving its performance under combined thermal and humidity-driven ageing factors, which collectively influence long-term stability in outdoor environments. Future research may consider the incorporation of additional stabilising agents—such as carbon quantum dots, titanium dioxide, or other UV-absorbing nanoparticles to improve the coating’s resistance to photo-oxidative degradation without compromising its optical transparency.

10.4. Conclusions

The results obtained from the ETICS mock-up campaign provide valuable insights into both the reproducibility of natural ageing phenomena under controlled conditions and the potential of the Chs–NS hybrid coating as a protective treatment for contemporary painted surfaces.

The comparative analysis between natural ageing (NA) and accelerated artificial ageing revealed a generally good correspondence in chromatic trends across most hues, particularly for yellow, orange, red, pink, violet, green, and light brown tones. This confirms that the adopted ageing protocol can effectively reproduce the main degradation pathways observed in-situ, thus validating its applicability

for predictive conservation studies. Nevertheless, certain discrepancies, especially for darker pigments such as black and dark brown, may highlight the influence of environmental factors (e.g., particulate deposition, moisture, biological growth) that are not fully replicated in laboratory conditions.

The evaluation of the Chs–NS hybrid coating demonstrated that its application does not induce perceptible chromatic alterations ($\Delta E_{00} < 1.4$ CIELAB units), fulfilling a key requirement for conservation treatments. After 650 hours of accelerated ageing, the coating proved effective in reducing colour variations in several colour systems, most notably light brown, dark blue, pink, and orange, suggesting a measurable retardation of photochemical degradation processes within the alkyd binder.

However, its protective efficacy varied among pigments, indicating that the interaction between the coating and the underlying paint layers, as well as the influence of the substrate, plays a crucial role in determining performance. These findings are consistent with previous observations on the “Anna Maria” mural (Chapter 8), where substrate composition and surface morphology were shown to affect paint stability.

To conclude, this study confirms the potential of the chitosan–nanosilica hybrid as a sustainable, low-impact material for the protection of modern painted surfaces, while also emphasizing the highlighting the complexity of coating–paint–substrate interactions. Beyond the development of new protective formulations, future research should increasingly focus on how chemistry and materials science can inform conservation decision-making, particularly by contributing to the definition of acceptable damage thresholds for contemporary mural paintings.

Quantitative insights into photochemical degradation pathways, colour change kinetics, and surface decohesion processes can support heritage scientists in distinguishing between tolerable material evolution and unacceptable loss of

legibility or artistic intent. In this perspective, laboratory ageing studies, combined with field monitoring, may play a crucial role not only in assessing material durability, but also in establishing evidence-based criteria to guide preventive conservation strategies for contemporary murals exposed to outdoor environments.

11. Collaboration with the artist and dissemination at school

11.1. Collaboration with Skim

The collaboration with the artist who created the mural *Anna Maria* proved fundamental both for the scientific development of the research and for the historical and artistic contextualization of the case study. From the very beginning, the artist demonstrated remarkable openness and interest toward the project, donating several of the original spray paints used for the execution of the mural. This contribution was essential to ensure that the experimental tests were conducted on the same materials actually employed in the artwork, thus guaranteeing the representativeness of the analysis.

During the collaboration, the artist shared his empirical knowledge regarding the behaviour of spray paints, particularly with respect to colour stability and the compatibility of different pigments when overlaid to achieve specific aesthetic effects. For instance, he noted that the superimposition of yellow and black spray paints can be problematic, as these two colours tend to repel each other, preventing homogeneous mixing on the surface.

He also explained the rationale behind his choice of nitro-based spray paints, which he considers offering superior application and coverage compared to acrylic-based sprays. However, he reported that for indoor murals – such as a recent work at the Meyer Children’s Hospital in Florence – he prefers acrylic paints, which are less toxic and more suitable for confined environments.

The artist expressed genuine curiosity and appreciation for the conservation-oriented perspective of this research, asking how long the mural *Anna Maria* might “survive” before significant deterioration occurs. This question also raises a broader issue concerning the planning and commissioning of large-scale public artworks. In the context of publicly funded murals, preliminary consideration of material durability, expected service life, and maintenance strategies could

represent an important component of the commissioning process. While artistic intention and aesthetic quality remain central, collaboration between artists, conservators, and commissioning authorities may help integrate sustainability criteria and preventive conservation principles from the outset. Such dialogue could support more informed material choices and clearer expectations regarding the long-term behaviour of contemporary spray-painted murals exposed to outdoor environments. Similar recommendations have been proposed in recent public art maintenance guidelines, which emphasize the importance of early dialogue between creators and conservation professionals [253].

Two years after the completion of the work, he was contacted again to discuss the progress of the study and to observe the current condition of the mural. During this visit, he was surprised by the extent of decay that had occurred in such a short period, attributing it mainly to southern exposure and the suboptimal quality of the ETICS thermal insulation system forming the substrate. From a conservation science perspective, the southern orientation of the mural implies prolonged daily exposure to solar radiation, with cumulative light doses that are known to accelerate photochemical degradation and whitening phenomena in modern paint systems. Although the experimental design of this research did not include a controlled comparison between different orientations, the observed decay patterns highlight the critical role of sunlight exposure duration and orientation as key environmental variables. These observations reinforce the importance of integrating exposure mapping and orientation-specific risk assessment into both experimental studies and preventive conservation strategies for outdoor murals. Moreover, the artist also recalled that during the first day of the mural's execution, he had to fill and smooth several irregularities in the wall to obtain a sufficiently even surface for painting.

The artist was also interviewed regarding the thermographic analyses, which had revealed hidden shapes and underdrawings beneath the surface paint layers. He

confirmed that these corresponded to compositional changes and “revisions” made during the painting process, particularly in areas such as the woman’s face and the decorative ribbon. Furthermore, he validated the interpretation of spray-painted guide grids used to establish the correct proportions and perspective of the main compositional elements, most notably the central figure, Anna Maria Agnoletti, and the seven poppies symbolizing the seven partisans executed in Sesto Fiorentino in 1944. This symbolic reference is reinforced by the depiction of a carved stone on the left side of the mural, representing the historical memorial stone inscribed with their names.

The artist also emphasized the central significance of Anna Maria Agnoletti herself – archivist, director of the State Archives, and a key figure of the Italian Resistance, serving as head of Radio Co.Ra and contributor to the newspaper *La Rinascita* – as the conceptual and moral core of the mural. These aspects of her life and legacy are symbolically represented within the composition through visual references to the archive, the newspaper, and the radio.

Finally, the artist mentioned the inclusion of a small, personal tribute within the composition: a letter “R” with wings, painted on the left side of the mural. This element was added upon request from the school community to commemorate Ruben, a student of the institution who had passed away shortly before the mural’s realization.

11.2. Reflections on the Importance of Collaboration between Artists and Heritage Scientists

The collaboration established with SKIM throughout this research highlights the broader importance of interdisciplinary cooperation between heritage scientists, conservators, and contemporary mural artists. Modern outdoor wall paintings and street artworks pose complex conservation challenges due to the intrinsic variability and instability of the materials employed: often industrial, synthetic, and rapidly evolving formulations. In this context, the artist’s direct contribution

provides unique insights that are otherwise inaccessible through analytical investigation alone.

From a technical and material standpoint, collaboration with artists is essential for accurately identifying the materials used in mural production. Street art is typically created using a wide range of modern products, including spray paints, synthetic polymer-based paints (acrylic, alkyd, vinyl, styrenic, or polyurethane), and unconventional additives. Artists frequently experiment with different brands or mix commercial and industrial materials to achieve specific visual effects, often without considering their long-term durability. The information obtained through interviews and dialogue with artists is therefore crucial for reconstructing the material composition, understanding application techniques, and interpreting analytical results correctly. This approach has already proven fundamental for developing digital documentation systems such as the SCIMA – Scheda Conservativa Informatizzata Mural Art, which relies on collaboration with both artists and curators to ensure accurate recording of materials and techniques [21]. From a conservation science perspective, this exchange of knowledge directly supports the development of more sustainable and compatible conservation strategies. Understanding the artist's choice of paints, perception of their stability, and preferred visual effects informs laboratory testing on material ageing, weathering resistance, and compatibility with potential protective coatings. In particular, the information gathered during this research contributed to the formulation of sustainable hybrid coating aimed at protecting synthetic polymer-based murals. Future advancements in conservation treatments – such as UV-shielding, anti-graffiti, or water-repellent coatings – depend on similar collaborative frameworks that integrate scientific testing with artistic validation. The artist's perspective also plays a central role in assessing the aesthetic acceptability of protective systems, since even minimal changes in gloss, colour saturation, or texture can significantly alter the visual balance of a mural.

Beyond technical aspects, ethical and legal considerations further underscore the need for active artist involvement in the conservation of contemporary murals. Living artists retain moral and intellectual property rights over their creations and, in some cases, may choose not to intervene in the natural degradation of their work. In this regard, conservation decisions should respect the artist's intention, whether prioritizing the preservation of the physical material or the conceptual and procedural dimensions of the artwork. Several international projects, including CAPuS, GRAArt, and SUPERSTAR, have promoted the establishment of ethical frameworks and institutional guidelines that encourage a "share-for-care" approach, where artists, conservators, and scientists jointly define conservation priorities and methods [21,254].

Comparable initiatives have also been developed in the field of contemporary art conservation, where structured dialogue with living artists has become an established methodological practice rather than an occasional consultation. For instance, the Artists Documentation Program (ADP) at the Menil Collection systematically records artists' testimonies concerning materials, techniques, anticipated ageing behaviour, and acceptable degrees of change, thereby informing future conservation decisions. Similarly, international networks such as the International Network for the Conservation of Contemporary Art (INCCA) have institutionalised artist interview protocols as a fundamental component of preventive conservation strategies. These initiatives recognise that contemporary artworks frequently employ industrial or experimental materials whose long-term behaviour cannot be fully predicted through analytical investigation alone. Within this broader international framework, the integration of artist testimony is widely acknowledged as best practice in the preservation of modern and contemporary art [255]. Documenting artistic intent, material selection, and expectations regarding durability allows conservators to better define acceptable

thresholds of change, to design compatible interventions, and to develop realistic maintenance strategies.

The collaboration between artists, conservators, and heritage scientists should therefore be viewed not merely as an auxiliary component of conservation research, but as a core methodological principle. Integrating the artist's empirical knowledge with analytical and diagnostic expertise enables the design of more effective, ethically grounded, and sustainable conservation strategies.

In this specific project, the dialogue established with the artist not only provided invaluable insights into the materials, techniques, and conceptual aspects of the mural's creation but also aligned the research with contemporary participatory conservation models. Building upon this dialogue between art and science, a second collaborative initiative was established with the high school hosting the mural, with the dual aim of facilitating long-term monitoring and fostering educational engagement among students.

11.3. Collaboration with “Anna Maria Enriques Agnoletti” High School
From the moment the real case study of the “Anna Maria” mural painting was included in this research, it was considered essential to establish also a collaboration with the high school on whose façade the artwork was created. This partnership was motivated not only by the practical need to obtain permission for periodic in-situ analyses aimed at monitoring the state of conservation of the mural over time, but also by the educational opportunity to engage the students in the cultural and scientific value of the artwork.

In agreement with the artist, the idea of involving the students was considered particularly meaningful. As the artist himself stated, “I created it for them (the students), and I hope they will take care of it”. Moreover, since the school is a science-oriented high school (Liceo Scientifico), the collaboration offered a valuable opportunity to introduce young students to the interdisciplinary field of

science applied to art and heritage conservation, demonstrating how chemistry, physics, and materials science contribute to the preservation of contemporary artworks.

To this end, a structured School–University Collaboration Project (Percorsi per le Competenze Trasversali e l'Orientamento – PCTO) was designed and implemented in agreement with the school principal and teaching staff. The project was launched during the 2023–2024 academic year and successfully repeated in 2024–2025, involving approximately 20 students from fourth-year classes.

The educational program was organized into several stages:

- Introductory lectures – Students were first introduced to the principles of heritage science, with a focus on the role of scientific research in the study, conservation, and protection of cultural heritage.
- Laboratory activities at school – Practical sessions were conducted in the school's chemistry laboratory, where students prepared the chitosan–nanosilica hybrid formulation and created concrete mock-ups coated with different spray paint colours. During these sessions, the concept of green chemistry was presented, emphasizing the importance of sustainability in modern research and its applications not only in industrial fields such as packaging and materials science but also in the conservation of cultural heritage.
- On-site analysis at the mural – During the in-situ analytical campaigns, students had the opportunity to observe and understand the basic principles behind diagnostic techniques such as colorimetry, gloss measurement, and thermography.
- University laboratory sessions – The final phase of the project took place at the research laboratories of the Department of Chemistry, University of Florence. Here, students were introduced to advanced instrumentation

used throughout this doctoral research, including optical and electron microscopes, centrifuges, infrared spectrometers, and ageing chambers. For educational purposes, some experimental demonstrations were also performed, such as contact angle and capillary absorption measurements, and ATR–FTIR analysis of modern paints.

The project met with great enthusiasm and curiosity. For many students, it represented their first encounter with the interdisciplinary domain of science applied to cultural heritage, revealing how scientific methods can be integrated with art and conservation. This initiative not only fostered awareness and respect toward the mural itself but also served as a model for future educational collaborations aimed at promoting scientific culture, cultural awareness, and civic engagement through heritage conservation.

While the collaboration described here was necessarily limited by the timeframe of the doctoral project, it provided a valuable foundation for the development of actionable and transferable strategies. The outcomes of this experience suggest that structured collaborations between institutions, universities and research centers, artists, and conservators could be translated into long-term monitoring plans, including periodic visual inspections, basic colorimetric documentation, and environmental awareness activities conducted at the local level.

In this perspective, educational initiatives such as the PCTO program could evolve into lightweight preventive conservation frameworks, where trained students and school staff contribute to early detection of degradation phenomena and to informed decision-making regarding maintenance and conservation needs. Although the implementation of such plans extends beyond the scope and duration of this doctoral research, the present collaboration demonstrates their feasibility and highlights the potential role of participatory models in the sustainable management of contemporary public artworks.

Research outputs and future perspectives

The doctoral research presented in this thesis has generated a series of interrelated scientific outcomes that collectively advance the understanding of sustainable materials for the conservation of contemporary muralism. Across its eleven chapters, the study started from theoretical considerations to practical experimentation, progressively addressing the cultural, chemical, and environmental dimensions of Street Art preservation.

The investigation began with a critical review of the state of the art and of the cultural context of Street Art and contemporary muralism, outlining their emergence as forms of urban cultural heritage and the specific challenges they pose to conservation practice.

Through the study of chitosan and nanosilica, two complementary materials were identified as candidates capable of meeting these specific demands.

This conceptual foundation led to the formulation of a promising chitosan–nanosilica hybrid coating designed to combine the sustainability and film-forming capacity of a biopolymer with the mechanical reinforcement and stability of an inorganic phase.

The hybrid was synthesised and characterised through spectroscopic, microscopic, and physico-chemical analyses, which confirmed the homogeneity and stability of the organic–inorganic system and its resistance to accelerated ageing.

Subsequent experiments tested the coating on representative concrete mock-ups, including surfaces painted with both acrylic and alkyd spray paints.

These trials showed that the hybrid formulation adheres well to the painted layers, improves surface cohesion, and preserves both the visual appearance and the water vapour permeability of the substrate.

The results indicated that the coating mitigates colour alteration and degradation processes without affecting the aesthetic or physical properties of the artwork.

The environmental implications of the formulation were also assessed through a preliminary life-cycle analysis, which revealed that the main environmental burden arises from nanosilica production and laboratory energy use, while the use of chitosan substantially enhances its sustainability profile.

The second part of the work was enriched by the inclusion of a real case study that emerged during the doctoral research itself: the mural *Anna Maria*, created by the street artist SKIM.

This opportunity made it possible to develop a parallel investigation combining the monitoring of the real artwork under outdoor conditions with the laboratory study of thirteen alkyd-based spray paints selected from the artist's original palette.

The paints were analysed using a combination of spectroscopic and microscopic techniques to identify their binders, pigments, and inorganic fillers.

This study provided new insights into the composition and degradation behaviour of modern paints, offering a reference framework for interpreting the field observations collected on the mural.

The in-situ monitoring of “*Anna Maria*” over time revealed the influence of environmental factors and substrate interactions on the evolution of the artwork's surface, while laboratory accelerated artificial ageing of the same spray paints enabled a direct comparison with the mural's natural degradation, improving the interpretation of the molecular and chromatic changes observed in-situ.

The experimental research concluded with the application of the hybrid coating on ETICS mock-ups reproducing modern architectural substrates. This stage confirmed the compatibility and durability of the formulation under artificial ageing conditions, whose effects were found to be consistent with those observed on the real mural.

Such correspondence indirectly supports the potential applicability of the hybrid coating to large-scale mural surfaces of artistic and cultural significance, highlighting its promise as a sustainable protective system for contemporary muralism.

Furthermore, the comparison between the natural ageing of the Anna Maria mural and the artificial accelerated ageing of the ETICS mock-ups made it possible to define an ageing protocol that closely reproduces the degradation behaviour observed in the real case study.

Although this protocol may not be universally applicable to all mural contexts, it provides interesting methodological insights for the design of future accelerated ageing procedures aimed at the preliminary evaluation of restoration, protection, and conservation products for Street Art and contemporary muralism.

In conclusion, the final stage of the project documented its collaborative dimension, including the partnership with the street artist SKIM and the outreach activity with the Anna Maria Enriques Agnoletti High School. These collaborations fostered dialogue between scientific and artistic communities and contributed to the dissemination of conservation science through education and public engagement.

In addition to the optimisation of the chitosan–nanosilica hybrid coating, future research should increasingly focus on predicting its long-term applicability and performance on a multi-scale, to keep durability at the core of sustainable interventive conservation strategies. While direct extrapolation to a 10-year timescale remains challenging, chemistry and materials science can provide valuable tools to inform such predictions, particularly through the study of degradation kinetics, cumulative light dose effects, and the evolution of surface cohesion and optical properties under controlled ageing conditions. In this perspective, accelerated ageing protocols, when critically correlated with field monitoring data, may support scenario-based durability assessments rather than

absolute lifetime predictions, helping conservators to distinguish between acceptable material evolution and unacceptable loss of legibility or functionality. Such approaches would allow durability to be integrated into cleaning–coating strategies not as a fixed endpoint, but as a parameter informed by material behaviour, exposure conditions, and planned maintenance cycles.

Within this framework, the incorporation of functional additives with protective properties – such as UV-shielding nanoparticles, radical scavengers, or antioxidants – should be evaluated not only in terms of immediate performance, but also for their influence on long-term stability and ageing pathways. This shift from product-centred optimisation toward durability-informed decision-making has the potential to guide both applied conservation practice and fundamental research on new protective systems for contemporary muralism.

Symbols and abbreviations

AFM – Atomic Force Microscopy

ATR–FTIR – Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy

CA – Contact Angle

CIE – Commission Internationale de l'Éclairage

CIELAB – International Commission on Illumination colour space (L^* , a^* , b^*)

Chs–NS – Chitosan–Nanosilica hybrid coating

DCF – Decoherence Factor

EDX – Energy Dispersive X-ray Spectroscopy

ETICS – External Thermal Insulation Composite System

FE–SEM – Field Emission Scanning Electron Microscopy

FORS – Fibre Optic Reflectance Spectroscopy

FTIR – Fourier Transform Infrared Spectroscopy

GU – Gloss Units

HR – Heating Rate

IR – Infrared

LCA – Life Cycle Assessment

LWIR – Long-Wave Infrared

MWIR – Mid-Wave Infrared

NETD – Noise Equivalent Temperature Difference

RH – Relative Humidity

RT – Room Temperature

SEM – Scanning Electron Microscopy

TGA – Thermogravimetric Analysis

UV – Ultraviolet

VIS – Visible spectrum

XRD – X-ray Diffraction

List of Figures

Fig. 1 Molecular structure of chitosan.

Fig. 2 ATR-FTIR spectra of the coating films.

Fig. 3 DLS intensity-weighted plots measured for Chitosan (0.5% ww), Nanosilica (0.5% ww), and Chs/NS (0.25%/0.25% ww).

Fig. 4 SEM images of the Chs-based coating (a), and the Chs-NS film (b-d).

Fig. 5 ATR-FTIR spectra of Chs (left side) and Chs-NS films (right side) under different aging conditions: Chs and Chs-NS films subjected to photo-oxidation - A1 (a, b), hydrothermal aging (c,d) and thermal aging (e, f) respectively.

Fig. 7 SEM images of aged Chs-based films subject to photo-oxidative aging tests.

Fig. 7 SEM images of aged Chs-NS hybrid films subject to photo-oxidative aging tests.

Fig. 8 Colour variations after the application of the films on the mock-ups.

Fig. 9 Film properties measured on the mock-ups: contact angle (a.), water vapour permeability (b.), and capillary water absorption (c.).

Fig. 10 Colour variation (ΔE) after the three aging tests (A1: UV-vis radiation; A2: 60 °C, 80% RH; A3: 60 °C) of the untreated and Chs or Chs-NS-treated spray-painted mock-ups.

Fig. 11 White and blue acrylic paints mock-ups treated and untreated after 200 days of thermal aging (A3).

Fig. 12 Colour variation (ΔE) after the aging test conducted on the untreated and Chs or Chs-NS-treated concrete mock-ups, coloured with alkyd spray paints.

Fig. 13 ATR–FTIR spectrum of the black spray paint, showing the vibrational bands that characterise the binder.

Fig. 14 ATR–FTIR and Raman spectra of white spray paint (W).

Fig. 15 FORS spectrum of the white spray paint (W).

Fig. 16 ATR–FTIR and Raman spectra of yellow spray paint (Y).

Fig. 17 FORS spectrum of the yellow spray paint (Y).

Fig. 18 ATR–FTIR and Raman spectra of orange spray paint (O).

Fig. 19 FORS spectrum of the orange spray paint (O).

Fig. 20 ATR–FTIR and Raman spectra of red spray paint (R).

Fig. 21 FORS spectrum of the red spray paint (R).

Fig. 22 ATR-FTIR and Raman spectra of pink spray paint (P).

Fig. 23 FORS spectrum of the pink spray paint (P).

Fig. 24 ATR-FTIR and Raman spectra of Light Violet spray paint (LV).

Fig. 25 FORS spectra of the light and dark violet spray paints (LV, and DV respectively).

Fig. 26 ATR-FTIR and Raman spectra of light blue spray paint (LB).

Fig. 27 FORS spectrum of the light blue spray paint (LB).

Fig. 28 ATR-FTIR and Raman spectra of dark blue spray paint (DB).

Fig. 29 FORS spectrum of the dark blue spray paint (DB).

Fig. 30 ATR-FTIR and Raman spectra a: laser source 532 nm; b: 785 nm laser source) of green spray paint (G).

Fig. 31 FORS spectrum of the green spray paint (G).

Fig. 32 ATR-FTIR and Raman spectra of light brown spray paint (LBr).

Fig. 33 FORS spectrum of the light brown spray paint (LBr).

Fig. 34 ATR-FTIR and Raman spectra of dark brown spray paint (DBr).

Fig. 35 FORS spectrum of the dark brown spray paint (DBr)

Fig. 36 Overview of the lower register of the mural, with mapping of the colour and gloss measurement areas from 0 to 24 months after the artwork's completion (May 2023 – May 2025) - white lines. Detail of the mapping on the left (a), central (b), and right (c).

Fig. 37 Mural painting Anna Maria by SKIM. The upper image was taken immediately after the completion of the work in 2023, while the lower image was taken two years later. Alterations in several colours can be observed.

Fig. 38 Histogram showing the ΔE values calculated by comparing the colorimetric coordinates of each mapped colour between 24 and 0 months after the completion of the mural painting. The legend highlights the colours corresponding to those characterized.

Fig. 39 Temporal evolution of ΔE values for selected spray paint colours over the two-year monitoring period of the mural painting. Colours correspond to those analysed in Section XX, highlighting the differing rates of chromatic change across the palette.

Fig. 40 Selected details of the mural painting showing efflorescences (highlighted within circles) and cracks (indicated by arrows).

Fig. 41 ATR-FTIR spectrum of the inorganic substrate (S) beneath the mural painting.

Fig. 42 Sampling areas for the efflorescences E1, E2, and E3.

Fig. 43 ATR-FTIR spectrum of efflorescences E1-3, sampled from the mural painting.

Fig. 44 a) Thermal image of the entire mural (3 – 5 μm range, passive mode with solar irradiation, $\varepsilon=0.9$, camera-to-object distance=25 m, atmospheric temperature=20°C, relative humidity=50%); b) thermal image of a portion of the

mural obtained by the application of the Digital Detail Enhancement (DDE) filter, that enhances high spatial frequencies, to emphasize the faint shapes beneath the blue sky, highlighted with white arrows in a) and b). c) Photograph of the region of interest.

Fig. 45 Area where E2 was sampled: a) visible-light image; b) and c) thermographic outputs in the 3 – 5 μm and 8 – 14 μm ranges, respectively. The thermograms reveal colder regions associated with the efflorescences, indicating the presence of underlying moisture. Yellow arrows point to the black spray lines beneath the outer paint layer, used to outline the figures.

Fig. 46 (a, c) Visible and DDE MWIR thermal images from the lower right corner; (b, d) region of interest analysed in active modality and highlighted in a. and c. by green and pink squares, respectively. b. and d. were generated by subtracting a pre-heating frame. The blue, yellow and white arrows indicate thermal discontinuities that are likely to be related to panel joints, fixing plugs and a pentimento, respectively.

Fig. 47 Comparison of ATR–FTIR spectra of the white (W) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations

Fig. 48 Comparison of ATR–FTIR spectra of the black (Bk) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 49 Comparison of ATR–FTIR spectra of the yellow (Y) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 50 Comparison of ATR–FTIR spectra of the Orange (O) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 51 Comparison of ATR–FTIR spectra of the Red (R) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 52 Comparison of ATR–FTIR spectra of the Pink (P) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 53 Comparison of ATR–FTIR spectra of the Light Violet (LV) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 54 Comparison of ATR–FTIR spectra of the Dark Violet (DV) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 55 Comparison of ATR–FTIR spectra of the Light Blue (LB) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 56 Comparison of ATR–FTIR spectra of the Dark Blue (DB) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 57 Comparison of ATR–FTIR spectra of the Green (G) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 58 Comparison of ATR–FTIR spectra of the Light Brown (LBr) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 59 Comparison of ATR–FTIR spectra of the Dark Brown (DBr) spray paint before ageing (0 h) and after 650 hours of accelerated artificial ageing, highlighting molecular variations.

Fig. 60 ΔE_{00} values measured for the mock-ups after 650 h of accelerated artificial aging.

Fig. 61 Scatter plot comparing dL' (lightness) and dC' (chroma) values of homologous colours subjected to natural aging (NA) on the mural and accelerated artificial aging on mock-ups, highlighting similarities and divergences in colour variation trends.

Fig. 62 ΔE_{00} values recorded for each alkyd-based colour following the application of the Chs–NS hybrid coating on the ETICS mock-ups.

Fig. 63 Photographic documentation of the ETICS mock-ups after the application of the Chs–NS hybrid coating (applied on the right-hand half of each sample) and subsequent artificial ageing (650 h). The untreated left-hand side served as control. The boundary between treated and untreated areas is marked by a dashed line.

Fig. 64 Histogram comparing the ΔE_{00} values measured before and after artificial ageing (650 h) for both treated and untreated portions of the ETICS mock-ups. Lower ΔE_{00} values for the treated areas indicate the protective effect of the Chs–NS coating against colour variation under accelerated ageing conditions.

List of Tables

Table 1 Main natural sources of chitin and relevance for chitosan production.

Table 2 Chitosan, nanosilica, and Chs-NS hybrid concentrations.

Table 3 Possible interaction mechanisms between chitosan (Chs) and nanosilica (NS).

Table 4 Zeta-potential of Chs, NS and Chs-NS solutions.

Table 5 Spray paints provided by the artist and analysed in this study.

Table 6 Overview of the prepared concrete mock-ups, paint types, and the corresponding accelerated ageing protocols applied to evaluate colour stability.

Table 7 Steps and parameters set for the accelerated artificial ageing of spray paint mock-ups.

Table 8 Decohesion factors measured for the different concrete mock-ups.

Table 9 Spray paints provided by the artist and analysed in this study.

Table 10 ATR–FTIR signals of the major binder of all spray paints investigated (s: strong, m: medium, w: weak, sh: shoulder).

Table 11 Integrated multi-analytical identification of pigments, dyes and extenders in the 13 spray paints.

Table 12 Assignments of pigments, dyes, and inorganic fillers identified in the 13 spray paint colours through ATR–FTIR and Raman spectroscopy.

Table 13 Elemental composition of spray paint samples as determined by EDX analysis.

Table 14 Assignments of pigments, dyes, and inorganic fillers identified in the 13 spray paint colours through FORS analysis. Abbreviations: VC = valence–conduction band transition; MO = molecular orbital transition (π – π^*); CT = charge transfer transition; LF = ligand field transition.

Table 15 Summary of the composition of the spray paints, listing identified organic dyes, inorganic pigments, and fillers.

Table 16 Thermogravimetric analysis (TGA) of selected spray paints, providing an approximate estimation of the relative amounts of organic (binder, stabilizers, organic dyes) and inorganic (fillers, inorganic pigments) components.

Table 17 Summary of ΔE values for all monitored colours across the different measurement sessions, providing an overview of the mural's colour stability over the two-year monitoring period.

Table 18 Signals and assignments for the inorganic substrate (S) beneath the mural painting wall.

Table 19 Signals and assignments for the efflorescences (E1-3), sampled from the mural painting.

Table 20 Comparison of ΔE values from natural aging (NA) of the mural and accelerated artificial aging of mock-ups, showing the closest temporal correspondences between laboratory and real exposure, supporting the evaluation of the predictive validity of the accelerated ageing protocol.

Table 21 Lightness (dL') and chroma (dC') values of homologous colours subjected to natural aging (NA) on the mural and accelerated artificial aging on mock-ups.

Acknowledgements

I would first like to express my deepest gratitude to my supervisors, Prof. Rodorico Giorgi and Prof. Giovanna Poggi, for their constant guidance, support, and trust throughout this research. Their expertise and thoughtful advice have been invaluable to my professional and personal growth during these years.

At the beginning of my PhD journey, I strongly wished to structure the work in a way that would connect people with different backgrounds and expertise: not only to enrich the research itself, but also to broaden my own skills throughout this formative experience. As the following lines will show, I am truly satisfied with how this goal was achieved.

My sincere thanks go to Elisa Gualini and Serena Morrocchesi for their collaboration, constructive discussions, and for contributing to the development of this research on the “Anna Maria” mural, making it richer and more complete.

I am also very grateful to Dr Marcello Picollo and Dr Giovanni Bartolozzi (CNR–IFAC) for granting access to their instrumentation and for their assistance in planning and data interpretation of the analytical work.

I am deeply grateful to Emma Vannini, Dr Alice Dal Fovo, and Dr Raffaella Fontana (CNR–INO) for enthusiastically embracing the idea of integrating thermography among the diagnostic techniques applied to the mural painting, and for their continuous openness to discussion and thoughtful interpretation of the results.

I would like to thank Dr Daniela Iacopino, Martina Piletti, and Dr Alida Russo from the Tyndall National Institute for hosting me during my research stay abroad and for helping me refine my skills in Raman spectroscopy, SEM–EDX analysis.

I am sincerely grateful to Sarah Nunberg for her collaboration on the Life Cycle Assessment study and for her valuable insights as a conservator. Her advice on the observation and interpretation of the Anna Maria mural greatly contributed to linking the analytical and practical aspects of this research.

I would also like to express my sincere appreciation to Ervin Cinti (Torchiani Srl) and Dr Peter Greenwood (Nouryon) for their interest and enthusiasm towards this project. I am particularly grateful for their willingness to share their expertise on the properties and potential applications of nanosilica, and for providing the material used during the experimental phase of this research. Their openness to dialogue between industry and academia has been both professionally stimulating and practically invaluable. I also wish to thank Torchiani for inviting me to present this research as a speaker at the Paint & Coatings exhibition in Milan (Fiera Milano, October 2025), an opportunity that allowed me to engage with a broader industrial audience and reflect on the applied relevance of this work.

My heartfelt thanks go to the teachers and students of Liceo Scientifico “A. M. Enriques Agnoletti”, whose enthusiasm, curiosity, and participation gave great meaning to this project.

A special thank-you goes to Francesco Forconi – known as SKIM – who showed remarkable generosity and curiosity both during the preliminary phases of the study and during the final discussions, when we shared with him the results collected over two years. His contribution, including providing the original spray paints and sharing his insights, has been invaluable. As a conservation scientist, this experience confirmed once again how collaboration across different fields and perspectives can lead to more complete and professionally enriching outcomes.

I am deeply grateful to my PhD colleagues – Dr Francesca Porpora, Dr Daniela Porcu, Dr Corinne Suraci, and Irene Lunghi – for their friendship, support, and for sharing with me so many formative experiences: conferences, courses, seminars, and projects.

Thank you sincerely for your kindness, encouragement, and presence. You all truly made a difference, both in the most rewarding and in the most challenging moments.

My heartfelt gratitude goes to my family, especially my parents, for their constant support throughout my university years.

A special thought goes to my grandparents, who always cheered for me and celebrated every achievement, teaching me the value of study, curiosity, and dedication. Your example, sacrifices, and support have guided me all along this path.

I wish to thank Stefano, for his constant support, patience, and understanding, for believing in this project and in me even when it meant sacrifices and long periods apart. Your presence and encouragement have been a true source of balance and strength throughout this journey.

Finally, a very special acknowledgement goes to my brother, who is now pursuing his first year of a PhD in Civil Engineering.

Thank you for these months as “colleagues”: this shared experience has brought us even closer.

I gladly pass you the baton and wish you to enjoy every stage of your doctoral journey. It may not always be easy, but it will certainly be enriching and full of meaningful encounters, experiences, and achievements. Looking back, you will realise how valuable every step has been.

Publications related to the PhD project

Cianci. C.; Andriulo, F.; Giorgi, R.

Formulation of a new sustainable hybrid coating for the conservation of Street-Art: characterization and application. Prog. Org. Coat. 2025, (200, 109026), 9 citations.

Cianci C., Gualini, E., Morrocchesi, S., Giorgi, R.

Sustainable conservation for Street-art: preliminary research of a green coating and monitoring of the degradation of a case study.

Methodologies and Strategies for Cultural Heritage Protection and Conservation Against Climate Changes, Natural and Anthropic Risks,
Ed. Springer Nature, March 2026.

Side Activities during the PhD period

Teaching support activity: Teaching assistant for the laboratory sessions of the course “Chemistry for Cultural Heritage with Laboratory”, academic years 2022–2023, 2023–2024, 2024–2025.

Tutoring activity: Chemistry. Academic tutor, academic years 2022–2023, 2023–2024, 2024–2025.

Science communication: Science Communicator at OpenLab – University of Florence, 2023–2025.

Dissemination activity: Outreach related to the project “Conservation of Anna Maria Mural” at A.M. Enriques Agnoletti High School (Sesto Fiorentino), school years 2023–2024 and 2024–2025.

References

- [1] L. Dei, *Conservation Treatments: Cleaning, Consolidation and Protection, Nanoscience for the Conservation of Works of Art* (2013) 77–92. <https://doi.org/10.1039/9781849737630-00077>.
- [2] ICOMOS-ISCS, *Illustrated glossary on stone deterioration patterns*, 2008.
- [3] P.R. Austin, C.J. Brine, J.E. Castle, J.P. Zikakis, Chitin: New facets of research, *Science* 212 (1981) 749–753. <https://doi.org/10.1126/SCIENCE.7221561>.
- [4] J.L. Shamshina, P. Berton, R.D. Rogers, *Advances in Functional Chitin Materials: A Review*, *ACS Sustain. Chem. Eng.* 7 (2019) 6444–6457. <https://doi.org/10.1021/ACSSUSCHEMENG.8B06372>.
- [5] M. Bisht, I.P.E. Macário, M.C. Neves, J.L. Pereira, S. Pandey, R.D. Rogers, J.A.P. Coutinho, S.P.M. Ventura, *Enhanced Dissolution of Chitin Using Acidic Deep Eutectic Solvents: A Sustainable and Simple Approach to Extract Chitin from Crayfish shell Wastes as Alternative Feedstocks*, *ACS Sustain. Chem. Eng.* 9 (2021) 16073–16081. <https://doi.org/10.1021/ACSSUSCHEMENG.1C04255>.
- [6] R. Devi, R. Dhamodharan, *Pretreatment in Hot Glycerol for Facile and Green Separation of Chitin from Prawn Shell Waste*, *ACS Sustain. Chem. Eng.* 6 (2017) 846–853. <https://doi.org/10.1021/ACSSUSCHEMENG.7B03195>.
- [7] I. Aranaz, A.R. Alcántara, M.C. Civera, C. Arias, B. Elorza, A.H. Caballero, N. Acosta, H. Velasco, D. Mecerreyes, R. Antonio, B. Gimeno, A. María Díez-Pascual, V.C. Moreno, A. Serra, *Chitosan: An Overview of Its Properties and Applications*, *Polymers* 2021, Vol. 13, Page 3256 13 (2021) 3256. <https://doi.org/10.3390/POLYM13193256>.
- [8] J. La Nasa, B. Campanella, F. Sabatini, A. Rava, W. Shank, P. Lucero-Gomez, D. De Luca, S. Legnaioli, V. Palleschi, M.P. Colombini, I. Degano, F. Modugno, *60 years of street art: A comparative study of the artists' materials through spectroscopic and mass spectrometric approaches*, *J. Cult. Herit.* 48 (2021) 129–140. <https://doi.org/10.1016/j.culher.2020.11.016>.
- [9] L. Pagnin, N. Guarnieri, F.C. Izzo, S. Goidanich, L. Toniolo, *Protecting Street Art from Outdoor Environmental Threats: What Are the*

- Challenges?, Coatings 13 (2023) 2044.
<https://doi.org/10.3390/coatings13122044>.
- [10] P. Mezzadri, Contemporary murals in the street and urban art field: Critical reflections between preventive conservation and restoration of public art, *Heritage* 4 (2021) 2515–2525. <https://doi.org/10.3390/heritage4030142>.
- [11] D. Dogheria, *Street Art, eDossier*, Giunti Editore, Firenze, 2014.
- [12] D. Cimino, R. Lamuraglia, I. Saccani, M. Berzioli, F.C. Izzo, Assessing the (In)Stability of Urban Art Paints: From Real Case Studies to Laboratory Investigations of Degradation Processes and Preservation Possibilities, *Heritage* 5 (2022) 581–609. <https://doi.org/10.3390/heritage5020033>.
- [13] E.M. Alonso-Villar, T. Rivas, J.S. Pozo-Antonio, G. Pellis, D. Sclarone, Efficacy of Colour Protectors in Urban Art Paintings under Different Conditions: From a Real Mural to the Laboratory, *Heritage* 6 (2023) 3475–3498. <https://doi.org/10.3390/heritage6040185>.
- [14] V. Gomes, A. Dionísio, J.S. Pozo-Antonio, Conservation strategies against graffiti vandalism on Cultural Heritage stones: Protective coatings and cleaning methods, *Prog. Org. Coat.* 113 (2017) 90–109. <https://doi.org/10.1016/j.porgcoat.2017.08.010>.
- [15] L. MacDowall, R. Schachter, *World Atlas of Street Art and Graffiti*, New Haven : Yale University Press, 2013.
- [16] L. Ciancabilla, L'Italia sui muri: nuove forme di scrittura-pittura fra vandalismo grafico e Graffiti-Writing, in: C. D'Achille, Ciociola; C. (Eds.), *L'italiano tra parola e immagine: iscrizioni, illustrazioni, fumetti*, GoWare, 2020: pp. 253–263. <https://cris.unibo.it/handle/11585/780973> (accessed October 1, 2025).
- [17] E.C.L. Rigante, F. Modugno, J. La Nasa, S. Pizzimenti, T.R.I. Cataldi, C.D. Calvano, Unveiling the Secret Chemistry of Street Art by a Multitechnique Approach, *Chempluschem* (2025). <https://doi.org/10.1002/cplu.202500059>.
- [18] V. Marazioti, A.M. Douvas, F. Katsaros, P. Koralli, C. Chochos, V.G. Gregoriou, S. Boyatzis, Y. Facorellis, Chemical characterisation of artists' spray-paints: A diagnostic tool for urban art conservation, *Spectrochim.*

Acta A Mol. Biomol. Spectrosc. 291 (2023).
<https://doi.org/10.1016/j.saa.2023.122375>.

- [19] Y. Zhang, F. Zenucchini, C. Ricci, P. Croveri, D. Scalarone, Analytical Evaluation of Laser Cleaning Effectiveness in the Context of Contemporary Muralism, *Applied Sciences (Switzerland)* 14 (2024).
<https://doi.org/10.3390/app14114799>.
- [20] T. Rivas, E.M. Alonso-Villar, J.S. Pozo-Antonio, Forms and factors of deterioration of urban art murals under humid temperate climate; influence of environment and material properties, *Eur. Phys. J. Plus* 137 (2022).
<https://doi.org/10.1140/EPJP/S13360-022-03473-1>.
- [21] L. Rivaroli, P. Moretti, A. Caricchio, A. Macchia, Mural art conservation data recording (Scima): The graart project, *Heritage* 4 (2021) 4222–4232.
<https://doi.org/10.3390/heritage4040232>.
- [22] G. Pellis, M. Bertasa, C. Ricci, A. Scarcella, P. Croveri, T. Poli, D. Scalarone, A multi-analytical approach for precise identification of alkyd spray paints and for a better understanding of their ageing behaviour in graffiti and urban artworks, *J. Anal. Appl. Pyrolysis* 165 (2022).
<https://doi.org/10.1016/j.jaap.2022.105576>.
- [23] J. Dickens, A. Rava, M.P. Colombini, M. Picollo, W. Shank, Keith Haring in Pisa and Melbourne: controversy and conservation, *Taylor & FrancisJ Dickens, A Rava, MP Colombini, M Picollo, W ShankStudies in Conservation*, 2016•Taylor & Francis 61 (2016) 29–37.
<https://doi.org/10.1080/00393630.2016.1193691>.
- [24] C. Cucci, G. Bartolozzi, M. De Vita, V. Marchiafava, M. Picollo, F. Casadio, The colors of Keith Haring: A spectroscopic study on the materials of the mural painting Tuttomondo and on reference contemporary outdoor paints, *Appl. Spectrosc.* 70 (2016) 186–196.
<https://doi.org/10.1177/0003702815615346>.
- [25] E. Hamilton, K. Dodson, S. Barack, K. Moomaw, Artist intention and the conservation of contemporary art, *AIC Objects Specialty Group Postprints* 22 (2015). www.conservation-us.org (accessed February 4, 2026).
- [26] R. Llamas-Pacheco, Some Theory for the Conservation of Contemporary Art, (2020). <https://doi.org/10.1080/00393630.2020.1733790>.

- [27] Project: Artists Documentation Program (ADP) | INCCA, (n.d.). <https://incca.org/project-artists-documentation-program-adp> (accessed February 4, 2026).
- [28] N. Guarnieri, A. Di Benedetto, D. Comelli, F. Mirani, D. Dellasega, L. Pagnin, S. Goidanich, L. Toniolo, Rapid chromatic alteration of Street Art: Mechanisms of deterioration of the painting materials of the 20 years of Freedom and Democracy mural, *Dyes and Pigments* 239 (2025). <https://doi.org/10.1016/j.dyepig.2025.112733>.
- [29] F. Sabatini, F. Albertin, B. Doherty, L. Monico, F. Rosi, D. Buti, A. Romani, A. Pecci, N. Abate, M. Sileo, A.M. Amodio, N. Masini, S. Pizzimenti, I. Degano, F. Modugno, B. Campanella, S. Legnaioli, L. Cartechini, Unveiling street art: A multimodal and multitechnique approach for analyzing and mapping painting materials on large murals, *Proceedings of the National Academy of Sciences* 122 (2025) e2504918122. <https://doi.org/10.1073/PNAS.2504918122>.
- [30] N. Guarnieri, L. Pagnin, L. Berti, S. Goidanich, D. Gulotta, F.C. Izzo, L. Toniolo, Preserving the contemporary mural “Musica Popolare” by Orticanoodles in Milan, Italy: Deterioration processes and protection performance of commercial coatings, *J. Cult. Herit.* 75 (2025) 326–332. <https://doi.org/10.1016/J.CULHER.2025.08.004>.
- [31] P. Sanmartín, J.S. Pozo-Antonio, Weathering of graffiti spray paint on building stones exposed to different types of UV radiation, *Constr. Build. Mater.* 236 (2020). <https://doi.org/10.1016/j.conbuildmat.2019.117736>.
- [32] F. Sabatini, J. La Nasa, I. Degano, B. Campanella, S. Legnaioli, I. Saccani, F. Modugno, Fluorescent Paints in Contemporary Murals: A Case Study, *Heritage* 6 (2023) 5689–5699. <https://doi.org/10.3390/HERITAGE6080299/S1>.
- [33] The ABC method a risk management approach to the preservation of cultural heritage, Canadian Conservation Institute = Institut canadien de conservation, 2016.
- [34] L. Pagnin, S. Goidanich, F.C. Izzo, Y. Zhang, D. Scalarone, L. Toniolo, Compatibility and Efficacy Evaluations of Organic Protective Coatings for Contemporary Muralism, *Coatings* 2025, Vol. 15, Page 166 15 (2025) 166. <https://doi.org/10.3390/COATINGS15020166>.

- [35] G. Germinario, I.D. van der Werf, L. Sabbatini, Chemical characterisation of spray paints by a multi-analytical (Py/GC–MS, FTIR, μ -Raman) approach, *Microchemical Journal* 124 (2016) 929–939. <https://doi.org/10.1016/j.microc.2015.04.016>.
- [36] World Heritage Centre - Managing Disaster Risks for World Heritage, (n.d.). <https://whc.unesco.org/en/managing-disaster-risks/> (accessed February 4, 2026).
- [37] C. Antomarchi, S. Michalski, Z. Aslan, A. Sabik, C. Malapitan, M. Foulquié, R. José Luiz Pedersoli Jr, CO-CREATION Concept and text José Luiz Pedersoli Jr., Scientia Pro Cultura ICCROM-International Centre for the Study of the Preservation and Restoration of Cultural Property Information design and visualisation, (n.d.).
- [38] Light, ultraviolet and infrared - Canada.ca, (n.d.). <https://www.canada.ca/en/conservation-institute/services/agents-deterioration/light.html> (accessed February 4, 2026).
- [39] International Commission on Illumination, Control of damage to museum objects by optical radiation, (2004) 30. <https://search.worldcat.org/title/55627950> (accessed February 4, 2026).
- [40] R. Giorgi, M. Baglioni, P. Baglioni, Nanofluids and chemical highly retentive hydrogels for controlled and selective removal of overpaintings and undesired graffiti from street art, *Anal. Bioanal. Chem.* 409 (2017) 3707–3712. <https://doi.org/10.1007/s00216-017-0357-z>.
- [41] M. Baglioni, G. Poggi, Y. Jaidar Benavides, F. Martínez Camacho, R. Giorgi, P. Baglioni, Nanostructured fluids for the removal of graffiti – A survey on 17 commercial spray-can paints, *J. Cult. Herit.* 34 (2018) 218–226. <https://doi.org/10.1016/j.culher.2018.04.016>.
- [42] O. Chiantore, M. Lazzari, Photo-oxidative stability of paraloid acrylic protective polymers, *Polymer (Guildf)*. 42 (2001) 17–27. [https://doi.org/10.1016/S0032-3861\(00\)00327-X](https://doi.org/10.1016/S0032-3861(00)00327-X).
- [43] P.M. Carmona-Quiroga, R.M.J. Jacobs, S. Martínez-Ramírez, H.A. Viles, Durability of anti-graffiti coatings on stone: natural vs accelerated weathering, *Journals.Plos.OrgPM Carmona-Quiroga, RMJ Jacobs, S Martínez-Ramírez, HA VilesPLOS One*, 2017•journals.Plos.Org 12 (2017). <https://doi.org/10.1371/JOURNAL.PONE.0172347>.

- [44] D. Jiménez-Desmond, J.S. Pozo-Antonio, A. Arizzi, Outdoor durability of nano-sized silica-based chromatic reintegrations. Influence of exposure conditions and pigment composition, *Dyes and Pigments* 235 (2025). <https://doi.org/10.1016/j.dyepig.2025.112651>.
- [45] E.M. Alonso-Villar, T. Rivas, J.S. Pozo-Antonio, Resistance to artificial daylight of paints used in urban artworks. Influence of paint composition and substrate, *Prog. Org. Coat.* 154 (2021). <https://doi.org/10.1016/j.porgcoat.2021.106180>.
- [46] V. Marazioti, A.M. Douvas, E.C. Vouvoudi, D. Bikiaris, K. Papadokostaki, D. Nioras, E. Gogolides, S. Orfanoudakis, T. Stergiopoulos, S. Boyatzis, Y. Facorellis, The Condition of Contemporary Murals in Sun-Exposed Urban Environments: A Model Study Based on Spray-Painted Mock-Ups and Simulated Light Ageing, *Heritage* 7 (2024) 3932–3959. <https://doi.org/10.3390/heritage7080186>.
- [47] O. Chiantore, L. Trossarelli, M. Lazzari, Photooxidative degradation of acrylic and methacrylic polymers, *Polymer (Guildf)*. 41 (2000) 1657–1668. [https://doi.org/10.1016/S0032-3861\(99\)00349-3](https://doi.org/10.1016/S0032-3861(99)00349-3).
- [48] C. Brandi, *Teoria del restauro*, 1913.
- [49] United Nations General Assembly, Transforming our world: the 2030 Agenda for Sustainable Development., 2015. <https://digitallibrary.un.org/record/1654217?v=pdf> (accessed January 31, 2026).
- [50] F.A. Vicente, M. Huš, B. Likozar, U. Novak, Chitin Deacetylation Using Deep Eutectic Solvents: Ab Initio-Supported Process Optimization, *ACS Sustain. Chem. Eng.* 9 (2021) 3874–3886. <https://doi.org/10.1021/acssuschemeng.0c08976>.
- [51] M. Ul-Islam, K.F. Alabbosh, S. Manan, S. Khan, F. Ahmad, M.W. Ullah, Chitosan-based nanostructured biomaterials: Synthesis, properties, and biomedical applications, *Advanced Industrial and Engineering Polymer Research* 7 (2024) 79–99. <https://doi.org/10.1016/j.aiepr.2023.07.002>.
- [52] C. Coquery, C. Negrell, N. Caussé, N. Pébère, G. David, Synthesis of new high molecular weight phosphorylated chitosans for improving corrosion protection, *Pure and Applied Chemistry* 91 (2019) 509–521.

<https://doi.org/10.1515/PAC-2018-0509/MACHINEREADABLECITATION/RIS>.

- [53] K. Ding, Y. Wang, H. Wang, L. Yuan, M. Tan, X. Shi, Z. Lyu, Y. Liu, H. Chen, 6-O-Sulfated Chitosan Promoting the Neural Differentiation of Mouse Embryonic Stem Cells, *ACS Appl. Mater. Interfaces* 6 (2014) 20043–20050. <https://doi.org/10.1021/AM505628G>.
- [54] K.L.B. Chang, M.C. Tai, F.H. Cheng, Kinetics and Products of the Degradation of Chitosan by Hydrogen Peroxide, *J. Agric. Food Chem.* 49 (2001) 4845–4851. <https://doi.org/10.1021/JF001469G>.
- [55] M.R. Kasaai, J. Arul, G. Charlet, Fragmentation of chitosan by ultrasonic irradiation, *Ultrason. Sonochem.* 15 (2008) 1001–1008. <https://doi.org/10.1016/J.ULTSONCH.2008.04.005>.
- [56] T. Wu, S. Zivanovic, D.G. Hayes, J. Weiss, Efficient Reduction of Chitosan Molecular Weight by High-Intensity Ultrasound: Underlying Mechanism and Effect of Process Parameters, *J. Agric. Food Chem.* 56 (2008) 5112–5119. <https://doi.org/10.1021/JF073136Q>.
- [57] N. Thadathil, S.P. Velappan, Recent developments in chitosanase research and its biotechnological applications: A review, *Food Chem.* 150 (2014) 392–399. <https://doi.org/10.1016/J.FOODCHEM.2013.10.083>.
- [58] J.C. Cabrera, P. Van Cutsem, Preparation of chitooligosaccharides with degree of polymerization higher than 6 by acid or enzymatic degradation of chitosan, *Biochem. Eng. J.* 25 (2005) 165–172. <https://doi.org/10.1016/J.BEJ.2005.04.025>.
- [59] K.M. Vårum, H.K. Holme, M. Izume, B.T. Stokke, O. Smidsrød, Determination of enzymatic hydrolysis specificity of partially N-acetylated chitosans, *Biochimica et Biophysica Acta (BBA) - General Subjects* 1291 (1996) 5–15. [https://doi.org/10.1016/0304-4165\(96\)00038-4](https://doi.org/10.1016/0304-4165(96)00038-4).
- [60] M.C. Chen, S.F. Huang, K.Y. Lai, M.H. Ling, Fully embeddable chitosan microneedles as a sustained release depot for intradermal vaccination, *Biomaterials* 34 (2013) 3077–3086. <https://doi.org/10.1016/J.BIOMATERIALS.2012.12.041>.

- [61] M. Dawoud, Chitosan coated solid lipid nanoparticles as promising carriers for docetaxel, *J. Drug Deliv. Sci. Technol.* 62 (2021) 102409. <https://doi.org/10.1016/J.JDDST.2021.102409>.
- [62] A.H. Salama, H. Elmotasem, A.A.A. Salama, Nanotechnology based blended chitosan-pectin hybrid for safe and efficient consolidative antiemetic and neuro-protective effect of meclizine hydrochloride in chemotherapy induced emesis, *Int. J. Pharm.* 584 (2020) 119411. <https://doi.org/10.1016/J.IJPHARM.2020.119411>.
- [63] B. Pilicheva, Y. Uzunova, I. Bodurov, A. Viraneva, G. Exner, S. Sotirov, T. Yovcheva, M. Marudova, Layer-by-layer self-assembly films for buccal drug delivery: The effect of polymer cross-linking, *J. Drug Deliv. Sci. Technol.* 59 (2020) 101897. <https://doi.org/10.1016/J.JDDST.2020.101897>.
- [64] N. Saracogullari, D. Gundogdu, F.N. Ozdemir, Y. Soyer, I. Erel-Goktepe, The effect of polyacid on the physical and biological properties of chitosan based layer-by-layer films, *Colloids Surf. A Physicochem. Eng. Asp.* 617 (2021) 126313. <https://doi.org/10.1016/J.COLSURFA.2021.126313>.
- [65] A. Mohebbali, M. Abdouss, Layered biocompatible pH-responsive antibacterial composite film based on HNT/PLGA/chitosan for controlled release of minocycline as burn wound dressing, *Int. J. Biol. Macromol.* 164 (2020) 4193–4204. <https://doi.org/10.1016/J.IJBIOMAC.2020.09.004>.
- [66] P.T.S. Kumar, V.K. Lakshmanan, R. Biswas, S. V. Nair, R. Jayakumar, Synthesis and biological evaluation of chitin hydrogel/nano ZnO composite bandage as antibacterial wound dressing, *J. Biomed. Nanotechnol.* 8 (2012) 891–900. <https://doi.org/10.1166/jbn.2012.1461>.
- [67] T. Moniz, S.A. Costa Lima, S. Reis, Marine polymeric microneedles for transdermal drug delivery, *Carbohydr. Polym.* 266 (2021) 118098. <https://doi.org/10.1016/J.CARBPOL.2021.118098>.
- [68] D. Raafat, H.G. Sahl, Chitosan and its antimicrobial potential--a critical literature survey, *Microb. Biotechnol.* 2 (2009) 186–201. <https://doi.org/10.1111/J.1751-7915.2008.00080.X>.
- [69] I.M. Helander, E.L. Nurmiaho-Lassila, R. Ahvenainen, J. Rhoades, S. Roller, Chitosan disrupts the barrier properties of the outer membrane of

- Gram-negative bacteria, *Int. J. Food Microbiol.* 71 (2001) 235–244. [https://doi.org/10.1016/S0168-1605\(01\)00609-2](https://doi.org/10.1016/S0168-1605(01)00609-2).
- [70] I. Galván Márquez, J. Akuaku, I. Cruz, J. Cheetham, A. Golshani, M.L. Smith, Disruption of protein synthesis as antifungal mode of action by chitosan, *Int. J. Food Microbiol.* 164 (2013) 108–112. <https://doi.org/10.1016/J.IJFOODMICRO.2013.03.025>.
- [71] R.C. Goy, D. De Britto, O.B.G. Assis, A review of the antimicrobial activity of chitosan, *Polimeros* 19 (2009) 241–247. <https://doi.org/10.1590/S0104-14282009000300013>.
- [72] E.I. Rabea, M.E.T. Badawy, C. V. Stevens, G. Smagghe, W. Steurbaut, Chitosan as antimicrobial agent: applications and mode of action, *Biomacromolecules* 4 (2003) 1457–1465. <https://doi.org/10.1021/BM034130M>.
- [73] M. Kong, X.G. Chen, K. Xing, H.J. Park, Antimicrobial properties of chitosan and mode of action: A state of the art review, *Int. J. Food Microbiol.* 144 (2010) 51–63. <https://doi.org/10.1016/J.IJFOODMICRO.2010.09.012>.
- [74] K. Xing, X.G. Chen, C.S. Liu, D.S. Cha, H.J. Park, Oleoyl-chitosan nanoparticles inhibits *Escherichia coli* and *Staphylococcus aureus* by damaging the cell membrane and putative binding to extracellular or intracellular targets, *Int. J. Food Microbiol.* 132 (2009) 127–133. <https://doi.org/10.1016/J.IJFOODMICRO.2009.04.013>.
- [75] K.R. Krishnapriya, M. Kandaswamy, Synthesis and characterization of a crosslinked chitosan derivative with a complexing agent and its adsorption studies toward metal(II) ions, *Carbohydr. Res.* 344 (2009) 1632–1638. <https://doi.org/10.1016/J.CARRES.2009.05.025>.
- [76] P. Feng, Y. Luo, C. Ke, H. Qiu, W. Wang, Y. Zhu, R. Hou, L. Xu, S. Wu, Chitosan-Based Functional Materials for Skin Wound Repair: Mechanisms and Applications, *Front. Bioeng. Biotechnol.* 9 (2021) 650598. <https://doi.org/10.3389/FBIOE.2021.650598/BIBTEX>.
- [77] H. Mellegård, S.P. Strand, B.E. Christensen, P.E. Granum, S.P. Hardy, Antibacterial activity of chemically defined chitosans: Influence of molecular weight, degree of acetylation and test organism, *Int. J. Food*

Microbiol. 148 (2011) 48–54.
<https://doi.org/10.1016/j.ijfoodmicro.2011.04.023>.

- [78] I. Younes, S. Sellimi, M. Rinaudo, K. Jellouli, M. Nasri, Influence of acetylation degree and molecular weight of homogeneous chitosans on antibacterial and antifungal activities, *Int. J. Food Microbiol.* 185 (2014) 57–63. <https://doi.org/10.1016/j.ijfoodmicro.2014.04.029>.
- [79] Sánchez, M. Mengíbar, G. Rivera-Rodríguez, B. Moerchbacher, N. Acosta, A. Heras, The effect of preparation processes on the physicochemical characteristics and antibacterial activity of chitooligosaccharides, *Carbohydr. Polym.* 157 (2017) 251–257. <https://doi.org/10.1016/J.CARBPOL.2016.09.055>.
- [80] S. Manan, M.W. Ullah, M. Ul-Islam, Z. Shi, M. Gauthier, G. Yang, Bacterial cellulose: Molecular regulation of biosynthesis, supramolecular assembly, and tailored structural and functional properties, *Prog. Mater. Sci.* 129 (2022) 100972. <https://doi.org/10.1016/J.PMATSCI.2022.100972>.
- [81] M. Rinaudo, Chitin and chitosan: Properties and applications, *Prog. Polym. Sci.* 31 (2006) 603–632. <https://doi.org/10.1016/J.PROGPOLYMSCI.2006.06.001>.
- [82] Y.A. Alli, S. Adewuyi, B.S. Bada, S. Thomas, H. Anuar, Quaternary Trimethyl Chitosan Chloride Capped Bismuth Nanoparticles with Positive Surface Charges: Catalytic and Antibacterial Activities, *J. Clust. Sci.* 33 (2022) 2311–2324. <https://doi.org/10.1007/S10876-021-02156-8/FIGURES/9>.
- [83] S. Torkaman, H. Rahmani, A. Ashori, S.H.M. Najafi, Modification of chitosan using amino acids for wound healing purposes: A review, *Carbohydr. Polym.* 258 (2021) 117675. <https://doi.org/10.1016/J.CARBPOL.2021.117675>.
- [84] J. Bian, A. Wang, Y. Sun, Q. Zhu, Adsorption of nitrate from water by core-shell chitosan wrinkled microspheres @LDH composite: Electrostatic interaction, hydrogen bonding and surface complexation, *Appl. Clay Sci.* 225 (2022) 106550. <https://doi.org/10.1016/J.CLAY.2022.106550>.
- [85] T. Chutimasakul, P. Na Nakhonpanom, W. Tirdtrakool, A. Intanin, T. Bunchuay, R. Chantiwas, J. Tantirungrotechai, Uniform Cu/chitosan beads

- as a green and reusable catalyst for facile synthesis of imines via oxidative coupling reaction, *RSC Adv.* 10 (2020) 21009–21018. <https://doi.org/10.1039/D0RA03884A>.
- [86] M.Y. Wong, B.A. Horri, B. Salamatina, Grafted copolymerized chitosan and its applications as a green biopolymer, *Biopolymer Grafting: Applications* (2017) 285–333. <https://doi.org/10.1016/B978-0-12-810462-0.00008-9>.
- [87] F. Croisier, C. Jérôme, Chitosan-based biomaterials for tissue engineering, *Eur. Polym. J.* 49 (2013) 780–792. <https://doi.org/10.1016/J.EURPOLYMJ.2012.12.009>.
- [88] J. Wang, C. Chen, Chitosan-based biosorbents: Modification and application for biosorption of heavy metals and radionuclides, *Bioresour. Technol.* 160 (2014) 129–141. <https://doi.org/10.1016/j.biortech.2013.12.110>.
- [89] S. Sundararaman, P. Deivasigamani, N. Gopakumaran, J.A. Kumar, J.S. Balasubramaniam, N.M. Kumar, Amalgamation and application of nano chitosan cross-linked with fish scales based activated carbon as an adsorbent for the removal of reactive dye (RB9), *IET Nanobiotechnol.* 14 (2020) 289–299. <https://doi.org/10.1049/IET-NBT.2019.0302>.
- [90] N. Aibani, R. Rai, P. Patel, G. Cuddihy, E.K. Wasan, Chitosan Nanoparticles at the Biological Interface: Implications for Drug Delivery, *Pharmaceutics* 2021, Vol. 13, Page 1686 13 (2021) 1686. <https://doi.org/10.3390/PHARMACEUTICS13101686>.
- [91] X. Li, X. Ji, K. Chen, X. Yuan, Z. Lei, M.W. Ullah, J. Xiao, G. Yang, Preparation and evaluation of ion-exchange porous polyvinyl alcohol microspheres as a potential drug delivery embolization system, *Materials Science and Engineering: C* 121 (2021) 111889. <https://doi.org/10.1016/J.MSEC.2021.111889>.
- [92] X. Li, X. Ji, K. Chen, M.W. Ullah, X. Yuan, Z. Lei, J. Cao, J. Xiao, G. Yang, Development of finasteride/PHBV@polyvinyl alcohol/chitosan reservoir-type microspheres as a potential embolic agent: from in vitro evaluation to animal study, *Biomater. Sci.* 8 (2020) 2797–2813. <https://doi.org/10.1039/C9BM01775E>.

- [93] C. Lim, D.S. Hwang, D.W. Lee, Intermolecular interactions of chitosan: Degree of acetylation and molecular weight, *Carbohydr. Polym.* 259 (2021) 117782. <https://doi.org/10.1016/J.CARBPOL.2021.117782>.
- [94] A.A. Kadam, B. Sharma, S.K. Shinde, G.S. Ghodake, G.D. Saratale, R.G. Saratale, D.Y. Kim, J.S. Sung, Thiolation of Chitosan Loaded over Super-Magnetic Halloysite Nanotubes for Enhanced Laccase Immobilization, *Nanomaterials* 2020, Vol. 10, Page 2560 10 (2020) 2560. <https://doi.org/10.3390/NANO10122560>.
- [95] R.F. Bombaldi de Souza, F.C. Bombaldi de Souza, A. Thorpe, D. Mantovani, K.C. Popat, Â.M. Moraes, Phosphorylation of chitosan to improve osteoinduction of chitosan/xanthan-based scaffolds for periosteal tissue engineering, *Int. J. Biol. Macromol.* 143 (2020) 619–632. <https://doi.org/10.1016/j.ijbiomac.2019.12.004>.
- [96] G. Lohiya, D.S. Katti, Carboxylated chitosan-mediated improved efficacy of mesoporous silica nanoparticle-based targeted drug delivery system for breast cancer therapy, *Carbohydr. Polym.* 277 (2022) 118822. <https://doi.org/10.1016/J.CARBPOL.2021.118822>.
- [97] W. Zhang, F. Gao, C. Cheng, L. Lu, H. Du, Y. Li, W. Hou, Y. Yang, X. Wang, Evaluation of sulfonated oxidized chitosan antifungal activity against *Fusarium graminearum*, *J. Biomater. Sci. Polym. Ed.* 33 (2022) 1495–1510. <https://doi.org/10.1080/09205063.2022.2068942>.
- [98] N.A. Negm, H.H.H. Hefni, A.A.A. Abd-Elaal, E.A. Badr, M.T.H. Abou Kana, Advancement on modification of chitosan biopolymer and its potential applications, *Int. J. Biol. Macromol.* 152 (2020) 681–702. <https://doi.org/10.1016/J.IJBIOMAC.2020.02.196>.
- [99] W. Gonciarz, E. Balcerczak, M. Brzeziński, A. Jeleń, A.J. Pietrzyk-Brzezińska, V.H.B. Narayanan, M. Chmiela, Chitosan-based formulations for therapeutic applications. A recent overview, *J. Biomed. Sci.* 32 (2025). <https://doi.org/10.1186/S12929-025-01161-7>.
- [100] M.I. Oliveira, S.G. Santos, M.J. Oliveira, A.L. Torres, M.A. Barbosa, Chitosan drives anti-inflammatory macrophage polarisation and pro-inflammatory dendritic cell stimulation, *Eur. Cell. Mater.* 24 (2012) 136–153. <https://doi.org/10.22203/ECM.V024A10>.

- [101] N. Duceppe, M. Tabrizian, Advances in using chitosan-based nanoparticles for in vitro and in vivo drug and gene delivery, *Expert Opin. Drug Deliv.* 7 (2010) 1191–1207. <https://doi.org/10.1517/17425247.2010.514604>.
- [102] E. Ardelean, D. Asandei, G. Asachi, E. Bobu, R. Nicu, Carboxymethyl-chitosan as consolidation agent for old documents on paper support, 2009. <https://www.researchgate.net/publication/268432618>.
- [103] F. Ciolacu, R. Nicu, T. Balan, E. Bobu, Chitosan Derivatives as Bio-based Materials for Paper Heritage Conservation, *Bioresources* 12 (2017) 735–747. <https://doi.org/10.15376/biores.12.1.735-747>.
- [104] E. Salim, W.S. Mohamed, R. Sadek, Evaluation of the Efficiency of traditional chitosan, nano chitosan and chitosan nanocomposites for consolidating aged papyrus paper, *Pigment and Resin Technology* (2022). <https://doi.org/10.1108/PRT-06-2022-0079>.
- [105] M. Christensen, E. Larnøy, H. Kutzke, A. Finn, K. Hansen, Treatment of waterlogged archaeological wood using Chitosan-and modified Chitosan solutions. Part I: Chemical compatibility and microstructure, *Journal of the American Institute for Conservation* 54 (2015) 3–13. <https://doi.org/10.1179/1945233014Y.00000000034>.
- [106] H.A.M. Afifi, R.R.A. Hassan, S.M. Menofy, An experimental study for consolidation of archaeological cartonnage using klucel g and chitosan, with nanocalcium hydroxide, *Scientific Culture* 7 (2021) 49–68. <https://doi.org/10.5281/zenodo.4465518>.
- [107] C. Giuliani, M. Pascucci, C. Riccucci, E. Messina, M. Salzano de Luna, M. Lavorgna, G.M. Ingo, G. Di Carlo, Chitosan-based coatings for corrosion protection of copper-based alloys: A promising more sustainable approach for cultural heritage applications, *Prog. Org. Coat.* 122 (2018) 138–146. <https://doi.org/10.1016/j.porgcoat.2018.05.002>.
- [108] F. Boccaccini, C. Giuliani, M. Pascucci, C. Riccucci, E. Messina, M.P. Staccioli, G.M. Ingo, G. Di Carlo, Toward a Green and Sustainable Silver Conservation: Development and Validation of Chitosan-Based Protective Coatings, *Int. J. Mol. Sci.* 23 (2022) 14454. <https://doi.org/10.3390/IJMS232214454/S1>.

- [109] M. Bassi, E. Sassoni, E. Franzoni, Experimental Study on an Innovative Biopolymeric Treatment Against Salt Deterioration of Materials in Cultural Heritage, *Front. Mater.* 8 (2021). <https://doi.org/10.3389/fmats.2021.583112>.
- [110] C. Marrone, E. Franzoni, Enhancing the durability of historic brick masonry: The role of diammonium phosphate and chitosan in reducing salt-induced damage, *J. Cult. Herit.* 73 (2025) 150–157. <https://doi.org/10.1016/j.culher.2025.03.004>.
- [111] M. Baglioni, G. Poggi, D. Chelazzi, P. Baglioni, Advanced materials in cultural heritage conservation, *Molecules* 26 (2021). <https://doi.org/10.3390/molecules26133967>.
- [112] M. Meléndez-Zamudio, I. Bravo-Flores, E. Ramírez-Oliva, A. Guerra-Contreras, G. Álvarez-Guzmán, R. Zárraga-Núñez, A. Villegas, M. Martínez-Rosales, J. Cervantes, An approach to the use of glycol alkoxysilane–polysaccharide hybrids in the conservation of historical building stones, *Molecules* 26 (2021). <https://doi.org/10.3390/molecules26040938>.
- [113] N.C. Silva, D. Castro, C. Neto, A.R. Madureira, M. Pintado, P.R. Moreira, Antimicrobial chitosan/TPP-based coatings for the prevention of biodeterioration of outdoor stone sculptures, *Prog. Org. Coat.* 189 (2024). <https://doi.org/10.1016/j.porgcoat.2024.108246>.
- [114] S. Mandal, C. Hazra, N. Joshi, P. Kumar, R. Sen, S. Das, K. Das, Development and performance evaluation of chitosan hydrogel based ZnO/CuO antibacterial and antialgal nanocoating for the control of biofouling in cultural heritage stones, *Constr. Build. Mater.* 489 (2025). <https://doi.org/10.1016/j.conbuildmat.2025.142236>.
- [115] G. Infurna, G. Cavallaro, G. Lazzara, S. Milioto, N.T. Dintcheva, Bionanocomposite films containing halloysite nanotubes and natural antioxidants with enhanced performance and durability as promising materials for cultural heritage protection, *Polymers (Basel)*. 12 (2020). <https://doi.org/10.3390/polym12091973>.
- [116] G. Infurna, G. Cavallaro, G. Lazzara, S. Milioto, N.T. Dintcheva, Understanding the effects of crosslinking and reinforcement agents on the performance and durability of biopolymer films for cultural heritage

- [117] M.R. Caruso, G. D'Agostino, S. Milioto, G. Cavallaro, G. Lazzara, A review on biopolymer-based treatments for consolidation and surface protection of cultural heritage materials, *J. Mater. Sci.* 58 (2023) 12954–12975. <https://doi.org/10.1007/s10853-023-08833-5>.
- [118] O. Abdel-Kareem, H. Abdel-Rahim, I. Ezzat, D.M. Essa, Evaluating the use of chitosan coated Ag nano-SeO₂ composite in consolidation of Funeral Shroud from the Egyptian Museum of Cairo, *J. Cult. Herit.* 16 (2015) 486–495. <https://doi.org/10.1016/j.culher.2014.09.016>.
- [119] X. Hao, X. Wang, W. Yang, J. Ran, F. Ni, T. Tong, W. Dai, L. Zheng, X. Shen, H. Tong, Comparisons of the restoring and reinforcement effects of carboxymethyl chitosan-silk fibroin (*Bombyx Mori/Antheraea Yamamai/Tussah*) on aged historic silk, *Int. J. Biol. Macromol.* 124 (2019) 71–79. <https://doi.org/10.1016/j.ijbiomac.2018.11.203>.
- [120] A. Zhgun, D. Avdanina, B. Shagdarova, G. Nuraeva, K. Shumikhin, Y. Zhuikova, A. Il'ina, E. Troyan, M. Shitov, V. Varlamov, The Application of Chitosan for Protection of Cultural Heritage Objects of the 15–16th Centuries in the State Tretyakov Gallery, *Materials* 15 (2022). <https://doi.org/10.3390/ma15217773>.
- [121] J.W. Rhim, Characterization of Biopolymer and Chitosan-Based Nanocomposites with Antimicrobial Activity, *Bio-Nanotechnology: A Revolution in Food, Biomedical and Health Sciences* (2013) 355–382. <https://doi.org/10.1002/9781118451915.CH19;CTYPE:STRING:BOOK>.
- [122] P. Baglioni, D. Chelazzi, R. Giorgi, Nanotechnologies in the Conservation of Cultural Heritage: A compendium of materials and techniques, *Nanotechnologies in the Conservation of Cultural Heritage: A Compendium of Materials and Techniques* (2014) 1–144. <https://doi.org/10.1007/978-94-017-9303-2>.
- [123] S.M. Viñas, Contemporary theory of conservation, *Contemporary Theory of Conservation* (2012) 1–239. <https://doi.org/10.4324/9780080476834>.
- [124] F. Cappitelli, C. Sorlini, Microorganisms Attack Synthetic Polymers in Items Representing Our Cultural Heritage, *Appl. Environ. Microbiol.* 74 (2007) 564. <https://doi.org/10.1128/AEM.01768-07>.

- [125] S. Ifuku, Chitin and Chitosan Nanofibers: Preparation and Chemical Modifications, *Molecules* 2014, Vol. 19, Pages 18367-18380 19 (2014) 18367–18380. <https://doi.org/10.3390/MOLECULES191118367>.
- [126] Z. Walsh, E.R. Janeček, M. Jones, O.A. Scherman, Natural polymers as alternative consolidants for the preservation of waterlogged archaeological wood, *Studies in Conservation* 62 (2017) 173–183. <https://doi.org/10.1179/2047058414Y.00000000149>.
- [127] Z. Walsh-Korb, L. Avérous, Wood-polymer composites and nanocomposites: Building and reconstruction materials of the future, in: *Handbook of Polymer Nanocomposites for Industrial Applications*, Elsevier, 2020: pp. 617–632. <https://doi.org/10.1016/B978-0-12-821497-8.00023-X>.
- [128] M. Christensen, H. Kutzke, F.K. Hansen, New materials used for the consolidation of archaeological wood-past attempts, present struggles, and future requirements, *J. Cult. Herit.* 13 (2012). <https://doi.org/10.1016/j.culher.2012.02.013>.
- [129] J.M.K. Wakefield, S. Braovac, H. Kutzke, R.A. Stockman, S.E. Harding, Tert-butyldimethylsilyl chitosan synthesis and characterization by analytical ultracentrifugation, for archaeological wood conservation, *European Biophysics Journal* 49 (2020) 781–789. <https://doi.org/10.1007/s00249-020-01450-z>.
- [130] T.G. Ambaye, M. Vaccari, S. Prasad, E.D. van Hullebusch, S. Rtimi, Preparation and applications of chitosan and cellulose composite materials, *J. Environ. Manage.* 301 (2022). <https://doi.org/10.1016/j.jenvman.2021.113850>.
- [131] W. Luangbudnark, J. Viyoch, W. Laupattarakasem, P. Surakunprapha, P. Laupattarakasem, Properties and biocompatibility of chitosan and silk fibroin blend films for application in skin tissue engineering, *The Scientific World Journal* 2012 (2012). <https://doi.org/10.1100/2012/697201>.
- [132] X. Wang, Y. Hu, Z. Zhang, B. Zhang, The application of thymol-loaded chitosan nanoparticles to control the biodeterioration of cultural heritage sites, *J. Cult. Herit.* 53 (2022) 206–211. <https://doi.org/10.1016/j.culher.2021.12.002>.

- [133] S. Martins, C. Salvador, A. Candeias, A.T. Caldeira, A. Pereira, Methodology for the Synthesis of Chitosan Derivatives to be Applied in Cultural Heritage, *International Journal of Conservation Science* 11 (2020) 867–874. www.ijcs.ro.
- [134] Mohammad A. Al-Dosari, Sawsan Darwish, Mahmoud Abd El-Hafez, Nagib Elmarzugi, Nadia Al-Mouallimi, Sayed Mansour, Effects of Adding Nanosilica on Performance of Ethylsilicat (TEOS) as Consolidation and Protection Materials for Highly Porous Artistic Stone, *J. Mater. Sci. Eng. A* 6 (2016). <https://doi.org/10.17265/2161-6213/2016.7-8.002>.
- [135] F. Book, M. Persson, E. Carmona, T. Backhaus, T. Lammel, Colloidal silica nanomaterials reduce the toxicity of pesticides to algae, depending on charge and surface area, *Environ. Sci. Nano* 9 (2022) 2402–2416. <https://doi.org/10.1039/d1en01180d>.
- [136] M.G. Mohamed, N.M. Ahmed, W.S. Mohamed, A.H. Ibrahim, H.M. Mohamed, The potential of new eco-friendly formulations in enhancing the protection of ceramic artifacts, *J. Cult. Herit.* 67 (2024) 404–413. <https://doi.org/10.1016/j.culher.2024.04.003>.
- [137] V.T. Nguyen, H.D. Phi, H.D. Phi, T. Van Trinh, T. Van Trinh, P. Van Mac, P. Van Mac, H.A. Nguyen, H.A. Nguyen, H.M. Dang, H.M. Dang, L.T. Nguyen, L.T. Nguyen, T.M. Duong, T.M. Duong, Effect of Silica Nanoparticles on Properties of Coatings Based on Acrylic Emulsion Resin, *Vietnam J. Sci. Technol.* 56 (2018) 117. <https://doi.org/10.15625/2525-2518/56/3b/12731>.
- [138] I. Capasso, A. Colella, F. Iucolano, Silica-based consolidants: Enhancement of chemical-physical properties of Vicenza stone in heritage buildings, *Journal of Building Engineering* 68 (2023). <https://doi.org/10.1016/j.jobbe.2023.106124>.
- [139] L. Kócs, M.H. Jilavi, D. Beckelmann, B. Schäfer, A. May, M. Koch, P.W. de Oliveira, Water-based silica coatings: An environmentally friendly process on an industrial scale of single-layer anti-reflective coatings for large substrates, *Ceram. Int.* 48 (2022) 4165–4171. <https://doi.org/10.1016/j.ceramint.2021.10.209>.
- [140] X. Zhang, W. Wen, H. Yu, F. Qiu, Q. Chen, D. Yang, Preparation, characterization of nano-silica/fluoroacrylate material and the application

- in stone surface conservation, *Journal of Polymer Research* 23 (2016). <https://doi.org/10.1007/s10965-016-0967-8>.
- [141] P. Greenwood, *Surface Modifications and Applications of Aqueous Silica Sols*, ProQuest LLC (2010).
- [142] P. Greenwood, B. Gevert, *Aqueous silane modified silica sols: Theory and preparation*, *Pigment & Resin Technology* 40 (2011) 275–284. <https://doi.org/10.1108/03699421111176171>.
- [143] K. Kolman, G. Poggi, M. Baglioni, D. Chelazzi, P. Baglioni, M. Persson, K. Holmberg, R. Bordes, pH-Controlled assembly of polyelectrolyte layers on silica nanoparticles in concentrated suspension, *J. Colloid Interface Sci.* 615 (2022) 265–272. <https://doi.org/10.1016/j.jcis.2022.01.120>.
- [144] T. Fistos, I. Fierascu, M. Doni, I.E. Chican, R.C. Fierascu, A Short Overview of Recent Developments in the Application of Polymeric Materials for the Conservation of Stone Cultural Heritage Elements, *Materials* 15 (2022). <https://doi.org/10.3390/ma15186294>.
- [145] A.M. Barberena-Fernández, M.T. Blanco-Varela, P.M. Carmona-Quiroga, Use of nanosilica- or nanolime-added TEOS to consolidate cementitious materials in heritage structures: Physical and mechanical properties of mortars, *Cem. Concr. Compos.* 95 (2019) 271–276. <https://doi.org/10.1016/j.cemconcomp.2018.09.011>.
- [146] M.A. Rogerio-Candelera, Science, technology and cultural heritage : proceedings of the Second International Congress on Science and Technology for the Conservation of Cultural Heritage, Sevilla, Spain, 24-27 June 2014, 2014.
- [147] M.A. Rogerio-Candelera, Science, technology and cultural heritage : proceedings of the Second International Congress on Science and Technology for the Conservation of Cultural Heritage, Sevilla, Spain, 24-27 June 2014, (2014).
- [148] K. Kolman, O. Nechyporchuk, M. Persson, K. Holmberg, R. Bordes, Preparation of silica/polyelectrolyte complexes for textile strengthening applied to painting canvas restoration, *Colloids Surf. A Physicochem. Eng. Asp.* 532 (2017) 420–427. <https://doi.org/10.1016/j.colsurfa.2017.04.051>.

- [149] N. Palladino, M. Hacke, G. Poggi, O. Nechyporchuk, K. Kolman, Q. Xu, M. Persson, R. Giorgi, K. Holmberg, P. Baglioni, R. Bordes, Nanomaterials for combined stabilisation and deacidification of cellulosic materials—the case of iron-tannate dyed cotton, *Nanomaterials* 10 (2020). <https://doi.org/10.3390/nano10050900>.
- [150] G. Zhao, X. Ma, Z. Shao, X. Huang, J. Huang, H. Luo, Breathable hyperbranched polysiloxane for the conservation of silicate cultural heritages, *J. Solgel Sci. Technol.* 106 (2023) 518–529. <https://doi.org/10.1007/s10971-022-05932-8>.
- [151] M.M.A. Nikje, Z.M. Tehrani, Novel Hybrid Membranes Based on Chitosan and Organically-Modified Nano-SiO₂, *Des. Monomers Polym.* 12 (2009) 315–322. <https://doi.org/10.1163/156855509X448280>.
- [152] Y. Liu, Z. Cai, L. Sheng, M. Ma, Q. Xu, Influence of nanosilica on inner structure and performance of chitosan based films, *Carbohydr. Polym.* 212 (2019) 421–429. <https://doi.org/10.1016/j.carbpol.2019.02.079>.
- [153] R.C.S. da Luz, M.V.G. Paixão, R. de C. Balaban, Nanosilica-chitosan hybrid materials: Preparation, characterization and application in aqueous drilling fluids, *J. Mol. Liq.* 279 (2019) 279–288. <https://doi.org/10.1016/j.molliq.2019.01.131>.
- [154] S. Trujillo, E. Pérez-Román, A. Kyritsis, J.L. Gómez Ribelles, C. Pandis, Organic-inorganic bonding in chitosan-silica hybrid networks: Physical properties, *J. Polym. Sci. B Polym. Phys.* 53 (2015) 1391–1400. <https://doi.org/10.1002/polb.23774>.
- [155] C. Pandis, S. Madeira, J. Matos, A. Kyritsis, J.F. Mano, J.L.G. Ribelles, Chitosan-silica hybrid porous membranes, *Materials Science and Engineering C* 42 (2014) 553–561. <https://doi.org/10.1016/j.msec.2014.05.073>.
- [156] J.N. Liang, L.P. Yan, Y.F. Dong, Y.F. Dong, X. Liu, X. Liu, G. Wu, G. Wu, G. Wu, N.R. Zhao, N.R. Zhao, N.R. Zhao, Robust and nanostructured chitosan-silica hybrids for bone repair application, *J. Mater. Chem. B* 8 (2020) 5042–5051. <https://doi.org/10.1039/d0tb00009d>.
- [157] L. Zhao, M. Wang, L. Zhang, S.M. Sadeghzadeh, Impact of chitosan extracted from shrimp shells on the shrinkage and mechanical properties

- of cement-based composites using dendritic fibrous nanosilica, *Heliyon* 10 (2024). <https://doi.org/10.1016/j.heliyon.2024.e31576>.
- [158] S. Shetranjiwalla, A. Fasulo, S. Rhoden, Eco-design and tunable structure-properties of chitosan-epoxy-glycerol-silicate biohybrids using integrated crosslinking, *Carbohydr. Polym.* 299 (2023). <https://doi.org/10.1016/j.carbpol.2022.120187>.
- [159] M. V. Reyes-Peces, A. Pérez-Moreno, D.M. De-Los-santos, M.D.M. Mesa-Díaz, G. Pinaglia-Tobaruela, J.I. Vilches-Pérez, R. Fernández-Montesinos, M. Salido, N. de la Rosa-Fox, M. Piñero, Chitosan-gptms-silica hybrid mesoporous aerogels for bone tissue engineering, *Polymers (Basel)*. 12 (2020) 1–24. <https://doi.org/10.3390/polym12112723>.
- [160] G. Toskas, C. Cherif, R.D. Hund, E. Laourine, B. Mahltig, A. Fahmi, C. Heinemann, T. Hanke, Chitosan(PEO)/silica hybrid nanofibers as a potential biomaterial for bone regeneration, *Carbohydr. Polym.* 94 (2013) 713–722. <https://doi.org/10.1016/j.carbpol.2013.01.068>.
- [161] T. Suzuki', Y. Mizushima, Characteristics of Silica-Chitosan Complex Membrane and Their Relationships to the Characteristics of Growth and Adhesiveness of L-929 Cells Cultured on the Biomembrane, 1997.
- [162] S.N. Jayash, P.R. Cooper, R.M. Shelton, S.A. Kuehne, G. Poologasundarampillai, Novel chitosan-silica hybrid hydrogels for cell encapsulation and drug delivery, *Int. J. Mol. Sci.* 22 (2021). <https://doi.org/10.3390/ijms222212267>.
- [163] R. Sabazoodkhiz, M. Rahmaninia, O. Ramezani, Interaction of chitosan biopolymer with silica nanoparticles as a novel retention/drainage and reinforcement aid in recycled cellulosic fibers, *Cellulose* 24 (2017) 3433–3444. <https://doi.org/10.1007/s10570-017-1345-3>.
- [164] S. Choi, H. Na, R.T. Rahman, J. Sim, J.B. Chang, Y.S. Nam, Chitosan-coated mesoporous silica particles as a plastic-free platform for photochemical suppression and stabilization of organic ultraviolet filters, *J. Photochem. Photobiol. B* 235 (2022). <https://doi.org/10.1016/j.jphotobiol.2022.112565>.
- [165] T. V. Podust, T. V. Kulik, B.B. Palyanytsya, V.M. Gun'Ko, A. Tóth, L. Mikhalovska, A. Menyhárd, K. László, Chitosan-nanosilica hybrid

- materials: Preparation and properties, *Appl. Surf. Sci.* 320 (2014) 563–569. <https://doi.org/10.1016/j.apsusc.2014.09.038>.
- [166] A.M. El Nahrawy, A.B. Abou Hammad, M.S. Abdel-Aziz, A.R. Wassel, Spectroscopic and Antimicrobial Activity of Hybrid Chitosan/Silica Membranes doped with Al₂O₃ Nanoparticles, *Silicon* 11 (2019) 1677–1685. <https://doi.org/10.1007/s12633-018-9986-x>.
- [167] S.F. Abaza, N.S. Elbialy, N. Mohamed, Incorporating silver nanoshell-coated mesoporous silica nanoparticles improves physicochemical and antimicrobial properties of chitosan films, *Int. J. Biol. Macromol.* 189 (2021) 792–801. <https://doi.org/10.1016/j.ijbiomac.2021.08.161>.
- [168] R. Saberi Riseh, M. Vatankhah, M. Hassanisaadi, J.F. Kennedy, Chitosan/silica: A hybrid formulation to mitigate phytopathogens, *Int. J. Biol. Macromol.* 239 (2023). <https://doi.org/10.1016/j.ijbiomac.2023.124192>.
- [169] I.A. Wonnice Ma, A. Sh, R. K, V. B, R. S, A.K. Arof, Anticorrosion properties of epoxy-nanochitosan nanocomposite coating, *Prog. Org. Coat.* 113 (2017) 74–81. <https://doi.org/10.1016/j.porgcoat.2017.08.014>.
- [170] Z. Wu, Y. Li, J. Tang, D. Lin, W. Qin, D.A. Loy, Q. Zhang, H. Chen, S. Li, Ultrasound-assisted preparation of chitosan/nano-silica aerogel/tea polyphenol biodegradable films: Physical and functional properties, *Ultrason. Sonochem.* 87 (2022). <https://doi.org/10.1016/j.ultsonch.2022.106052>.
- [171] E. Ksinopoulou, A. Bakolas, A. Moropoulou, Consolidation effectiveness of modified Si-based nanocomposites applied to limestones, *Materials and Structures/Materiaux et Constructions* 51 (2018). <https://doi.org/10.1617/s11527-018-1281-1>.
- [172] Y.J. Cao, M. Camaiti, M. Endrizzi, G. Forti, E. Vergani, I. Forti, Enhanced consolidation efficacy and durability of highly porous calcareous building stones enabled by nanosilica-based treatments, *Sci. China Technol. Sci.* 66 (2023) 2197–2212. <https://doi.org/10.1007/s11431-022-2343-y>.
- [173] H. Baykara, A. Riofrio, N. Garcia-Troncoso, M. Cornejo, K. Tello-Ayala, J. Flores Rada, J. Caceres, Chitosan-Cement Composite Mortars: Exploring Interactions, Structural Evolution, Environmental Footprint and

- Mechanical Performance, *ACS Omega* 9 (2024) 24978–24986. <https://doi.org/10.1021/acsomega.4c02040>.
- [174] P.A. Hassan, S. Rana, G. Verma, Making sense of Brownian motion: Colloid characterization by dynamic light scattering, *Langmuir* 31 (2015) 3–12. https://doi.org/10.1021/LA501789Z/ASSET/IMAGES/MEDIUM/LA-2014-01789Z_0013.GIF.
- [175] F. Niroomand, A. Khosravani, H. Younesi, Fabrication and properties of cellulose-nanochitosan biocomposite film using ionic liquid, *Cellulose* 23 (2016) 1311–1324. <https://doi.org/10.1007/s10570-016-0872-7>.
- [176] S.H. Lim, S.M. Hudson, Synthesis and antimicrobial activity of a water-soluble chitosan derivative with a fiber-reactive group, *Carbohydr. Res.* 339 (2004) 313–319. <https://doi.org/10.1016/j.carres.2003.10.024>.
- [177] R. Sabazoodkhiz, M. Rahmaninia, O. Ramezani, Interaction of chitosan biopolymer with silica nanoparticles as a novel retention/drainage and reinforcement aid in recycled cellulosic fibers, *Cellulose* 24 (2017) 3433–3444. <https://doi.org/10.1007/s10570-017-1345-3>.
- [178] R.C.S. da Luz, M.V.G. Paixão, R. de C. Balaban, Nanosilica-chitosan hybrid materials: Preparation, characterization and application in aqueous drilling fluids, *J. Mol. Liq.* 279 (2019) 279–288. <https://doi.org/10.1016/j.molliq.2019.01.131>.
- [179] E.J. Lee, D.S. Shin, H.E. Kim, H.W. Kim, Y.H. Koh, J.H. Jang, Membrane of hybrid chitosan-silica xerogel for guided bone regeneration, *Biomaterials* 30 (2009) 743–750. <https://doi.org/10.1016/j.biomaterials.2008.10.025>.
- [180] C.P. Li, M.C. Weng, S.L. Huang, Preparation and characterization of pH sensitive chitosan/3-glycidyloxypropyl trimethoxysilane (GPTMS) hydrogels by Sol-Gel method, *Polymers (Basel)* 12 (2020) 1326. <https://doi.org/10.3390/POLYM12061326>.
- [181] L.S. Connell, F. Romer, M. Suárez, E.M. Valliant, Z. Zhang, P.D. Lee, M.E. Smith, J. V. Hanna, J.R. Jones, Chemical characterisation and fabrication of chitosan-silica hybrid scaffolds with 3-glycidoxypropyl trimethoxysilane, *J. Mater. Chem. B* 2 (2014) 668–680. <https://doi.org/10.1039/c3tb21507e>.

- [182] S. Deville, E. Saiz, R.K. Nalla, A.P. Tomsia, Freezing as a path to build complex composites, *Science* (1979). 311 (2006) 515–518. <https://doi.org/10.1126/science.1120937>.
- [183] J.G. Varghese, R.S. Karuppannan, M.Y. Kariduraganavar, Development of hybrid membranes using chitosan and silica precursors for pervaporation separation of water + isopropanol mixtures, *J. Chem. Eng. Data* 55 (2010) 2084–2092. <https://doi.org/10.1021/je9003993>.
- [184] L.S. Connell, F. Romer, M. Suárez, E.M. Valliant, Z. Zhang, P.D. Lee, M.E. Smith, J. V. Hanna, J.R. Jones, Chemical characterisation and fabrication of chitosan-silica hybrid scaffolds with 3-glycidoxypopyl trimethoxysilane, *J. Mater. Chem. B* 2 (2014) 668–680. <https://doi.org/10.1039/c3tb21507e>.
- [185] E. Szymańska, K. Winnicka, Stability of chitosan - A challenge for pharmaceutical and biomedical applications, *Mar. Drugs* 13 (2015) 1819–1846. <https://doi.org/10.3390/md13041819>.
- [186] M. Kurek, A. Guinault, A. Voilley, K. Galić, F. Debeaufort, Effect of relative humidity on carvacrol release and permeation properties of chitosan based films and coatings, *Food Chem.* 144 (2014) 9–17. <https://doi.org/10.1016/j.foodchem.2012.11.132>.
- [187] I. Yakimets, S.S. Paes, N. Wellner, A.C. Smith, R.H. Wilson, J.R. Mitchell, Effect of water content on the structural reorganization and elastic properties of biopolymer films: A comparative study, *Biomacromolecules* 8 (2007) 1710–1722. <https://doi.org/10.1021/bm070050x>.
- [188] M. Dash, F. Chiellini, R.M. Ottenbrite, E. Chiellini, Chitosan—A versatile semi-synthetic polymer in biomedical applications, *Prog. Polym. Sci.* 36 (2011) 981–1014. <https://doi.org/10.1016/j.progpolymsci.2011.02.001>.
- [189] I. Younes, M. Rinaudo, Chitin and chitosan preparation from marine sources. Structure, properties and applications, *Mar. Drugs* 13 (2015) 1133–1174. <https://doi.org/10.3390/md13031133>.
- [190] R. Lamuraglia, A. Campostrini, E. Ghedini, A. De Lorenzi Pezzolo, A. Di Michele, G. Franceschin, F. Menegazzo, M. Signoretto, A. Traviglia, A New Green Coating for the Protection of Frescoes: From the Synthesis to the Performances Evaluation, *Coatings* 13 (2023). <https://doi.org/10.3390/coatings13020277>.

- [191] M. Bertasa, C. Ricci, A. Scarcella, F. Zenucchini, G. Pellis, P. Croveri, D. Scalarone, Overcoming challenges in street art murals conservation: A comparative study on cleaning approach and methodology, *Coatings* 10 (2020) 1–23. <https://doi.org/10.3390/coatings10111019>.
- [192] Novo-Gloss Trio 20/60/85 Glossmeter - Rhopoint instruments webpage, (n.d.). <https://www.rhopointinstruments.com/product/novo-gloss-trio-20-60-85-glossmeter/> (accessed November 27, 2024).
- [193] UNI EN 15802:2010. Available online: <https://store.uni.com/en/uni-en-15802-2010>, (n.d.).
- [194] UNI EN 15801:2010, (2010). <https://store.uni.com/en/uni-en-15801-2010> (accessed November 25, 2024).
- [195] UNI EN 15803:2010, (2010). <https://store.uni.com/en/uni-en-15803-2010> (accessed November 25, 2024).
- [196] G. Torraca, P. Mora, Fissativi per pitture murali, *Bollettino Dell'Istituto Centrale Del Restauro* (1965) 109–132.
- [197] M. Drdácý, J. Lesák, S. Rescic, Z. Slížková, P. Tiano, J. Valach, Standardization of peeling tests for assessing the cohesion and consolidation characteristics of historic stone surfaces, *Materials and Structures/Materiaux et Constructions* 45 (2012) 505–520. <https://doi.org/10.1617/s11527-011-9778-x>.
- [198] P.O. Bussiere, J.L. Gardette, G. Rapp, C. Masson, S. Therias, New insights into the mechanism of photodegradation of chitosan, *Carbohydr. Polym.* 259 (2021). <https://doi.org/10.1016/j.carbpol.2021.117715>.
- [199] B. Bashiri, A.C.D.A.S. Pinheiro, S. Tappi, P. Rocculi, A. Kaleda, R. Vilu, Life cycle assessment of laboratory-scale chitosan production: comparison of high-pressure processing-assisted and conventional methods, *Proceedings of the Estonian Academy of Sciences* 74 (2025) 1–14. <https://doi.org/10.3176/proc.2025.1.01>.
- [200] T. Roukas, Citric and gluconic acid production from fig by *Aspergillus niger* using solid-state fermentation, 2000. www.nature.com/jim.
- [201] L.M.I. Canals, A. Azapagic, G. Doka, D. Jefferies, H. King, C. Mutel, T. Nemecek, A. Roches, S. Sim, H. Stichnothe, G. Thoma, A. Williams, Approaches for Addressing Life Cycle Assessment Data Gaps for Bio-

- based Products, J. Ind. Ecol. 15 (2011) 707–725. <https://doi.org/10.1111/J.1530-9290.2011.00369.X>.
- [202] R. Di Cagno, R. Coda, M. De Angelis, M. Gobbetti, Exploitation of vegetables and fruits through lactic acid fermentation, Food Microbiol. 33 (2013) 1–10. <https://doi.org/10.1016/J.FM.2012.09.003>.
- [203] A. Ghanbari, M.M. Attar, A study on the anticorrosion performance of epoxy nanocomposite coatings containing epoxy-silane treated nano-silica on mild steel substrate, Journal of Industrial and Engineering Chemistry 23 (2015) 145–153. <https://doi.org/10.1016/J.JIEC.2014.08.008>.
- [204] R.. Pant, L.. Zampori, Suggestions for updating the organisation environmental footprint (OEF) method, Publications Office of the European Union, 2019.
- [205] L. Pagnin, N. Guarnieri, F.C. Izzo, S. Goidanich, L. Toniolo, Protecting Street Art from Outdoor Environmental Threats: What Are the Challenges?, Coatings 13 (2023). <https://doi.org/10.3390/coatings13122044>.
- [206] L. Pagnin, R. Calvini, R. Wiesinger, J. Weber, M. Schreiner, Photodegradation Kinetics of Alkyd Paints: The Influence of Varying Amounts of Inorganic Pigments on the Stability of the Synthetic Binder, Front. Mater. 7 (2020) 600887. <https://doi.org/10.3389/FMATS.2020.600887/BIBTEX>.
- [207] P. Vandenabeele, PRACTICAL RAMAN SPECTROSCOPY: AN INTRODUCTION, Practical Raman Spectroscopy: An Introduction (2013) 1–167. <https://doi.org/10.1002/9781119961284>.
- [208] G.D. Smith, R.J.H. Clark, Raman microscopy in archaeological science, J. Archaeol. Sci. 31 (2004) 1137–1160. <https://doi.org/10.1016/j.jas.2004.02.008>.
- [209] M. Picollo, M. Bacci, A. Casini, F. Lotti, S. Porcinai, B. Radicati, L. Stefani, Fiber Optics Reflectance Spectroscopy: A Non-destructive Technique for the Analysis of Works of Art, Optical Sensors and Microsystems (2002) 259–265. https://doi.org/10.1007/0-306-47099-3_23.

- [210] J.K. Delaney, P. Ricciardi, L.D. Glinsman, M. Facini, M. Thoury, M. Palmer, E.R. De La Rie, Use of imaging spectroscopy, fiber optic reflectance spectroscopy, and X-ray fluorescence to map and identify pigments in illuminated manuscripts, *Studies in Conservation* 59 (2014) 91–101. <https://doi.org/10.1179/2047058412Y.00000000078>.
- [211] R.F. Kokaly, R.N. Clark, G.A. Swayze, K.E. Livo, T.M. Hoefen, N.C. Pearson, R.A. Wise, W. Benzel, H.A. Lowers, R.L. Driscoll, A.J. Klein, USGS Spectral Library Version 7, (2017). <https://doi.org/10.3133/ds1035>.
- [212] B.A., B.P. and S.Q.L. eds. Price, Infrared and Raman Users Group Spectral Database, Vol. 1 & 2 (2014). <http://irug.org/> (accessed May 13, 2025).
- [213] C. Defeyt, P. Vandenabeele, B. Gilbert, J. Van Pevenage, R. Cloots, D. Strivay, Contribution to the identification of α -, β - And μ -copper phthalocyanine blue pigments in modern artists' paints by X-ray powder diffraction, attenuated total reflectance micro-fourier transform infrared spectroscopy and micro-Raman spectroscopy, *Journal of Raman Spectroscopy* 43 (2012) 1772–1780. <https://doi.org/10.1002/JRS.4125>;CSUBTYPE:STRING:SPECIAL;PAGE:STRING:ARTICLE/CHAPTER.
- [214] N.C. Scherrer, Z. Stefan, D. Francoise, F. Annette, K. Renate, Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 73 (2009) 505–524. <https://doi.org/10.1016/j.saa.2008.11.029>.
- [215] W. Fremout, S. Saverwyns, Identification of synthetic organic pigments: the role of a comprehensive digital Raman spectral library, *Journal of Raman Spectroscopy* 43 (2012) 1536–1544. <https://doi.org/10.1002/JRS.4054>.
- [216] A. Rousaki, P. Vandenabeele, M. Berzioli, I. Saccani, L. Fornasini, D. Bersani, An in-and-out-the-lab Raman spectroscopy study on street art murals from Reggio Emilia in Italy, *Eur. Phys. J. Plus* 137 (2022). <https://doi.org/10.1140/epjp/s13360-022-02423-1>.
- [217] E.M. Bauer, T. De Caro, P. Tagliatesta, M. Carbone, Unraveling the real pigment composition of tattoo inks: the case of bi-components phthalocyanine based greens, *Dyes and Pigments* 167 (2019) 225–235. <https://doi.org/10.1016/J.DYEPIG.2019.04.018>.

- [218] A. Bosi, A. Ciccola, I. Serafini, M. Guiso, F. Ripanti, P. Postorino, R. Curini, A. Bianco, Street art graffiti: Discovering their composition and alteration by FTIR and micro-Raman spectroscopy, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 225 (2020). <https://doi.org/10.1016/j.saa.2019.117474>.
- [219] L. Burgio, R.J.H. Clark, Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 57 (2001) 1491–1521. [https://doi.org/10.1016/S1386-1425\(00\)00495-9](https://doi.org/10.1016/S1386-1425(00)00495-9).
- [220] I.M. Bell, R.J.H. Clark, P.J. Gibbs, Raman spectroscopic library of natural and synthetic pigments (pre-~ 1850 AD), *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 53 (1997) 2159–2179. [https://doi.org/10.1016/S1386-1425\(97\)00140-6](https://doi.org/10.1016/S1386-1425(97)00140-6).
- [221] M. Bacci, M. Picollo, G. Trumpy, M. Tsukada, D. Kunzelman, Non-invasive identification of white pigments on 20th-century oil paintings by using fiber optic reflectance spectroscopy, *Journal of The American Institute for Conservation* 46 (2007) 27–37. <https://doi.org/10.1179/019713607806112413;PAGE:STRING:ARTICLE/CHAPTER>.
- [222] C. Montagner, M. Bacci, S. Bracci, R. Freeman, M. Picollo, Library of UV–Vis–NIR reflectance spectra of modern organic dyes from historic pattern-card coloured papers, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 79 (2011) 1669–1680. <https://doi.org/10.1016/J.SAA.2011.05.033>.
- [223] S. Carlesi, G. Bartolozzi, C. Cucci, V. Marchiafava, M. Picollo, The artists' materials of Fernando Melani: A precursor of the Poor Art artistic movement in Italy, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 104 (2013) 527–537. <https://doi.org/10.1016/J.SAA.2012.11.094>.
- [224] S. Carlesi, G. Bartolozzi, C. Cucci, V. Marchiafava, M. Picollo, J. La Nasa, F. Di Girolamo, M. Dilillo, F. Modugno, I. Degano, M.P. Colombini, S. Legnaioli, G. Lorenzetti, V. Palleschi, Discovering “the Italian Flag” by Fernando Melani (1907–1985), *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 168 (2016) 52–59. <https://doi.org/10.1016/J.SAA.2016.05.027>.

- [225] R. Johnston-Feller, Color Science in the Examination of Museum Objects - Nondestructive Procedures, (2001).
- [226] V. Marchiafava, G. Bartolozzi, C. Cucci, M. De Vita, M. Picollo, Colour measurements for monitoring the conservation of contemporary artworks, *Journal of the International Colour Association* (2014) 36–42. <http://www.aic-colour-journal.org/> (accessed October 7, 2025).
- [227] A.A.M. Farag, Optical absorption studies of copper phthalocyanine thin films, *Opt. Laser Technol.* 39 (2007) 728–732. <https://doi.org/10.1016/J.OPTLASTEC.2006.03.011>.
- [228] G. Pellis, M. Bertasa, C. Ricci, A. Scarcella, P. Croveri, T. Poli, D. Scalarone, A multi-analytical approach for precise identification of alkyd spray paints and for a better understanding of their ageing behaviour in graffiti and urban artworks, *J. Anal. Appl. Pyrolysis* 165 (2022). <https://doi.org/10.1016/j.jaap.2022.105576>.
- [229] J. Honzíček, E. Matušková, Š. Voneš, J. Vinklárek, Helmet Phthalocyaninato Iron Complex as a Primary Drier for Alkyd Paints, *Materials* 14 (2021) 1220. <https://doi.org/10.3390/MA14051220>.
- [230] M. Picollo, G. Basilissi, C. Cucci, L. Stefani, M. Tsukada, Ultraviolet, Visible and Near Infrared Reflectance Spectra of Modern Pictorial Materials in the 200–2500 nm range, (2024). <https://iris.cnr.it/handle/20.500.14243/274174> (accessed February 15, 2026).
- [231] G. Sharma, W. Wu, E.N. Dalal, The CIEDE2000 color-difference formula: Implementation notes, supplementary test data, and mathematical observations, *Color Res. Appl.* 30 (2005) 21–30. <https://doi.org/10.1002/COL.20070;WGROU:STRING:PUBLICATION>.
- [232] M.R. Luo, G. Cui, B. Rigg, The development of the CIE 2000 colour-difference formula: CIEDE2000, *Color Res. Appl.* 26 (2001) 340–350. <https://doi.org/10.1002/col.1049>.
- [233] R.F. Witzel, R.W. Burnham, J.W. Onley, Threshold and suprathreshold perceptual color differences, *J. Opt. Soc. Am.* 63 (1973) 615–625. <https://doi.org/10.1364/JOSA.63.000615>.

- [234] J. Fang, Y. Xuan, Q. Li, Preparation of polystyrene spheres in different particle sizes and assembly of the PS colloidal crystals, *Sci. China Technol. Sci.* 53 (2010) 3088–3093. <https://doi.org/10.1007/S11431-010-4110-5>.
- [235] S. Gunasekaran, G. Anbalagan, Spectroscopic characterization of natural calcite minerals, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 68 (2007) 656–664. <https://doi.org/10.1016/J.SAA.2006.12.043>.
- [236] M.B. Toffolo, L. Regev, S. Dubernet, Y. Lefrais, E. Boaretto, FTIR-Based Crystallinity Assessment of Aragonite–Calcite Mixtures in Archaeological Lime Binders Altered by Diagenesis, *Minerals* 2019, Vol. 9, Page 121 9 (2019) 121. <https://doi.org/10.3390/MIN9020121>.
- [237] C.M. Müller, A. Molinelli, M. Karlowatz, A. Aleksandrov, T. Orlando, B. Mizaikoff, Infrared attenuated total reflection spectroscopy of quartz and silica micro- and nanoparticulate films, *Journal of Physical Chemistry C* 116 (2012) 37–43. <https://doi.org/10.1021/JP205137B>.
- [238] Q. Xia, X.J. Zhao, S.J. Chen, W.Z. Ma, J. Zhang, X.L. Wang, Effect of solution-blended poly(styrene-co-acrylonitrile) copolymer on crystallization of poly(vinylidene fluoride), *Express Polym. Lett.* 4 (2010) 284–291. <https://doi.org/10.3144/EXPRESSPOLYMLET.2010.36>.
- [239] Architectural coatings - Synthomer, (n.d.). <https://www.synthomer.com/markets-and-products/coatings-emea/architectural/> (accessed August 24, 2025).
- [240] External Thermal Composite Insulation Systems (ETICS)/ Exterior Insulation & Finish Systems (EIFS), (n.d.). <https://www.dow.com/en-us/market/mkt-building-construction/sub-build-wall-systems-insulation-facade/app-build-wallinsulation-etics.html> (accessed August 24, 2025).
- [241] N. Simões, I. Simões, C. Serra, A. Tadeu, Thermographic inspection of external thermal insulation systems with mechanical fixing, *https://doi.org/10.1117/12.2180711* 9485 (2015) 341–350. <https://doi.org/10.1117/12.2180711>.
- [242] S.M. Cakić, I.S. Ristić, J.M. Vladislav, J. V. Stamenković, D.T. Stojiljković, IR-change and colour changes of long-oil air drying alkyd paints as a result of UV irradiation, *Prog. Org. Coat.* 73 (2012) 401–408. <https://doi.org/10.1016/J.PORGCOAT.2010.12.002>.

- [243] L. Ortiz-Herrero, I. Cardaba, S. Setien, L. Bartolomé, M.L. Alonso, M.I. Maguregui, OPLS multivariate regression of FTIR-ATR spectra of acrylic paints for age estimation in contemporary artworks, *Talanta* 205 (2019). <https://doi.org/10.1016/j.talanta.2019.120114>.
- [244] A. Ciccola, M. Guiso, F. Domenici, F. Sciubba, A. Bianco, Azo-pigments effect on UV degradation of contemporary art pictorial film: A FTIR-NMR combination study, *Polym. Degrad. Stab.* 140 (2017) 74–83. <https://doi.org/10.1016/j.polymdegradstab.2017.04.004>.
- [245] L. Pagnin, S. Goidanich, N. Guarnieri, F.C. Izzo, J.J.H. Henriquez, L. Toniolo, Street Art in the Rain: Evaluating the Durability of Protective Coatings for Contemporary Muralism Through Accelerated Rain Ageing, *Coatings* 2025, Vol. 15, Page 924 15 (2025) 924. <https://doi.org/10.3390/COATINGS15080924>.
- [246] F. Cadena, L. Irusta, M.J. Fernandez-Berridi, Performance evaluation of alkyd coatings for corrosion protection in urban and industrial environments, *Prog. Org. Coat.* 76 (2013) 1273–1278. <https://doi.org/10.1016/j.porgcoat.2013.03.017>.
- [247] M. Anghelone, D. Jembrih-Simbürger, V. Pintus, M. Schreiner, Photostability and influence of phthalocyanine pigments on the photodegradation of acrylic paints under accelerated solar radiation, *Polym. Degrad. Stab.* 146 (2017) 13–23. <https://doi.org/10.1016/j.polymdegradstab.2017.09.013>.
- [248] J. Bentley, G.P.A. Turner, Introduction to Paint Chemistry and principles of paint technology, 4th ed., SPRINGER-SCIENCE+BUSINESS MEDIA, B.v., 1998. <https://doi.org/10.1007/978-1-4899-3180-1>.
- [249] F.N. Jones, M.E. Nichols, S.P. Pappas, Organic coatings: science and technology, 4th ed., John Wiley & Sons, Inc, 2017.
- [250] N.S. Allen, Handbook of photochemistry and photophysics of polymer materials, John Wiley & Sons, Inc., Hoboken, New Jersey, 2010.
- [251] J.F. Rabek, Photodegradation of Polymers, 1st ed., Springer Berlin Heidelberg, Berlin, Heidelberg, 1996. <https://doi.org/10.1007/978-3-642-80090-0>.

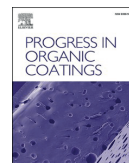
- [252] J.S. Pozo-Antonio, E.M. Alonso-Villar, T. Rivas, I. Márquez, Evaluation of a protective acrylic finish applied to surfaces painted with acrylic paints for outdoor or indoor uses, *Dyes and Pigments* 212 (2023) 111141. <https://doi.org/10.1016/J.DYEPIG.2023.111141>.
- [253] Public Art Maintenance Best Practices | Artwork Archive, (n.d.). <https://www.artworkarchive.com/blog/public-art-maintenance-best-practices> (accessed February 15, 2026).
- [254] L. Pagnin, N. Guarnieri, F.C. Izzo, S. Goidanich, L. Toniolo, Protecting Street Art from Outdoor Environmental Threats: What Are the Challenges?, *Coatings* 2023, Vol. 13, Page 2044 13 (2023) 2044. <https://doi.org/10.3390/COATINGS13122044>.
- [255] ADP - Artists Documentation Program, (n.d.). <https://adp.menil.org/> (accessed February 15, 2026).

Appendix – Scientific Publication Arising from this Doctoral Research



Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Formulation of a new sustainable hybrid coating for the conservation of street-art: Characterization and application

Chiara Cianci^a, Fabrizio Andriulo^b, Rodorico Giorgi^{a,*}^a Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, Via della Lastruccia 3, Sesto Fiorentino, 50019 Florence, Italy^b Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, Sesto Fiorentino, 50019 Florence, Italy

ARTICLE INFO

Keywords:

Street-art

Chitosan

Hybrids

Nanosilica

Green conservation

ABSTRACT

Street-Art murals are spreading and transforming urban areas worldwide; however, proper and effective conservation procedures for this emerging form of art are lacking. Outdoor murals are made of inorganic pigments or dyes blended with synthetic organic binders applied on inorganic substrates, mainly concrete, and are exposed to serious degradation due to light, temperature, and humidity fluctuations, pollutants, and biological agents that hinder their conservation. This research focuses on the formulation and application of chitosan and nanosilica hybrid coating by exploiting the good film-forming ability, optical and antimicrobial properties, and sustainability of chitosan. The capability of silica to boost the chitosan film properties was investigated, with special reference to the compatibility of hybrid films with paints and concrete substrates. The new formulation was characterized by ATR-FTIR, SEM imaging, DLS, and zeta potential measurements. The hybrid coating was applied on concrete spray paint-coloured mock-ups, and the film properties in terms of adhesion, water vapor permeability, and hydrophobicity are reported. The long-term stability of the coating was assessed by three different accelerated aging tests, and the colorimetric variations were measured.

1. Introduction

Street-Art is an emerging contemporary form of art that, in the last decades, has led to a significant transformation in urban areas worldwide thanks to its great expressive impact. Unlike in the past, muralism is now perceived as a valuable contribution to society and local areas, rather than being seen as an act of vandalism. Rather, this novel form of art has gained social recognition and piqued the interest of administrations, municipalities, and citizens who actively started commissioning or economically supporting the creation of new murals, as well as in public spaces. At the same time, conservators and heritage scientists have also become more aware of the cultural value of these unique outdoor works of art, and, in recent years, some reflections and debates have been initiated regarding their preservation [1–4]. Still, no specifically defined materials and conservation procedures have been developed for this emerging form of art, and the professionals call for a more in-depth study of materials and techniques employed to generate specific protocols [5].

These outdoor artworks are exposed to numerous factors such as light, temperature and humidity fluctuations, water, pollutants, fine particulate matter, and biological agents that accelerate their

deterioration over time. Additionally, vandalism can also threaten the legibility and longevity of these artworks. It is important to note that these degradation processes act synergistically, and further investigation is necessary to fully understand these complex phenomena [6].

Furthermore, the chemical composition of the materials employed in street artworks, their quality, and the constant interaction with the atmospheric environment are key factors in defining distinct conservation strategies for murals. Differently from traditional wall paintings, graffiti are made of synthetic organic paints directly applied on different inorganic substrates such as concrete, brick walls, plasters, and mortars. The range of materials used in Street-Art is wide, especially considering the numerous techniques involved in creating the artwork. Spray cans, brushes, and rollers are commonly used to paint large wall surfaces and achieve unique aesthetic effects.

From the chemical point of view, these synthetic paints comprise a propellant - commonly butane, isobutane, or propane - a binder medium that is responsible for the paint film formation, on which are dispersed organic and inorganic pigments, a solvent for the pigment/binder mixture; and additives (plasticizers, dispersing agents, defoamers, surfactants, etc.). The different classes of spray paints are distinguished according to their binder media: alkyd, styrene acrylic, acrylic-based

* Corresponding author.

E-mail address: rodorico.giorgi@unifi.it (R. Giorgi).<https://doi.org/10.1016/j.porgcoat.2024.109026>

Received 6 November 2024; Received in revised form 10 December 2024; Accepted 18 December 2024

Available online 26 December 2024

0300-9440/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

resins, and vinyl emulsions. The extreme variability of the artistic techniques and substrates, and the continuous changes in the formulation and quality of the commercial products employed by the artists make the constant and continuous characterization, selection, and study of compatible restoration and protective products particularly challenging [7–10].

The materials employed by the street artists are exposed to various forms of deterioration. Some of the most common include cracks and detachments of the painting layer from the support, discoloration, and fading of the background, particulate matter deposits, and washouts. The type and severity of these degradation patterns are strongly influenced by environmental factors such as climate conditions, traffic, humidity, and the orientation of the painted wall. Prolonged exposure to sunlight and pollutants is particularly damaging to murals and can lead to significant deterioration of their appearance. Furthermore, the intrinsic characteristics of the artistic materials such as the paint layer and the substrate used can accelerate the decay of mural artworks. Compared to traditional materials, spray paints are less resistant to environmental factors, especially sunlight. In fact, if the substrate is not prepared correctly, it may not allow the paint to adhere well to its surface, leading to problems such as cracks, water infiltration, and deposits of atmospheric particulates [11–16]. Physical and mechanical factors can cause embrittlement, cracking, morphology changes, and craquelure formation leading to paint loss due to environmental exposure (thermal excursions, wet and dry cycles, and mechanical action of raindrops). All these processes occur simultaneously, and a list of the various degradation phenomena that affect contemporary muralism has been drawn up by the CAPuS project [17].

The increasing spread of Street-Art calls for the formulation of specifically designed protective coatings that meet all the requirements for the protection and, desirably, for the consolidation of the murals. These new materials must be compatible with the surfaces, show good optical properties to preserve the aesthetic characteristics of the painting layer and be effective in protecting the latter against alterations. In this context, it is also important to use neutral-pH products to prevent chemical reactions with the painted surface or the wall support that could alter the brightness and colour stability of the painting or damage the inorganic porous materials underneath. Moreover, the surface should not appear more hydrophobic after the treatment, to avoid the alteration of the breathability of the complex substrate composed of inorganic and organic materials, i.e. concrete and spray paint, respectively. Finally, the coating must be durable under outdoor conditions while being cost-effective for their use on large-wall surfaces, and it must be sustainable and nontoxic for both the conservators and the environment [18,19].

In recent years, biopolymers and waste-derived materials have attracted interest as suitable substitutes for synthetic protective coatings [20,21] due to their sustainability and potential compliance with the *reversibility-retreatability* requirement. Although biodegradable polymers cannot be properly defined as reversible, they are expected to completely disappear from the substrate once their protective action has ceased, without influencing further treatments on the original surface or jeopardizing the environment. For this reason, biopolymers might be considered *intrinsically reversible*, as they do not leave any permanent residue in the stone and do not cause any unforeseen consequences in subsequent conservation work [22].

Among biopolymers, chitosan would be a particularly promising candidate due to its sustainability, biodegradability, film-forming ability, antimicrobial activity, and cost-effectiveness. Chitosan is a polysaccharide obtained through the partial deacetylation of chitin, the second most abundant biopolymer after cellulose. This material can be produced by the valorisation of marine biomass, in particular, crustacean shell waste [23]. Its numerous properties make this polysaccharide an interesting material in various fields such as cosmetics, pharmaceuticals, medicine, food, agriculture, and water treatment [24,25]. Moreover, it has recently been used for the synthesis of sustainable anti-

corrosion coatings for metal substrates [26,27]. In Cultural Heritage, it was also studied for the formulation of consolidating systems for paper [28–30], wood consolidation [31,32], stone protection and consolidation [33–35], frescoes protection [36], and for the treatment of cotton and linen-based ethnographic objects [37].

In this research, we describe the formulation of an effective chitosan-based coating as a suitable option for application in urban art conservation. However, chitosan shows significant limitations in terms of mechanical properties and compatibility with the inorganic substrate, which may lead to poor protective action, especially in terms of thermal and mechanical properties. Additionally, chitosan needs to be dissolved under lower pH conditions because it contains amine groups that become protonated in acidic environments. Typically, pH is increased to acceptable value (concrete is alkaline) by adding an alkaline aqueous solution. However, this method was not suitable for our purposes, as neutralization would result in salt formation and, consequently, efflorescence on the artwork's substrate. A new strategy was developed to achieve a final pH-neutral solution, which is a requirement for applying the product on art substrates safely.

Several studies have focused on enhancing the mechanical strength of chitosan, by formulating composite materials with nanosilica [38–44]. Due to its exceptional properties such as high surface energy, small size, stable structure, and strong mechanical strength, nanosilica has shown promising results for the preparation of composite biomaterials [45].

For that, this research considers the combination of chitosan with an inorganic material as a potentially effective approach to obtain hybrid materials with improved physicochemical properties that meet the specific requirements of Street-Art techniques. Specifically, nanosilica is commonly employed as an additive in waterborne coatings, to ensure compatibility with both organic painting films and inorganic substrates [46,47]. Notably, nanosilica-based materials have demonstrated remarkable compatibility with stone substrates, providing durability, surface cohesion, and strength under various environmental conditions [48]. In our research we explored the potentiality of using functionalized nanosilica with epoxy silane moieties, which can boost the film stability and adhesion capability.

The resulting hybrid coating would possess the collective properties of both inorganic and organic components, including good tensile strength, flexibility, and chemical and thermal stability. [49,50].

The characterization of the films was conducted using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy images (SEM), dynamic light scattering (DLS) and zeta potential measurements. Chemical stability, colour and gloss variations, water vapor permeability, and hydrophobicity are evaluated on spray-painted concrete mock-ups before and after the application of the composites, and its long-term stability is assessed by means of photochemical, hydrothermal, and thermal aging tests.

2. Materials and methods

Chitosan (Chs, medium molecular weight, viscosity 200–800 cP, 75–85 % deacetylated), D-(+)-gluconic δ -lactone (GDL, purity ≥ 99.9 %), and dialysis tubing (high retention seamless cellulose tubing, MWCO 14000, 99.9 % retention) were purchased from Sigma Aldrich. Before using, Chs was washed in boiling water for 1 h, filtered, rinsed with distilled water to remove impurities, and let dry at room temperature for 48 h. Ultrapure Milli-Q water (resistivity 18.2 M Ω ·cm at 25 °C) was used where needed.

Nano silica dispersion (NS) Levasil® CC301 by Nouryon was used as received. It is a neutral aqueous dispersion of colloidal silica (approx. 30 % solids by weight). The anionic NS particles have an epoxy-silane-modified surface.

For the preparation of the mock-ups, white concrete (purchased by Knauf) and sand (SiO₂, 50–70 mesh particle size, Sigma Aldrich) were used. Two acrylic spray-can paints were selected and purchased from

Table 1
Chitosan, nanosilica, and Chs-NS hybrid concentrations.

	Chs - Chitosan	NS - Levasil® CC301	Chs-NS hybrid
Concentration %ww	0.5	0.5	0.25/0.25

Table 2
Concrete mock-ups prepared.

Colour	Not treated	Treatment	
		Chs 0.5 %	Chs-NS 0.25/0.25 %
White	Not aged, A1, A2, A3	Not aged, A1, A2, A3	Not aged, A1, A2, A3
Blue	Not aged, A1, A2, A3	Not aged, A1, A2, A3	Not aged, A1, A2, A3

Low Kobra: LOW1171 – “Strong Blue” and LOW001 – “Pure White” and used as received.

2.1. Coatings preparation

Chitosan powder with a 0.6 % w/v concentration was dissolved in an aqueous 0.05 M gluconic acid solution. The solution was heated at 30 °C for 24 h under continuous stirring. The solution reached a pH of about 3.5. Then, to remove the insoluble residues, the solution was centrifuged at 4500 rpm twice for 5 min. The pH adjustment of the centrifuged solution was achieved by dialysis, using a membrane cell for 24 h against 1 L water. This operation was chosen to avoid the addition of alkaline solutions that lead to the formation of salts which could be hazardous for the application of the coating on porous substrates. After dialysis, the Chs aqueous solution resulted clear and transparent, and its pH was about 6.0. As the final concentration is calculated gravimetrically, the desired final concentration was adjusted for the analysis or the application on the mock-ups according to the values reported in Table 1. The chitosan-nano silica (Chs-NS) hybrid solution was prepared by mixing and magnetically stirring the Chs-based solution and NS at the selected ratios (Table 1). A portion of each resulting solution was kept at room temperature for 24 h before the application on the mock-ups (par. 2.2). The remaining portion of each solution was cast on a glass plate and let dry at room temperature for at least 48 h to obtain coating films for the characterization analysis and film's aging tests (par. 2.3, 2.4, and 2.5).

2.2. Mock-ups preparation

Concrete mock-ups of $5.5 \times 5.5 \times 1 \text{ cm}^3$ were prepared to replicate the characteristics of the most usual form of Street-Art. White concrete was mixed with sand and water according to the volume ratios described by the concrete producer, 2.5:2 respectively. The paste was then let dry in wooden moulds for two weeks at room temperature. When the setting was complete, the front surface of each mock-up was coloured by spraying one of the acrylic sprays to mimic the street art technique. Different replicates were prepared according to the colour. The colours used, white and blue, were selected to better detect the colour variations both as the coatings are applied, and during the aging processes, i.e. yellowing or formation of whitish residues. Once coloured, the mock-ups were left set for a week at room temperature before the coating treatment and the consequent colour measurements, film analysis, and aging tests.

The chitosan-based coating and the hybrid system were applied on concrete mock-ups by brush and let dry for 1 week before measurements and aging tests. The different combinations of mock-ups are summarized in Table 2.

2.3. Accelerated aging tests

To assess the colour stability of the treated and untreated mock-ups,

different accelerated aging tests were considered. Each test carried out on the concrete mock-ups lasted 200 days.

The description of the different conditions is here reported:

“A1”- *Photo-oxidative aging*.

A set of treated and untreated mock-ups were irradiated with UV–vis light to induce photo-oxidative degradation. The samples were stored in a closed box with a Neon Light Colour 765 Basic daylight Beghelli® Lamp (380–700 nm, 160 mW/lm.). The climatic conditions inside the chamber ($T = 36 \pm 2 \text{ °C}$ and $\text{RH } 40 \pm 5 \%$) were recorded through a digital thermohygrometer (Gauge). The mock-ups' surface was exposed to about 11,000 Lux of homogeneous illumination; the distance from the lamp is 10 cm.

“A2”- *Hydrothermal aging*.

A set of mock-ups was hermetically closed into sealed vessels with a vial with saturated KCl solution and put into oven at 60 °C to get a constant RH of 80 % inside the vessels.

“A3”- *Thermal aging*.

A set of mock-ups was put in oven at a constant temperature of 60 °C in a dry environment (about 40 %).

A summary of the mock-ups prepared and aged is reported in Table 2.

Additionally, the Chs and Chs-NS-based films were also cast and allowed to dry without being applied on the mock-ups. This method ensured an accurate characterization of their physical and chemical properties.

Moreover, this approach facilitated a focused investigation of the coatings' behaviour as standalone materials, independently of their application on the mock-ups. Specifically, aging tests were also conducted on the films alone to evaluate their molecular transformations when in contact with an inert surface such as the glass of Petri dishes.

Aging tests were conducted on the films alone to evaluate their molecular transformations when in contact with an inert surface, such as the glass of Petri dishes. Preliminary observations from the aging tests of the coatings applied to the mock-ups indicated that molecular changes occurred within the first 20 days of artificial aging. Therefore, this time range was selected for studying the molecular behaviour of Chs and Chs-NS films.

Moreover, Chs and Chs-NS coatings directly cast on glass Petri dishes were subjected to the same aging conditions of the mock-ups for 20 days to analyse the aging effect on the physical and molecular structure of the films.

2.4. ATR-FTIR

Attenuated total reflection Fourier Transformation Infrared spectroscopy (ATR-FTIR) measurements were conducted on the coating films using a Thermo Nicolet Nexus 870 spectrometer equipped with a liquid nitrogen-cooled HgCdTe detector and a single reflection diamond crystal ATR unit. Spectra were recorded in the $4000\text{--}650 \text{ cm}^{-1}$ range by acquiring 128 scans for each spectrum with a 4 cm^{-1} spectral resolution.

2.5. Field emission scanning electron microscopy (FE-SEM)

Field Emission SEM (FE-SEM) images were recorded with a Sigma scanning electron microscope (Carl Zeiss Microscopy Deutschland GmbH, Germany). The images were acquired at a working distance of 1.8 mm playing with an acceleration potential of 10 kV using a secondary electron detector as well as an in-lens secondary electron detector with an acceleration potential of 5 kV. The Chs and Chs-NS films were gold coated with an automatic sputter coater (Agar Scientific Ltd., UK).

2.6. Size distribution and zeta potential

Dynamic light scattering (DLS) measurements at $\theta = 90^\circ$ and the ζ -potential determination was performed using a Brookhaven

Instrument 90 Plus (Brookhaven, Holtsville, NY). Each measurement was an average of 10 repetitions of 1 min each, and measurements were repeated 10 times. 3 repeats were carried out for each sample. 659 nm laser light radiation. The measurements were carried out at 25 °C. Particle size distributions were obtained from the fitting of the measured autocorrelation functions using the CONTIN method [51].

2.7. Colour measurements

Colour measurements on treated mock-ups, before and after aging, were performed using an X-rite SP60 spectrophotometer equipped with an integrating sphere having a circular sampling spot (diameter = 1.5 cm). Colorimetric coordinates were obtained using standard illuminant D65 and a standard observer at 2°. The untreated mock-ups were taken as standard. Each measurement was an average of 5 acquisitions taken in 5 different spots on each mock-up surface (30.25 cm²).

The colour difference (ΔE), according to the CIE Lab equation, and its standard deviation ($\sigma_{\Delta E}$) was obtained using the equations below, respectively:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

$$\sigma_{\Delta E} = \sqrt{\left(\frac{\Delta L}{\Delta E}\right)^2 \cdot (\sigma_{L_1}^2 + \sigma_{L_0}^2) + \left(\frac{\Delta a}{\Delta E}\right)^2 \cdot (\sigma_{a_1}^2 + \sigma_{a_0}^2) + \left(\frac{\Delta b}{\Delta E}\right)^2 \cdot (\sigma_{b_1}^2 + \sigma_{b_0}^2)} \quad (2)$$

where ΔL , Δa , and Δb are the differences between the values obtained on the same sample before and after each step, and L_0 , A_0 , b_0 correspond to the values obtained before the application or aging, while L_1 , a_1 , b_1 are referred to the colorimetric coordinates obtained by measuring the mock-ups after the application or the aging.

In the Heritage Science field, it is assumed that, when the ΔE values are higher than 3, the chromatic difference is visibly detectable to the naked eye [52].

2.8. Gloss measurements

The gloss of the unaged, aged, treated and untreated mock-ups was evaluated using a glossmeter (Novo-Gloss Trio 20/60/85 Glossmeter, Rhopoint Instruments Ltd., UK). The measurement area is 4.4 mm × 44 mm. Gloss is measured in gloss units (GU). Initially, the specular reflection was measured at an incident angle of 60°, which is the standard measurement angle. However, since the gloss values for each sample were below 10 GU, the measurement angle of 85° was selected, as this angle is known to provide better resolution for low gloss surfaces [53]. Measurements were conducted three times for each of the three replicates of each mock-up.

2.9. Film properties

The hydrophobicity of the coating was measured on the mock-ups following the UNI EN 15802 document [54], by measuring the static contact angle formed by a water droplet on the surface. The procedure is recorded by a Canon EOS 60D camera, with a 100 mm f/2.8 Macro lens. The image processing was carried out with *ImageJ* software by using the *Contact angle* plug-in. The results are presented as the mean of 10 repetitions conducted on each sample, with the data dispersion calculated as the standard deviation. The water capillary absorption of both treated and untreated mock-ups was measured following the procedure outlined in the UNI EN 15801 regulation [55]. The results reflect the mean value obtained from three replicates of each sample.

Additionally, the water vapor permeability was measured on concrete mock-ups according to the steps specified in the UNI EN 15803 document [56]. Even in this case, the results reflect the mean value obtained from three replicates of each sample.

The Scotch Tape Test [58,59] was conducted on the surface of various concrete mock-ups to assess the adhesion of the Chs and Chs-NS films once applied on the mock-ups. A 3 M Magic tape™ was employed and each strip was weighed using an analytical scale and then applied to cover 10 cm² of the mock-up's surface. The tape was peeled off at a 90° angle one minute after application and weighed again. The decohesion factor (DCF) was calculated to assess the adhesion properties of the coating films on the concrete surfaces using the following equation:

$$DCF = \frac{W_1 - W_0}{S} \quad (3)$$

where W_0 and W_1 are the weights (in mg) of the same strip before and after application on the surface, respectively, and S is the area (in cm²) of the tape application. The results were calculated as the mean value of the measurements on three replicates of each sample. On each replicate, 3 measurements were performed. The uncertainty of the measurement is represented as the standard deviation.

3. Results and discussion

3.1. Coating preparation

The Chs coating prepared through the protocol described in the previous section (2.1) results in a transparent and colourless solution. In particular, the washing procedure of the chitosan powder already described previously [26] had a positive impact on the clear and colourless appearance of the solution. Chs is soluble in acidic media and,

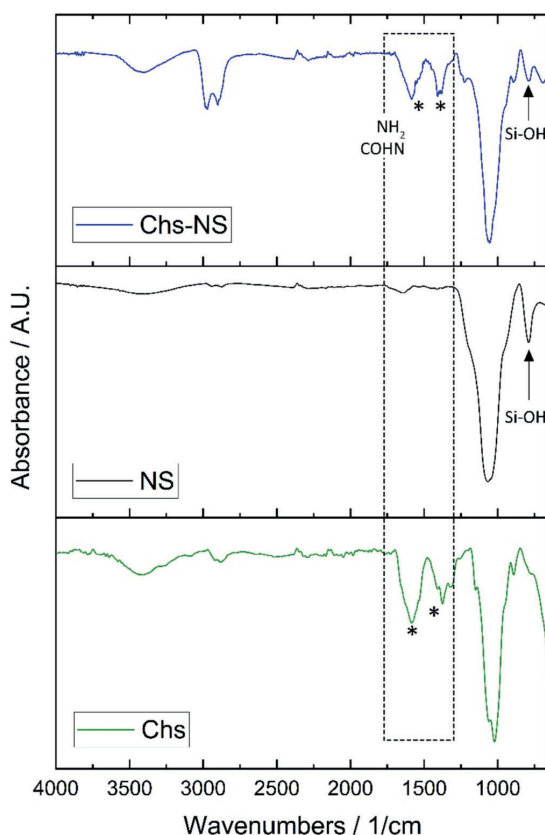


Fig. 1. ATR-FTIR spectra of the coating films.

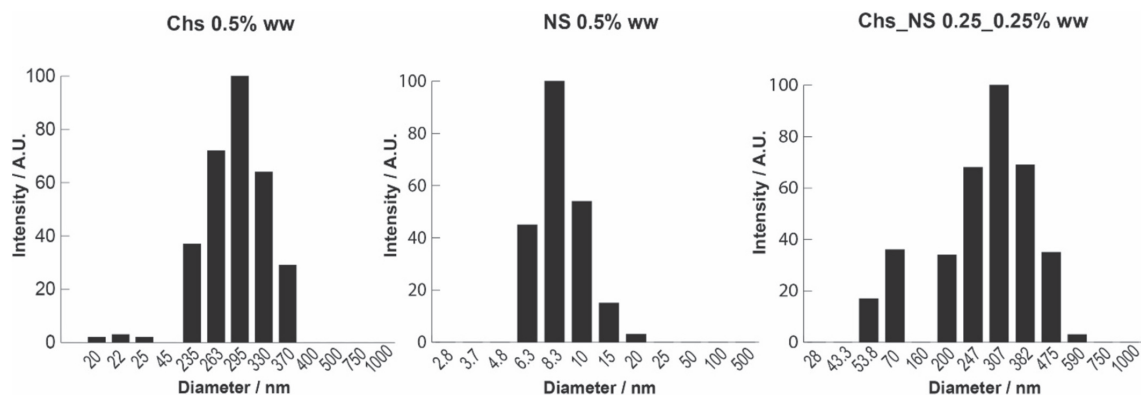


Fig. 2. DLS intensity-weighted plots measured for Chitosan (0.5 % ww), Nanosilica (0.5 % ww), and Chs/NS (0.25 %/0.25 % ww).

usually, after its solubilization its pH is raised using NaOH aqueous solutions [33]. In this study, we opted for a dialysis process to avoid the introduction of other materials into the solution which would lead to the formation of harmful salts for the conservation of stones and building materials in general. Also, Chs films obtained after the evaporation of the solution are transparent and colourless, as well as the Chs-NS ones. The Chs-NS mass ratio equal to 1 resulted in the most suitable composition to have a transparent solution and film.

3.2. Exploring the interactions of chitosan and nanosilica

The chemical structure of the films obtained by the single components (Chs and NS) and the hybrid one, were studied by ATR-FTIR spectra (Fig. 1).

The spectrum referred to the Chs-based film presents the following typical functional group of the polysaccharide: a broad band at 3435 cm^{-1} due to the stretching vibration of O—H groups which almost overlaps with the stretching vibration of N—H in the $3300\text{--}3150\text{ cm}^{-1}$ region [57]; the bands at 2922 and 2877 cm^{-1} attributed to the C—H symmetric and asymmetric stretching, respectively; a shoulder at 1655 cm^{-1} due to the C=O stretching of the secondary amide in acetylated units of chitosan; a broad band at 1590 cm^{-1} attributed to N—H bending of the primary amine [58]; the bands at 1411 cm^{-1} , 1378 cm^{-1} , and 1322 cm^{-1} are attributed to the C—H₂ bending, the asymmetrical C—H bending of the C—H₂ group, and the amide III band, respectively. The shoulder at 1153 cm^{-1} is attributed to the C—O—C glycosidic bond of the pyranose ring; the peaks at 1064 and 1020 cm^{-1} are due to the vibrations of C—O, C—OH, C—OC, CH₂OH, and C—O—C functional groups.

The NS spectrum presents a peak at 1050 cm^{-1} attributed to the Si—O—Si internal asymmetrical stretching; a peak at 955 cm^{-1} due to the vibration of the silanol groups Si—OH, and a peak at 808 cm^{-1} attributed to the symmetric stretching of Si—O—Si bonds [59].

As shown in Fig. 1, the spectrum of the hybrid film is likely the overlapping of the spectra of the single components, matching most of the absorption values described above and confirming the loading of NS in the Chs matrix. However, some changes are detectable in the $1700\text{--}1400\text{ cm}^{-1}$ range, due to the angular deformations of the NH₂ group at 1590 cm^{-1} and CONH group at around 1400 cm^{-1} , respectively. This phenomenon can be explained by the variation of the electric dipole moment of the NH₂ and CONH groups due to the angular deformation due to the hydrogen bonding between the silanol groups of silica and amine groups of chitosan [60]. Moreover, the decrease of the silanol groups signal at 808 cm^{-1} in the hybrid film if compared to the NS spectrum can corroborate the hypotheses of a hydrogen bonding interaction between the two components [59]. Additionally, the intense band in the $950\text{--}1190\text{ cm}^{-1}$ range in Chs spectrum becomes broader in

Table 3
Zeta-potential of Chs, NS and Chs-NS solutions.

ζ-Potential	Chs	NS	Chs-NS
Mean (mV)	51.40 ± 1.35	-11.00 ± 0.41	62.64 ± 2.55

the Chs-NS due to the Si—O—Si and Si—OH vibrations [61].

The presence of epoxy silane structures [47] on the NS surface was considered to describe the interaction between Levasil CC301 and Chs. It is well known that chitosan may give covalent bonds with epoxy silanes through a sol-gel method [62]. Moreover, several possible mechanisms may occur when chitosan and GPTMS interact. These mechanisms may include: (i) the covalent coupling of the epoxide ring to the primary amine, which forms a secondary amine; (ii) covalent coupling between the hydroxyl groups of the chitosan via the epoxy ring; (iii) condensation of silane groups with hydroxyl groups of Chs; (iv) hydrogen bonding which can occur between amine, amide, and hydroxyl groups; (v) ionic bonding between positively charged amine groups of Chs and the negatively charged silanes, and finally (vi) ionic bonds between protonated amines and negatively charged oxygen of the epoxide group [63].

Since the reactions of amine with the epoxy group on GPTMS occurred at acidic pH – as the epoxy rings open and react with hydroxyl groups of chitosan to form C—O—C bonds, or with the protonated $-\text{NH}_3^+$ groups [64,65] and the pH of Chs solution when NS is added is just about 6 – we can assume that the interactions between NS and Chs mainly consist in ionic and hydrogen bonding [66].

The Chs, NS, and Chs-NS solutions were analysed using DLS and zeta potential measurements, investigating concentration values of 0.2 % for each component. The DLS Intensity plots (Fig. 2) show that Chs exhibits a wide distribution of dimensions in the nanoscale in the $235\text{--}370\text{ nm}$ range, with the presence of some smaller structures in the $20\text{--}30\text{ nm}$ range. NS shows a monodisperse and narrow size distribution at about 10 nm , according to the data provided by the producer. The hybrid solution has a size distribution like the Chs solution with polydisperse structures in the $50\text{--}70\text{ nm}$ and $200\text{--}590\text{ nm}$ ranges. This increase of the size distribution in the hybrid system can be better explained by the data obtained by the zeta potential measurements which highlighted the positive charge of the Chs solution and the negative of the NS alone, $+51.40\text{ mV}$ and -11.00 mV , respectively (Table 3). The hybrid solution has a positive charge which results higher than the value measured in Chs. This phenomenon can be explained by hypothesizing that the biopolymer, once combined with NS, rearranges itself surrounding the silica particles increasing the exposition of the positive charges of the protonated amine groups. As shown above, Chs and NS can interact with

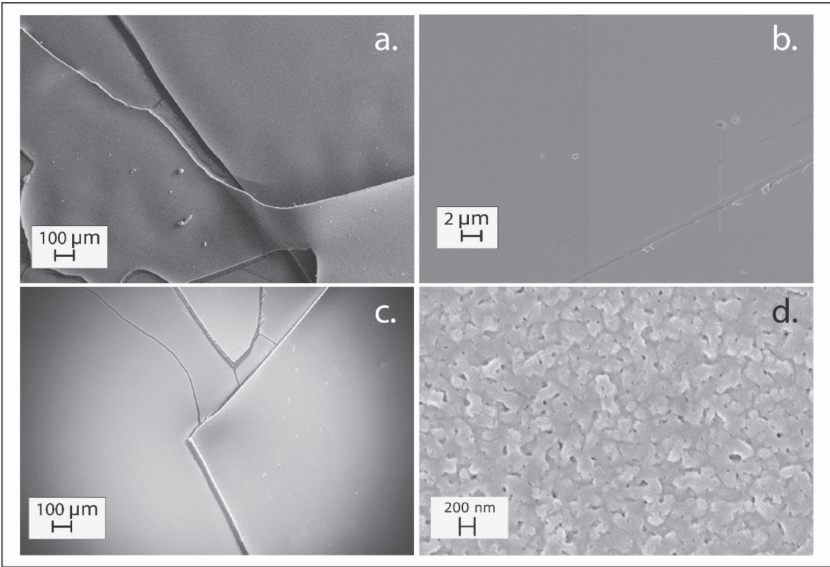


Fig. 3. SEM images of the Chs-based coating (a), and the Chs-NS film (b-d).

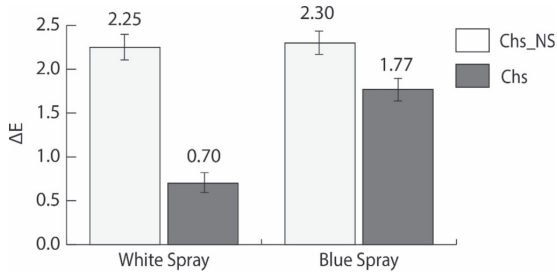


Fig. 4. Colour variations after the application of the films on the mock-ups.

each other by hydrogen bonding, thus decreasing the contribution of the negatively charged OH groups.

The surface morphology of the chitosan-based and hybrid films was observed by SEM analyses (Fig. 3). The Chs-based films show a compact, smooth, and homogeneous structure (Fig. 3a), without defects. These characteristics are also detected macroscopically as a transparent and homogeneous film is obtained. The surface of the hybrid films (Fig. 3b-d) shows a homogeneous distribution of NS within the polymeric matrix.

3.3. Film properties

The properties of Chs and Chs-NS films were evaluated through colorimetric measurements on the concrete mock-ups, and in terms of adhesion, contact angle, capillary water absorption, and water vapor permeability.

The colorimetric tests were performed on blue and white spray-painted concrete mock-ups to better assess the colour changes that occur after the application of the different coatings. The calculation of the ΔE through the equation reported in par. 2.7 allows to compare the values L , a , b coordinates of the paint colours before and after the treatment. The values obtained are reported in Fig. 4. These results demonstrate that both the coating solutions do not significantly alter the colour appearance of the acrylic spray paints applied on the mock-ups,

Table 4

Decohesion factors measured for the different concrete mock-ups.

Mock-ups	DCF (mg/cm ²)	Standard deviation
Pristine concrete		
Not treated	6.86	0.01
Chs 0.5 %	4.62	0.01
Chs-NS 0.25–0.25 %	3.26	0.01
Blue Spray		
Not treated	4.7	0.01
Chs 0.5 %	3.22	0.01
Chs-NS 0.25–0.25 %	2.18	0.04
White Spray		
Not treated	4.58	0.05
Chs 0.5 %	2.58	0.01
Chs-NS 0.25–0.25 %	1.86	0.01

since the ΔE always results lower than 3, which makes the potential application of these coatings on street artworks safe, from the aesthetical point of view.

The Scotch tape test [67,68] was conducted on the surface of the various concrete mock-ups – both treated and untreated – to evaluate the adhesion of the coating to the substrate, and the consolidating effect of the formulations. The decohesion factor (DCF) (par. 2.9) was calculated and reported as the average of five measurements for each specimen in Table 4.

The comparative measurement of the effects of applying the Chs and Chs-NS coatings highlighted an effective performance of the treatments in terms of consolidation of the substrate. Specifically, the hybrid formulation demonstrated the best performance on both the coloured and pristine concrete specimens, followed by the Chs-based coating. The DCF in untreated concrete results were approximately 2 times higher compared to the values measured on the Chs-NS-treated mock-ups. These results confirm the improved adhesion of the coating to the substrate due to the addition of NS to the Chs solution.

Furthermore, the tests conducted to investigate the interaction between the mock-ups and the water highlighted the promising performance of the films. By comparing the results of the treated and untreated mock-ups (Fig. 5), the coatings based on Chs or Chs-NS do not impact the

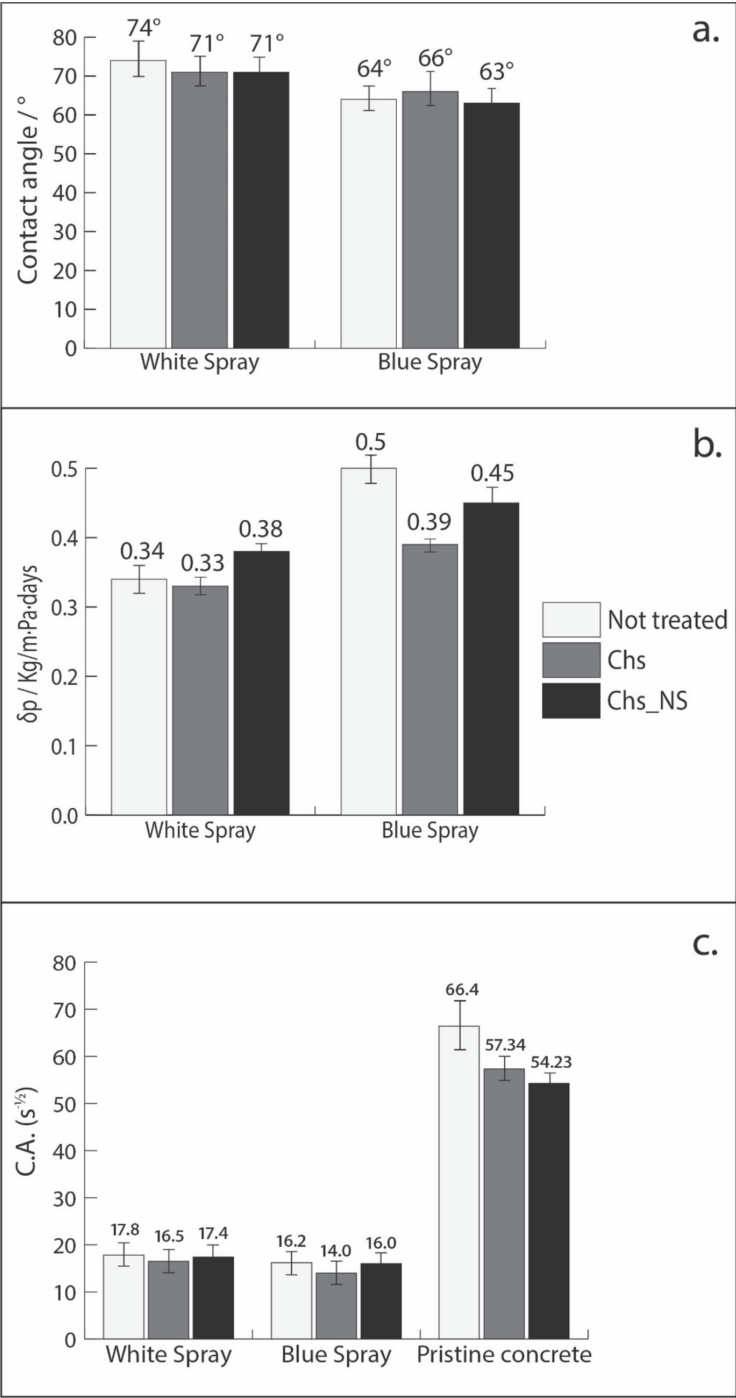


Fig. 5. Film properties measured on the mock-ups: contact angle (a.), water vapor permeability (b.), and capillary water absorption (c.)

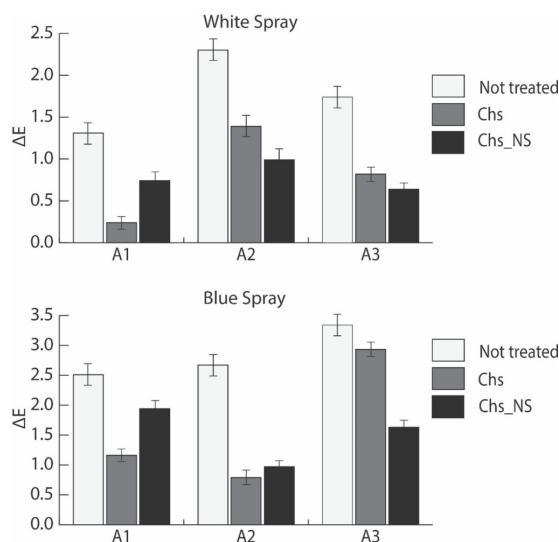


Fig. 6. Colour variation (ΔE) after the three aging tests (A1: UV–vis radiation; A2: 60 °C, 80 % RH; A3: 60 °C) of the untreated and Chs or Chs-NS-treated spray-painted mock-ups.

breathability of the substrate and its interaction with water. More in detail, the contact angle of the surface of the mock-ups slightly decreases due to the Chs and NS hydrophilicity (Fig. 5a). Even the water vapor permeability (Fig. 5b) does not significantly change after the application of the treatments. It can be noted that the exchange of water between Street-Art substrates and the environment, is already strongly impacted by the synthetic paints employed by the street artists. Thus, the application of protecting coatings that do not further affect these aspects would be preferred. Indeed, the capillary water absorption values are very similar in treated and untreated mock-ups, while the highest impact on hydrophobicity and breathability of the porous substrate is due to the application of the synthetic paint, as can be observed in Fig. 5c, by comparing the uncoloured concrete with the coloured and untreated mock-ups. In general, the application of Chs and Chs-NS coatings would not lead to further waterproofing of the substrate, leaving the permeability of the Street-Art walls unaltered.

3.4. Accelerated artificial aging effect

The long-term durability of Chs-NS and Chs-based coatings was studied through three kinds of accelerated aging tests described in paragraph 2.3. The degradation effects were analysed by FTIR-ATR analysis on Chs and Chs-NS films aged for 20 days, to detect any variation in the molecular structure of the materials. According to the literature, the main degradation phenomena that may affect Chs are depolymerization followed by deacetylation, oxidation, and interchain crosslinking [69].

Considering Chs-based film, the spectra reported in the *Supplementary Material (SM)* section (SM - Fig. 1) show a good resistance of the polysaccharide film toward photo-oxidative degradation (A1), and thermal degradation (A3) since the comparison between the aged and unaged films does not highlight any significant variation of the signals. The spectrum of the Chs exposed to hydrothermal degradation (A2) shows many variations in the signals attributed to the N–H and amide II vibrations. These phenomena can be ascribed to the interaction of the Chs with the moisture water. It is important to note that in the A2 setup,

RH is 80 % and Chs as a hydrophilic polymer can undergo structure reorganization of the molecules due to the plasticizing effect of the water molecules which can also determine the crystalline-amorphous transition impacting the molecular mobility of Chs [70,71]. As mentioned in 3.2, Chs-NS spectrum has numerous peaks and, by considering the overlapping of some signals and the complexity of the possible degradation phenomena that can affect the biopolymer, the study of the Chs-NS behaviour toward accelerated aging is a very complex issue. Moreover, the spectra of the aged hybrid films exposed to the different conditions (A1–3) only showed a slight shift in the 3000–2800 cm^{-1} range, while any significant variations of the spectra are reported in the other ranges. It is important to observe that the absorption bands in the 1260–800 cm^{-1} range belonging to the glycosidic ring, particularly the band at about 1150 cm^{-1} corresponding to the glycosidic bond - do not show any significant variation, thus it can be confirmed that no depolymerization phenomena are observed when the Chs and hybrid films are aged. Therefore, the Chs and hybrid films can be considered chemically stable for their application as protective coatings on outdoor mural paintings.

SEM images recorded after the aging test on the Chs and Chs-NS based films did not show any significant change in the morphology of the surface, and they can be observed in the SM - Fig. 2, and SM - Fig. 3.

As mentioned above (3.3), the obtained films resulted transparent and very stable also when applied on the spray-painted mock-ups, [56] and the colour variation of the coated and aged (A1–3) samples was monitored by comparing the results with the colour variation detected on aged and untreated mock-ups used as a control. The coloured concrete samples did not exhibit any visible changes after the application of coatings, even after the accelerated aging tests. The ΔE values calculated by the comparison of the colorimetric coordinates of unaged and aged samples are shown in Fig. 6. More in detail, the control mock-ups (not treated samples) always showed higher ΔE values highlighting a more severe colour variation due to the artificial aging conditions (A1–3) on the uncoated acrylic paints. By comparing the results obtained for the blue and the white spray-painted mock-ups, it can be noticed that the latter have lower ΔE . This phenomenon may be ascribed to the presence of titanium dioxide as a pigment on the white spray. TiO_2 is a well-known white pigment (PW6) employed in the coating industry, and the rutile crystalline structure shows a marked photostability due to its reducing action against the photooxidation reactions [6]. The Chs and hybrid coatings showed to have a good protective action toward the different aging conditions. The Chs-based films resulted in lower ΔE values when applied on the mock-ups exposed to the UV–vis radiation (A1). No yellowing or crack formations were detected on the film, differently from what was observed by Bussiere et al. on chitosan films exposed to thermal-photo oxidative degradation [72]. Considering the hydrothermal aging, conducted at 60 °C and RH 80 %, Chs and Chs-NS coatings showed lower and similar ΔE values, demonstrating effective protection if compared to the uncoated aged, coloured samples. Finally, the mock-ups subjected to thermal aging (A3) highlighted the effectiveness of the hybrid coating, which showed the lowest ΔE values. The aesthetic changes on the treated and untreated mock-ups after thermal aging (A3) are shown in Fig. 7. The Chs and Chs-NS coatings remain stable even when applied to concrete samples that have been coloured with acrylic spray paints, and all treated samples have ΔE values under the limit of detection of the human eye after the accelerated artificial aging. These results indicate the potential use of Chs and Chs-NS solutions for the formulation of new environmentally friendly protective products for street art.

The gloss values measured on treated, untreated, aged, and unaged mock-ups all resulted to be 0 GU. By these results, we can affirm that all the mock-ups have a matte aspect, due to their rough surfaces, and the aging and or the application of the Chs and Chs-NS coatings does not affect this characteristic.



Fig. 7. White and blue mock-ups treated and untreated after 200 days of thermal aging (A3). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

In this research, a new chitosan and nanosilica-based formulation has been developed to protect Street-Art. The hybrid material was tested on spray-painted concrete and its stability evaluated through accelerated aging tests. The preparation of the chitosan solution was improved to avoid harmful salts forming on inorganic substrates after applying the coating. The addition of nanosilica made the coating more compatible with the inorganic substrate without altering the optical properties of the applied coating. The interaction between chitosan and nanosilica was examined using different analytical techniques, revealing a stable hybrid dispersion. The coating protects against UV-visible light radiation, temperature, and humidity, preserving vibrant colours. The breathability of the substrate is maintained even after the application of the coating and the addition of nanosilica to the biopolymer films enhanced the adhesion of the protective coating to the substrate. These results are a significant step toward a sustainable coating for outdoor murals, which requires specific materials and approaches for conservation.

CRedit authorship contribution statement

Chiara Cianci: Writing – original draft, Methodology, Investigation. **Fabrizio Andriulo:** Methodology, Conceptualization. **Rodorigo Giorgi:** Writing – review & editing, Supervision, Project administration,

Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors wish to express their sincere gratitude to Ervin Cinti (Torchiani s.r.l.) for providing the Levasil products. Dr. Andrea Casini is kindly acknowledged for assistance with the SEM measurements and Dr. Serena Morrocchesi and Elisa Gualini for helping with aging tests. The publication was contributed by a researcher (FA) with a research contract in the framework of CHANGES project, funded by the European Union-PNRR NextGenerationEU in accordance with Article 24, paragraph 3a of Law No. 240 of December 30, 2010, as amended and Ministerial Decree No. 1365 of November 8, 2022. CSGI is also acknowledged for partly funding this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2024.109026>.

Data availability

Data will be made available on request.

References

- [1] T. Sawicki, The conservation of murals – a new trend in protecting works of art, *Acta Universitatis Lodzensis. Folia Philosophica. Ethica-Aesthetica-Practica* (2022) 81–95, <https://doi.org/10.18778/0208-6107.40.04>.
- [2] L. Rainer, T.J. Paul, G. Trust, The conservation of outdoor contemporary murals, *Conservation; The Getty Conservation Institute: Los Angeles, CA, USA* 8 (2003) 4–9.
- [3] E.G. Gayo, From post-graffiti to contemporary mural art, *SAUC - Street Art and Urban Creativity* 3 (2017) 26–28. doi:10.25765/SAUC.V3I1.60.
- [4] L. Rivaroli, P. Moretti, A. Caricchio, A. Macchia, Mural art conservation data recording (Scima): the graart project, *Heritage* 4 (2021) 4222–4232, <https://doi.org/10.3390/heritage4040232>.
- [5] J. La Nasa, B. Campanella, F. Sabatini, A. Rava, W. Shank, P. Lucero-Gomez, D. De Luca, S. Legnaioli, V. Palleschi, M.P. Colombini, I. Degano, F. Modugno, 60 years of street art: a comparative study of the artists' materials through spectroscopic and mass spectrometric approaches, *J. Cult. Herit.* 48 (2021) 129–140, <https://doi.org/10.1016/j.culher.2020.11.016>.
- [6] L. Pagnin, N. Guarnieri, F.C. Izzo, S. Goidanich, L. Toniolo, Protecting street art from outdoor environmental threats: what are the challenges? *Coatings* 13 (2023) 2044, <https://doi.org/10.3390/coatings13122044>.
- [7] G. Germinario, L.D. van der Werf, L. Sabbatini, Chemical characterisation of spray paints by a multi-analytical (Py/GC-MS, FTIR, μ -RAM) approach, *Microchem. J.* 124 (2016) 929–939, <https://doi.org/10.1016/j.microc.2015.04.016>.
- [8] M. Baglioni, G. Poggi, Y. Jaidar Benavides, F. Martínez Camacho, R. Giorgi, P. Baglioni, Nanostructured fluids for the removal of graffiti – a survey on 17 commercial spray-can paints, *J. Cult. Herit.* 34 (2018) 218–226, <https://doi.org/10.1016/j.culher.2018.04.016>.
- [9] G. Pellis, M. Bertasa, C. Ricci, A. Scarcella, P. Croveri, T. Poli, D. Scalzone, A multi-analytical approach for precise identification of alkyd spray paints and for a better understanding of their ageing behaviour in graffiti and urban artworks, *J. Anal. Appl. Pyrolysis* 165 (2022), <https://doi.org/10.1016/j.jaap.2022.105576>.
- [10] T.J.S. Learner, *Analysis of Modern Paints*, Los Angeles, California, 2004.
- [11] E.M. Alonso-Villar, T. Rivas, J.S. Pozo-Antonio, Sol-silicate versus organic paints: durability after outdoor and ultraviolet radiation exposures, *Prog. Org. Coat.* 168 (2022) 106843, <https://doi.org/10.1016/j.porgcoat.2022.106843>.
- [12] E.M. Alonso-Villar, T. Rivas, J.S. Pozo-Antonio, Resistance to artificial daylight of paints used in urban artworks, Influence of paint composition and substrate, *Prog. Org. Coat.* 154 (2021), <https://doi.org/10.1016/j.porgcoat.2021.106180>.
- [13] O. Chiantore, L. Trossarelli, M. Lazzari, Photooxidative degradation of acrylic and methacrylic polymers, *Polymer (Guildf)* 41 (2000) 1657–1668, [https://doi.org/10.1016/S0032-3861\(99\)00349-3](https://doi.org/10.1016/S0032-3861(99)00349-3).
- [14] F.C. Izzo, E. Balliana, E. Perra, E. Zendri, Accelerated Ageing Procedures to Assess the Stability of an Unconventional Acrylic-Wax Polymeric Emulsion for Contemporary Art, *Polymers* 2020, Vol. 12, Page 1925 12 (2020) 1925. doi: <https://doi.org/10.3390/POLYM12091925>.
- [15] A. Ciccola, I. Serafini, M. Guiso, F. Ripanti, F. Domenici, F. Sciubba, P. Sostorino, A. Bianco, Spectroscopy for contemporary art: discovering the effect of synthetic organic pigments on UVB degradation of acrylic binder, *Polym. Degrad. Stab.* 159 (2019) 224–228, <https://doi.org/10.1016/j.POLYMEDEGRADSTAB.2018.11.027>.
- [16] A. Timoncini, E. Brattich, E. Bernardi, C. Chiavari, L. Tositti, Safeguarding outdoor cultural heritage materials in an ever-changing troposphere: challenges and new guidelines for artificial ageing test, *J. Cult. Herit.* 59 (2023) 190–201, <https://doi.org/10.1016/J.CULHER.2022.12.003>.
- [17] Conservation of Art in Public Spaces (CAPUS)-Illustrated Glossary, (n.d.). <https://www.capusproject.eu/glossary/> (accessed March 4, 2024).
- [18] O. García, K. Malaga, Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on cultural heritage porous materials, *J. Cult. Herit.* 13 (2012) 77–82, <https://doi.org/10.1016/j.culher.2011.07.004>.
- [19] A. Artesani, F. Di Turo, M. Zucchelli, A. Travaglia, Recent advances in protective coatings for cultural heritage—an overview, *Coatings* 10 (2020), <https://doi.org/10.3390/coatings10030217>.
- [20] Y. Ocak, A. Sofuoğlu, F. Tihminlioglu, H. Böke, Protection of marble surfaces by using biodegradable polymers as coating agent, *Prog. Org. Coat.* 66 (2009) 213–220, <https://doi.org/10.1016/j.porgcoat.2009.07.007>.
- [21] M. Frediani, L. Rosi, M. Camaiti, D. Berti, A. Mariotti, A. Comucci, C. Vannucci, I. Malesci, Polylactide/Perfluoropolyether block copolymers: potential candidates for protective and surface modifiers, *Macromol. Chem. Phys.* 211 (2010) 988–995, <https://doi.org/10.1002/MACP.201000034>.
- [22] S. Andreotti, E. Franzoni, P. Fabbri, P. Fabbri, Poly(hydroxyalkanoate)s-based hydrophobic coatings for the protection of stone in cultural heritage, *Materials* 11 (2018), <https://doi.org/10.3390/ma11010165>.
- [23] J.L. Vidal, T. Jin, E. Lam, F. Kerton, A. Moores, Blue is the new green: valorization of crustacean waste, *Current Research in Green and Sustainable Chemistry* 5 (2022) 100330, <https://doi.org/10.1016/j.crgsc.2022.100330>.
- [24] R.C. Goy, D. De Britto, O.B.G. Assis, A review of the antimicrobial activity of chitosan, *Polímeros* 19 (2009) 241–247, <https://doi.org/10.1590/S0104-14282009000300013>.
- [25] N. Morin-Crini, E. Lichtfouse, G. Torri, G. Crini, Applications of Chitosan in Food, Pharmaceuticals, Medicine, Cosmetics, Agriculture, Textiles, Pulp and Paper, Biotechnology, and Environmental Chemistry, *Environmental Chemistry Letters* 2019 17 4 (2019), 1667–1692, <https://doi.org/10.1007/s10311-019-00904-X>.
- [26] C. Giuliani, M. Pascucci, C. Riccucci, E. Messina, M. Salzano de Luna, M. Lavorgna, G.M. Ingo, G. Di Carlo, Chitosan-based coatings for corrosion protection of copper-based alloys: a promising more sustainable approach for cultural heritage applications, *Prog. Org. Coat.* 122 (2018) 138–146, <https://doi.org/10.1016/j.porgcoat.2018.05.002>.
- [27] F. Boccazzini, C. Giuliani, M. Pascucci, C. Riccucci, E. Messina, M.P. Staccioli, G. M. Ingo, G. Di Carlo, Toward a green and sustainable silver conservation: development and validation of chitosan-based protective coatings, *Int. J. Mol. Sci.* 23 (2022) 14454, <https://doi.org/10.3390/IJMS232214454/S1>.
- [28] E. Ardelean, D. Asandei, G. Asachi, E. Bobu, R. Nicu, Carboxymethyl-Chitosan as Consolidation Agent for Old Documents on Paper Support. <https://www.researchgate.net/publication/268432618>, 2009.
- [29] E. Salim, W.S. Mohamed, R. Sadek, Evaluation of the efficiency of traditional chitosan, nano chitosan and chitosan nanocomposites for consolidating aged papyrus paper, *Pigm. Resin Technol.* (2022), <https://doi.org/10.1108/PRT-06-2022-0079>.
- [30] F. Ciolacu, R. Nicu, T. Balan, E. Bobu, Chitosan derivatives as bio-based materials for paper heritage conservation, *Bioresources* 12 (2017) 735–747, <https://doi.org/10.15376/biores.12.1.735-747>.
- [31] J.M.K. Wakefield, S. Braovac, H. Kutzke, R.A. Stockman, S.E. Harding, Tert-butylidimethylsilyl chitosan synthesis and characterization by analytical ultracentrifugation, for archaeological wood conservation, *Eur. Biophys. J.* 49 (2020) 781–789, <https://doi.org/10.1007/s00249-020-01450-z>.
- [32] M. Christensen, H. Kutzke, F.K. Hansen, New materials used for the consolidation of archaeological wood-past attempts, present struggles, and future requirements, *J. Cult. Herit.* 13 (2012), <https://doi.org/10.1016/j.culher.2012.02.013>.
- [33] M. Bassi, E. Sassoni, E. Franzoni, Experimental study on an innovative biopolymeric treatment against salt deterioration of materials in cultural heritage, *Front Mater* 8 (2021), <https://doi.org/10.3389/fmats.2021.583112>.
- [34] S. Andreotti, E. Franzoni, P. Fabbri, P. Fabbri, Poly(hydroxyalkanoate)s-Based Hydrophobic Coatings for the Protection of Stone in Cultural Heritage, *Materials* 2018, Vol. 11, Page 165 11 (2018) 165. doi: <https://doi.org/10.3390/M11010165>.
- [35] S. Andreotti, E. Franzoni, E. Ruiz-Agudo, G.W. Scherer, P. Fabbri, E. Sassoni, C. Rodríguez-Navarro, New polymer-based treatments for the prevention of damage by salt crystallization in stone, *Materials and Structures/Materiaux et Constructions* 52 (2019), <https://doi.org/10.1617/s11527-018-1309-6>.
- [36] R. Lamuraglia, A. Campostrini, E. Ghedini, A. De Lorenzi Pezzolo, A. Di Michele, G. Franceschini, F. Menegazzo, M. Signoretto, A. Travaglia, A new green coating for the protection of frescoes: from the synthesis to the performances evaluation, *Coatings* 13 (2023), <https://doi.org/10.3390/coatings13020277>.
- [37] L. Indrie, M. Bonet-Arakil, D.C. Ilies, A.V. Albu, G. Ilies, G.V. Herman, Ștefan Baias, M. Costea, Heritage ethnographic objects - Antimicrobial effects of chitosan treatment, *Industria Textila* 72 (2021) 284–288, <https://doi.org/10.35530/IT.072.03.1812>.
- [38] H. Haghighi, F. Licciardello, P. Fava, H.W. Siesler, A. Pulvirenti, Recent advances on chitosan-based films for sustainable food packaging applications, *Food Packag. Shelf Life* 26 (2020), <https://doi.org/10.1016/j.fpsl.2020.100551>.
- [39] S.P. Miguel, A.F. Moreira, I.J. Correia, Chitosan based-asymmetric membranes for wound healing: a review, *Int. J. Macromol.* 127 (2019) 460–475, <https://doi.org/10.1016/j.ijbiomac.2019.01.072>.
- [40] A.B. da Silva, K.B. Rufato, A.C. de Oliveira, P.R. Souza, E.P. da Silva, E.C. Muniz, B. H. Vilsinski, A.F. Martins, Composite materials based on chitosan/gold nanoparticles: from synthesis to biomedical applications, *Int. J. Biol. Macromol.* 161 (2020) 977–998, <https://doi.org/10.1016/j.ijbiomac.2020.06.113>.
- [41] X. Ji, H. Shao, X. Li, M.W. Ullah, G. Luo, Z. Xu, L. Ma, X. He, Z. Lei, Q. Li, X. Jiang, G. Yang, Y. Zhang, Injectable immunomodulation-based porous chitosan microspheres/HPCH hydrogel composites as a controlled drug delivery system for osteochondral regeneration, *Biomaterials* 285 (2022), <https://doi.org/10.1016/j.biomaterials.2022.121530>.
- [42] Q. Meng, S. Zhong, J. Wang, Y. Gao, X. Cui, Advances in chitosan-based microcapsules and their applications, *Carbohydr. Polym.* 300 (2023), <https://doi.org/10.1016/j.carbpol.2022.120625>.
- [43] A. Balakrishnan, A.G.F. Thottian, K. Govind Babu, P. Kumar, Drug susceptibility testing of circulating lung cancer cells for personalized treatment, *Med. Oncol.* 40 (2023), <https://doi.org/10.1007/s12032-022-01860-3>.
- [44] M. Ul-Islam, K.F. Alabbosh, S. Manan, S. Khan, F. Ahmad, M.W. Ullah, Chitosan-based nanostructured biomaterials: synthesis, properties, and biomedical applications, *Advanced Industrial and Engineering Polymer Research* 7 (2024) 79–99, <https://doi.org/10.1016/j.aiepr.2023.07.002>.
- [45] T.V. Podust, T.V. Kulik, B.B. Palyantysya, V.M. Gun'ko, A. Tóth, L. Mikhalevskaya, A. Menyhárd, K. László, Chitosan-nanosilica hybrid materials: preparation and properties, *Appl. Surf. Sci.* 320 (2014) 563–569, <https://doi.org/10.1016/j.apsusc.2014.09.038>.
- [46] V.T. Nguyen, H.D. Phi, H.D. Phi, T. Van Trinh, T. Van Trinh, P. Van Mac, P. Van Mac, H.A. Nguyen, H.A. Nguyen, H.M. Dang, H.M. Dang, L.T. Nguyen, L. T. Nguyen, T.M. Duong, T.M. Duong, Effect of silica nanoparticles on properties of coatings based on acrylic emulsion resin, *Vietnam J Sci Technol* 56 (2018) 117, <https://doi.org/10.15625/2525-2518/56/3b/12731>.
- [47] P. Greenwood, B. Gevert, Aqueous silane modified silica sols: theory and preparation, *Pigm. Resin Technol.* 40 (2011) 275–284, <https://doi.org/10.1108/03699421111176171>.

- [48] Y.J. Cao, M. Camaiti, M. Endrizzi, G. Forti, E. Vergani, I. Forti, Enhanced consolidation efficacy and durability of highly porous calcareous building stones enabled by nanosilica-based treatments, *Sci. China Technol. Sci.* 66 (2023) 2197–2212, <https://doi.org/10.1007/s11431-022-2343-y>.
- [49] B.P. Tripathi, V.K. Shahi, Functionalized organic-inorganic nanostructured N-p-carboxy benzyl chitosan-silica-PVA hybrid polyelectrolyte complex as proton exchange membrane for DMFC applications, *J. Phys. Chem. B* 112 (2008) 15678–15690, https://doi.org/10.1021/JP806337B/SUPPL_FILE/JP806337B_SI_001.PDF.
- [50] G.C. Pradhan, S. Dash, S.K. Swain, Barrier properties of nano silicon carbide designed chitosan nanocomposites, *Carbohydr. Polym.* 134 (2015) 60–65, <https://doi.org/10.1016/j.CARBPOL.2015.06.081>.
- [51] P.A. Hassan, S. Rana, G. Verma, Making sense of Brownian motion: colloid characterization by dynamic light scattering, *Langmuir* 31 (2015) 3–12, https://doi.org/10.1021/LA501789Z/ASSET/IMAGES/MEDIUM/LA-2014-01789Z_0013.GIF.
- [52] M. Bertasa, C. Ricci, A. Scarcella, F. Zenucchini, G. Pellis, P. Croveri, D. Scalapone, Overcoming challenges in street art murals conservation: a comparative study on cleaning approach and methodology, *Coatings* 10 (2020) 1–23, <https://doi.org/10.3390/coatings10111019>.
- [53] Novo-Gloss Trio 20/60/85 Glossmeter - Rhopoint instruments webpage, (n.d.). <https://www.rhopointinstruments.com/product/novo-gloss-trio-20-60-85-gloss-meter/> (accessed November 27, 2024).
- [54] UNI EN 15802:2010. Available online: <https://store.uni.com/en/uni-en-15802-2010>, (n.d.).
- [55] UNI EN 15801:2010, (2010), <https://store.uni.com/en/uni-en-15801-2010> (accessed November 25, 2024).
- [56] UNI EN 15803:2010, (2010), <https://store.uni.com/en/uni-en-15803-2010> (accessed November 25, 2024).
- [57] F. Niroomand, A. Khosravani, H. Younesi, Fabrication and properties of cellulose-nanochitosan biocomposite film using ionic liquid, *Cellulose* 23 (2016) 1311–1324, <https://doi.org/10.1007/s10570-016-0872-7>.
- [58] S.H. Lim, S.M. Hudson, Synthesis and antimicrobial activity of a water-soluble chitosan derivative with a fiber-reactive group, *Carbohydr. Res.* 339 (2004) 313–319, <https://doi.org/10.1016/j.carres.2003.10.024>.
- [59] R. Sabazoodkhiz, M. Rahmaninia, O. Ramezani, Interaction of chitosan biopolymer with silica nanoparticles as a novel retention/drainage and reinforcement aid in recycled cellulosic fibers, *Cellulose* 24 (2017) 3433–3444, <https://doi.org/10.1007/s10570-017-1345-3>.
- [60] R.C.S. da Luz, M.V.G. Paixão, R. de C. Balaban, Nanosilica-chitosan hybrid materials: preparation, characterization and application in aqueous drilling fluids, *J. Mol. Liq.* 279 (2019) 279–288, <https://doi.org/10.1016/j.molliq.2019.01.131>.
- [61] E.J. Lee, D.S. Shin, H.E. Kim, H.W. Kim, Y.H. Koh, J.H. Jang, Membrane of hybrid chitosan-silica xerogel for guided bone regeneration, *Biomaterials* 30 (2009) 743–750, <https://doi.org/10.1016/j.biomaterials.2008.10.025>.
- [62] C.P. Li, M.C. Weng, S.L. Huang, Preparation and characterization of pH sensitive chitosan/3-glycidyloxypropyl trimethoxysilane (GPTMS) hydrogels by sol-gel method, *Polymers (Basel)* 12 (2020) 1326, <https://doi.org/10.3390/POLYM12061326>.
- [63] L.S. Connell, F. Romer, M. Suárez, E.M. Valliant, Z. Zhang, P.D. Lee, M.E. Smith, J. V. Hanna, J.R. Jones, Chemical characterisation and fabrication of chitosan-silica hybrid scaffolds with 3-glycidyloxypropyl trimethoxysilane, *J. Mater. Chem. B* 2 (2014) 668–680, <https://doi.org/10.1039/c3tb21507e>.
- [64] S. Deville, E. Saiz, R.K. Nalla, A.P. Tomsia, Freezing as a path to build complex composites, *Science* 311 (2006) 1515–1518, <https://doi.org/10.1126/science.1120937>.
- [65] J.G. Varghese, R.S. Karuppannan, M.Y. Kariduraganavar, Development of hybrid membranes using chitosan and silica precursors for pervaporation separation of water + isopropanol mixtures, *J. Chem. Eng. Data* 55 (2010) 2084–2092, <https://doi.org/10.1021/jc9003993>.
- [66] L.S. Connell, F. Romer, M. Suárez, E.M. Valliant, Z. Zhang, P.D. Lee, M.E. Smith, J. V. Hanna, J.R. Jones, Chemical characterisation and fabrication of chitosan-silica hybrid scaffolds with 3-glycidyloxypropyl trimethoxysilane, *J. Mater. Chem. B* 2 (2014) 668–680, <https://doi.org/10.1039/c3tb21507e>.
- [67] G. Torracca, P. Mora, Fissatvi per pitture murali, *Bollettino Dell'Istituto Centrale Del Restauro* (1965) 109–132.
- [68] M. Drdáký, J. Lesák, S. Rescic, Z. Slížková, P. Tiano, J. Valach, Standardization of peeling tests for assessing the cohesion and consolidation characteristics of historic stone surfaces, *Materials and Structures/Materiaux et Constructions* 45 (2012) 505–520, <https://doi.org/10.1617/s11527-011-9778-x>.
- [69] E. Szymańska, K. Winnicka, Stability of chitosan - a challenge for pharmaceutical and biomedical applications, *Mar. Drugs* 13 (2015) 1819–1846, <https://doi.org/10.3390/md13041819>.
- [70] M. Kurek, A. Guinault, A. Voilley, K. Galić, F. Debeaufort, Effect of relative humidity on carvacrol release and permeation properties of chitosan based films and coatings, *Food Chem.* 144 (2014) 9–17, <https://doi.org/10.1016/j.foodchem.2012.11.132>.
- [71] I. Yakimets, S.S. Paes, N. Wellner, A.C. Smith, R.H. Wilson, J.R. Mitchell, Effect of water content on the structural reorganization and elastic properties of biopolymer films: a comparative study, *Biomacromolecules* 8 (2007) 1710–1722, <https://doi.org/10.1021/bm070050x>.
- [72] P.O. Bussiere, J.L. Gardette, G. Rapp, C. Masson, S. Therias, New insights into the mechanism of photodegradation of chitosan, *Carbohydr. Polym.* 259 (2021), <https://doi.org/10.1016/j.carbpol.2021.117715>.