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Review

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Protecting Street Art from Outdoor Environmental Threats: What Are the Challenges?

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Abstract: Street Art is an artistic expression in constant development, whose interest has grown in recent years among society, public administrations, conservators, and heritage scientists. This growing awareness has given rise to a series of debates between professionals with the intent to expand the knowledge relating to conservation practices and possible protection solutions. Additionally, the paint materials used by contemporary artists are in constant development; therefore, difficulty has emerged in the identification of their degradation processes when exposed to environmental conditions and in the consequent selection of a specific protection system. This review presents an overview of the recent literature and experiences in the field of knowledge and preservation of Street Art, focusing on the type and nature of paint formulations, the main deterioration processes of painted artworks in outdoor conditions, and the most recent advances in materials and methods for the conservation and protection of Street Art. This review aims to emphasise how the approach to the challenge of preservation of Street Art is complex, aspiring to the need for optimised diagnostic protocols for the development of innovative and effective protective coatings. This paper is a starting point to provide suggestions and indications for the development of further research projects within the framework of preservation and protection of contemporary muralism.

Keywords: street art; contemporary muralism; conservation; protective coatings; anti-graffiti; painting materials; deterioration

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1. Introduction

Nowadays, through the streets of many cities in the world, it is quite common to see examples of contemporary muralism, an extremely versatile form of painting, full of social and cultural significance, with the intent to be accessible to everyone [1].

Since the 1960s, this artistic movement was recognised with the name of Street Art, bringing a very strong and significant spirit of social revenge. In fact, it focused on the principle of rebellion as the very essence of the movement, based on protest, provocation, and the idea of fighting the system by going against the law. However, since the 1980s, the artistic activity linked to Street Art began to change. Artists started to focus on social themes, merging them with the urban lifestyle of the city with the purpose of astonishing with impactful artworks. These works of art began to have a correlation to contemporary visual art practices, and thus taking the name of Urban Art [2,3].

For this reason, Urban Art was decreasingly perceived as vandalism, and recently, it has been recognised as an established and growing form of art [4]. With their artworks, street artists still want to express their political, ethical, and social idea/issue, which is aimed at being handed down from the current population to the future one [5]. In this way, they contribute to the aesthetic and ethical enrichment of the urban space thanks to the extraordinary communicative power of Urban Art [6]; the citizens gained a new artistic awareness, beginning to appreciate the themes and the pictorial techniques, with the consequent renewal and improvement of popular-class blocks and more critical neighbourhoods. The artistic messages of this type of artwork are expressed using the wall as substrate, experimenting with a wide variety of painting techniques. The choice of painting on external walls is a necessity to extend the accessibility of these artworks to the majority of the population [5,7]. The history of outdoor murals began in the 20th century, with the first appearances in Mexico, followed by the Chicano mural movement in the late 1960s [1,8]. As mentioned above, the great impact of Street Art as a socially recognised artistic expression has given, and still gives, artists the opportunity to produce murals on a large scale, developing what is known as contemporary muralism [9,10]. This phenomenon met the interest of administrations, municipalities, and private individuals who began to take an active part in the realisation of these artworks (in some cases by commissioning the artworks themselves or by providing the necessary painting materials), but also by starting to take care of them, with prevention and conservation activities over time [5,8].

However, conservation practices for such artworks are challenging. Since it is a new preventive topic, there are no defined and assessed conservative and protective procedures. Although street artists are supported by public administrations and increasingly by society, their artistic expressions are often realised on the façades of buildings in decay or not well maintained, with the risk of being replaced at any time by other street artists. On the other hand, according to some artists' interviews, like those mentioned by Cadetti [1], artists themselves do not always think about the future of their artworks in terms of durability and conservation practices. Actually, in order to improve the preservation of contemporary murals, the involvement of artists from the very beginning would be a winning strategy [11].

The first discussions about this topic contributed to opening a dialogue among artists, conservators, municipalities, heritage scientists, and material suppliers. Awareness emerged among artists due to the various artistic techniques and the continuous changes in the formulation and quality of paint materials. This aspect is important because it brings to light a series of problems related to the adequate selection of restoration, conservation, and protection practices of contemporary mural artworks. The latter is particularly controversial for several reasons: the ethical aspect related to the artists will be about the destiny of the artwork, the economic and legal aspect related to conservation and protection practices, and the outdoor location where these artworks are exposed [12]. The last point is linked to the inevitable atmospheric degradation process of the artistic materials employed, a factor yet to be fully investigated and understood. An example of the different aspects still to be studied is the role of the substrate. It generally comprises plasters and mortars that, if not adequately prepared, can make the compatibility with the pictorial materials difficult, jeopardising their correct adhesion and over time favouring degradation phenomena such as cracks, water infiltrations, and atmospheric particulate deposits [13]. The chemical nature of the materials, their quality, and the constant interaction with the atmospheric environment are important factors to define distinct strategies for the protection of contemporary mural artworks.

The possibility of prolonging the life of contemporary murals is based on a twofold activity: on the one hand, the realisation of digital archives and, on the other hand, the conservation or restoration activities aimed at stopping or reducing the materials from ageing and alteration. Concerning the realisation of digital archives, it essentially comprises cataloguing and documenting urban mural artworks (including a specific activity of condition report). It should be noted that for such an important activity there is not yet a specific standard approach, and the development of standard cataloguing protocols is in progress, through various international research projects [5]. Collecting thorough, comprehensive information material will be the basis for the creation of a reliable digital archive and, more generally, knowledge about these kinds of mural paintings.

Regarding the possibility of reducing the deterioration kinetic of painting materials by acting directly on the painting surfaces through restoration interventions, many authors have commented on the distinctive condition of contemporary murals, according to which they are not yet defined as cultural heritage, and therefore may not deserve active conservation by any means. Indeed, the ephemeral character of these artworks is often invoked, while some conservators [14] affirm that "*the goal to achieve their material integrity and legibility, at least while the generation that created them is alive*" should be pursued vigorously.

The present review aims at presenting the state of the art of the research and practice related to the degradation and conservation of street art materials, focusing on the possibility of using protective coating systems, as reported in recent scientific literature.

The review considers the most commonly used classes of protective products and presents both laboratory and in situ research experiences reported in the literature. It is important to highlight that the scientific literature on this topic is still quite limited. This review collects the most recent studies and scientific evaluations and aims at highlighting the needs and critical points for the development of protective materials and the optimisation of suitable conservation practices.

2. Research Projects and Debates about Contemporary Muralism

In the last two decades, a very active debate about the peculiarities and needs related to contemporary murals has arisen (Figure 1).

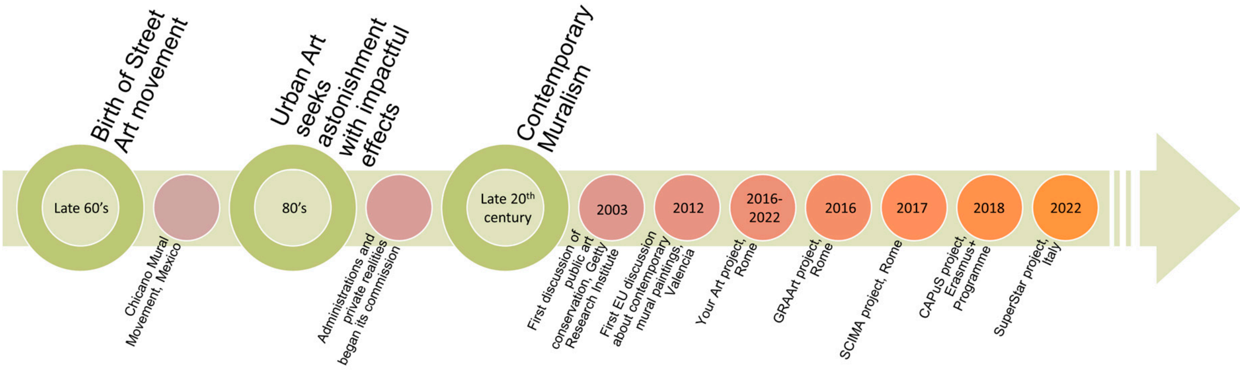

Figure 1. Schematic timeline listing the main debates and research projects regarding the preservation of Street Art over the years.

One of the first debates related to the art conservation in public places occurred in 2003 at the Getty Research Institute in Los Angeles (USA) [8]. The debate was initially centred on the lack of attention paid to the maintenance and preservation of these contemporary murals which, in most cases, are not even included in the maintenance plan due to the limited availability of funds. Therefore, one of the most relevant questions that was discussed is: who is responsible for this public art? During the debate, it became clear that there is no single person/institution responsible as the committee requesting the artwork may not have the resources to maintain it, the owner of the building may not have the interest in preserving it and, the artist (if alive) owns the copyright of its artwork; therefore, he/she could decide both to repaint it or to let it degrade according to his/her wishes.

Another question was: should conservation follow the strict guidelines used in museum environments? Considering that, as previously discussed, different professionals/institutions are typically responsible for the fate of a specific contemporary mural, this issue is still under discussion case by case. The objectives of restoration practices and their suitability are not easily defined, in some cases, the main aim is the stabilisation of the painting on the wall support, while in others the focus is on the restoration of the artwork's original colour with the risk of erasing its historical value [7,8,10].

Although the questions addressed did not always have a single answer, the key concept that emerged from this initial discussion was that a balanced collaboration is vital to the preservation of a contemporary mural, and therefore it is necessary to cultivate and strengthen relationships between artists, conservators, and art curators, starting from the moment of the mural's creation and long before conservation action is needed.

Also, this issue has begun to be addressed at the EU level. One of the first European discussions on Street Art conservation was held in 2012 at the University of Valencia (Spain) with the conference titled "Modern and Contemporary Mural Painting: Conservation, Treatment and Access". This event resumed the previous American debate and updated the issue related to the restoration of murals, focusing the attention on the need to maintain a constant dialogue with the various professionals and to establish a more conscious approach to Street Art methodologies [12].

In conjunction with this awareness, several scientific projects were carried out in the years between 2016 and 2022, focused on the conservation and protection of street artworks combining a scientific and conservative point of view. One of these is the project called Your Art: Yococu Urban Art born from the collaboration of YOCOCU Association (YOuth in COnservation of Cultural Heritage) and M.U.Ro (Museum of Urban Art in Rome) [15]. From this project, it was possible to address the delicate issue of the relationship between the urban context and Street Art, focusing the attention on the fundamental aspects related to legal issues, the documentation of the artworks, and their conservation. A great lack of knowledge has emerged regarding the monitoring and archiving activities on street artworks, the techniques and materials used by the artists, the atmospheric conditions that significantly emphasise the degradation of the artworks, and how to intervene for their conservation and protection [15].

From these first exchanges, subsequent projects were developed, such as the GRAArt [16], another project coordinated by YOCOCU. This project was born with two fundamental objectives: first, to retrace the history of Ancient Rome through street artworks created in peripheral areas of the capital, aiming at redeveloping such areas by giving them an artistic and social identity; second, to digitally document these street artworks through the creation of an ad hoc website, useful both for the community to publicise this artistic movement, and for professionals to monitor their conservation conditions over time. In fact, the entire team of professionals involved had the chance to collaborate, share their knowledge, and discuss urban art conservation.

A later project is SCIMA (Computerised Conservation Card for Mural Art), a digitalisation project on conservation data specific for contemporary mural art [17].

Similar to the GRAArt project, SCIMA began to centralise and then virtually archive the technical information of the different contemporary murals, while constantly updating them. It aimed to develop a common lexicon and to make this tool accessible to everyone in order to describe the technical, technological, and morphological characteristics of the degradation of mural artworks.

In recent years, the CAPuS project (Conservation of Art in Public Spaces concerning Street Art), supported via the Key Action 2 (Knowledge Alliances) of the Erasmus+ Programme, [18] aimed to increase the knowledge in the field of public art conservation by encouraging the direct collaboration between the researcher and restorer, via outlining specific treatment protocols and providing a constant dissemination to institutions, to the public, and professionals [19]. The main outputs of the project were the guidelines for the conservation of public works of art, based on two themes: the study of the state of conservation of the artworks and the determination of appropriate strategies for the conservation and preservation. It was developed by combining the results both from laboratory experiments and real case studies, emphasising how the conservative approach and the practical intervention must always be case specific.

One of the main factors that emerged from all these projects (that should not be underestimated) is the importance of the exchange of knowledge born from the relationship between professionals involved in the conservation of street artworks. For this reason, the ongoing project, SuperStar—Sustainable Preservation Strategies for Street Art [20], funded by the Italian Ministry of Research and University, carried out a survey on the practice of Street Art conservation, with a series of interviews and questionnaires addressed to restorers, conservation scientists, technicians, and artists to better understand their points of view and their experiences in the field. The obtained results allowed for the orientation of the research towards specific approaches to conservation, choice of materials and methods, and specific investigation protocols. The objective of the project is to define innovative guidelines for the conservation of Street Art and to guarantee the safeguarding of its powerful social and cultural message in the urban context.

The objectives of the SuperStar project are addressed to study the properties of paint materials and to reveal the critical aspects for conservation. Also, the project propses a holistic experimental approach to the knowledge of Street Art, combining a series of non-invasive and micro-invasive spectroscopic, chromatographic, and thermo-analytic methods.

Moreover, suitable cleaning methods, protective coatings, and anti-graffiti systems are developed and tested both on site and in laboratory conditions, including artificial accelerated ageing procedures. In this context, and in close collaboration with the Municipalities of Milan and Turin (Italy), relevant case studies are being studied to develop integrated monitoring and conservation guidelines for their long-term sustainability.

3. Paint Formulations Used for Street Art

At the beginning of the 20th century, innovations in the chemical–technological field and the growing interest in new paint materials among artists led to the fast implementation of new synthetic polymers in the artistic sector [21–23]. A further development was observed in the painting technique at the beginning of "graffiti writing" and Street Art. In fact, in addition to brushes, rollers and spray cans became painting tools used in order to cover greater areas, draw large artistic subjects, and achieve desired chromatic effects [24–26]. In recent years, a technological evolution of these paint materials has been assessed, and thus making their characterisation more complex due to the constant changes in formulations by manufacturers. Moreover, street artists often replace or mix artistic products with others for industrial or domestic use to enhance specific effects. These continuous changes and variables make the diagnostic phase difficult and complicate the conservation procedures. One of the most used materials and most ascribable to the creation of street artworks is the spray can, which comprises synthetic paints and propellants (commonly butane, isobutane, or propane) that allow the paint to be spread in small droplets (aerosol), with the advantages of accelerating the drying process, and creating greater chromatic tones on different surfaces.

From the chemical point of view [27–29], synthetic paints used in spray cans mainly comprise (i) a *binder medium*, a transparent film-forming material in which the pigment particles are dispersed and, once the drying process is complete, they form the pictorial film; (ii) *pigments* which give colour to the paint; (iii) a *solvent* capable of solubilising the pigment/binder mixture; (iv) *additives*, for several different purposes and to lend specific properties to the paint layers (Figure 2) [30,31]. From recent studies on the identification of Street Art spray paint materials [32,33], the mostly used binder media are alkyd, styrene acrylic, acrylic-based resins, and vinyl emulsions. However, spray cans are not the only painting tools used by street artists. In some cases, paint cans and the application by brushes and rollers are preferred both for economic reasons, for the easier applicability that allows for spreading the product over larger areas, and for the possibility to act directly on the paint mixture obtaining the ideal colour rendering the desired results by artists. In this case, the same synthetic polymers present in the spray cans were reported also in paint cans, with the addition of acrylic, styrene acrylic, and vinyl emulsions [34,35].

Pigments in modern paints can generally be divided into inorganic and organic: inorganic pigments, are chosen for their stability over time [36], while organic pigments are chosen for their lively colours, although they are less stable (except for blue phthalocyanines [37]). As widely reported in literature, pigments can promote or reduce some degradation reactions (such as photodegradation) [38].

As previously introduced, an important component in paints (spray and cans) is the solvent. The most common are aliphatic hydrocarbons, aromatic toluene, xylene, naphthenic, or oxygenated solvents like alcohols. Ketones and esters or glycol are also used. In water-based formulations, they are present together with water and surfactants.

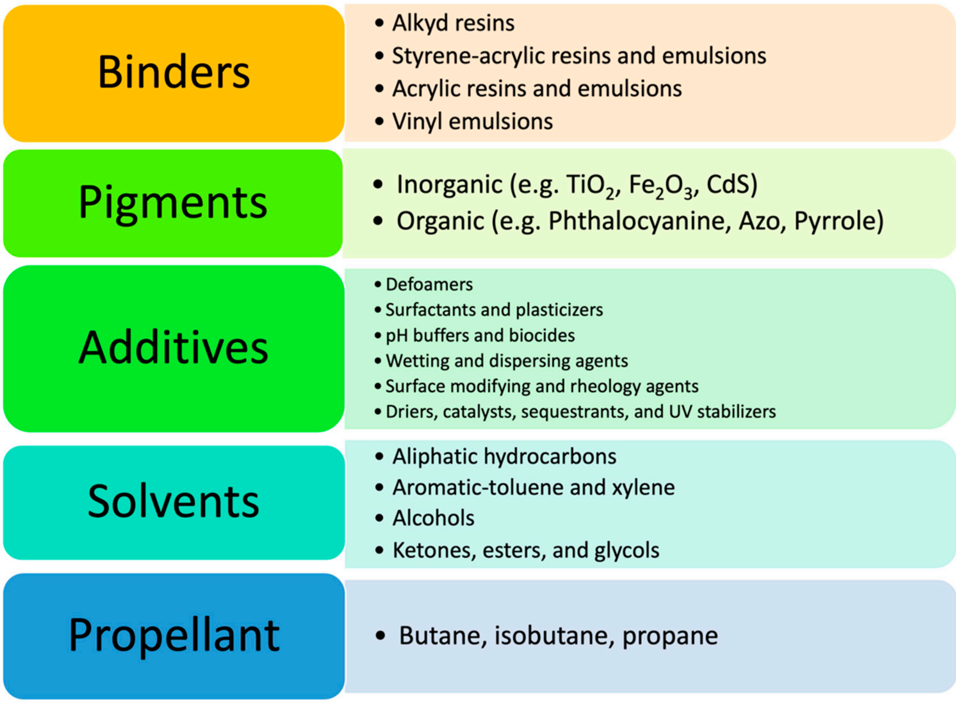

Figure 2. Schematic representation of the main components of paints used in street artworks.

Finally, various additives are added to synthetic paints, allowing for the prevention of surface morphological defects during application (e.g., bubbles, poor levelling, flocculation, sedimentation), improvement of certain properties of the paint film (e.g., chromatic homogeneity, adequate adhesion to the support, appropriate mixing), and prolonging of the paint stability to various degradation factors (e.g., thermal and UV light stability). They are added in small quantities, generally between 0.01 and 1%, and can be classified as follows [39]:

(1) Defoamers. They are generally used to reduce the tendency of the surfactant to foam; generally using mineral or silicone oils.

(2) Plasticisers. They allow for increasing the plastic properties and the fluidity of the paints. In addition, they are used to control the paint film formation process. The correct formation of the film is essential to guarantee the final paint film adhesion to the support, elasticity, and hardness [40]. Some recent examples found in alkyd paints are di-isobutyl phthalate (DIBP), diethyl phthalate (DEP), dibutyl phthalate (DBP), and in polyvinyl paints are di-iso-octyl adipate (DIOA), di-iso-butylitaconate (DITA), ethyl citrate, and the 2-ethylhexyl diester of hexanedioic acid [41].

(3) Wetting and dispersing agents. Wetting agents are additives with a polar-apolar surfactant structure and low molecular weight capable of reducing the interfacial tension between the binder and the pigment surface. On the other hand, dispersing agents are stabilising compounds which are absorbed by the pigment via establishing repulsive forces between individual pigment particles. Stabilisation is ensured by electrostatic charge repulsion or by steric hindrance due to molecular structures projecting from the pigment surface in the binder [42]. These additives can prevent the flocculation problem when different pigments are mixed in the same paint. An example of a commercial product is Disperbyk®, an alkylammonium salt of polycarboxylic acid used in water-based systems to stabilise a wide variety of pigments and fillers against flocculation [43].

(4) Surfactants. They lower the surface tension which, in the solution, leads to the adsorption of surfactants at the air–water interface. Furthermore, they can form micelles, resulting in a stabilising effect in paints. The two most studied and identified

examples in modern paints are polyethylene glycol (PEG) and polyethylene oxide (PEO) [44,45].

(5) Surface modifying agents. They are useful for regulating the difference in surface tension of the paint when applied to a support (in fact, if the paint has a higher surface tension than the support, it will be poorly wettable) and to prevent any morphological defects caused by the deposit of particulate matter. An example is the use of silicone additives [39].

(6) Rheology additives. Also called thickeners, they allow for the improvement of the viscosity of the paint work by polymer chain entanglement and hydrogen bonding with water molecules. Cellulose derivatives are the most common group.

(7) Driers and catalysts. They allow for the acceleration of the drying process of the paints. Dryers are generally organometallic compounds, where the active part (the metal) is generally represented by cobalt and manganese (primary dryers), lead, calcium, zinc, zirconium, and barium (secondary dryers).

(8) Preservatives. Biocides are added to prevent microbial growth on the dried polymeric film.

(9) pH buffers. They can stabilise the pH range (e.g., ammonia).

(10) Freeze-thaw agents. They lower the freezing point of the system as the water component in the polymer can freeze, expand in volume, and damage the polymeric film. For this purpose, water-soluble solvents, such as ethylene glycol or propylene glycol, are added.

(11) Sequestrants. They are used for the removal of metal ions in the paint mixture during production, preventing them from precipitating any anionic surfactants or dispersants (e.g., sodium hexametaphosphate).

(12) UV absorbers and stabilisers. These additives are of recent use. In fact, some synthetic polymers, such as some acrylic-based ones, are not stable under UV light exposure, causing the modification of their mechanical, chemical, and optical properties. Some examples are benzotriazoles and hindered amine light stabilisers (HALS). They have demonstrated the capacity to increase the chemical stability of the coating as they are chemically formulated to absorb the high energy of ultraviolet light and protect the coating product from exposure to this energy [46].

However, the chemical characterisation of the paints available on the market is much more complex and depends not only on the commercial formulations, but also on the chromatic needs of the artists, which may lead them to mix several paints together. For this reason, in order to broaden the knowledge related to their actual composition, several studies [25,33,47–49] have focused on the extensive evaluation of various commercial spray paints used over the years by street artists, in order to identify the nature of binders and pigments added for their formulation. Results of these investigations are summarised in Table 1.

Additional studies were carried out in order to integrate the results obtained from the analysis of the pure paints with those obtained from the pictorial layers of contemporary mural artworks [19,32,50–58]. These analyses have made it possible to identify the materials used by the artists over the last 60 years, to understand the commercial product trends among artists, and whether the same artist used different or the same paint materials at different time periods or places. A general overview of this information, listing the main examined case studies, is presented in Table 2.

From the evaluation of the results obtained, the presence of hybrid structures is evident such as alkyd resins combined with acrylic or nitrocellulose structures. These blends are used to improve the properties of the main polymer (in this case alkyd) [59]. In fact, polymers such as epoxies, acrylic, polyurethanes, or siloxanes are combined with alkyd resins through the formation of covalent bonds given by the double bonds or the acid or hydroxyl terminal functions. These new compounds allow for the improvement of mechanical properties of the paint such as adhesion, hardness, and resistance to the solvent, acid, and alkaline solutions [60]. The most identified pigments in modern artistic paints belong to the organic group, probably due to their ability to give more vivid colours compared to the inorganic ones, which attracts artists to use them more for their artworks, pushing manufacturers to add these kinds of pigments in modern paint formulations [61]. An example is phthalocyanine (as a blue pigment, PB15 and green pigment, PG7), which is the most important modern synthetic organic pigment used in artists' paint formulations [62]. However, the presence of various inorganic pigments is observed, including red ochre, lead chromate (yellow pigment, PY34) still used in industrial paints despite its toxicity [63], and titanium dioxide (white pigment, PW6). The latter is the most important white pigment used in the coating industry. It is employed both as an additional pigment to confer different shades of colour and as a filler because it is able to better scatter the visible light, thereby imparting whiteness, brightness, and opacity when it is incorporated into a coating. Furthermore, it is non-toxic and does not turn black when exposed to sulfuric acid from acid rain [64]. However, titanium dioxide can have different crystalline structures including rutile and anatase. The first form is photostable and it is preferable for reducing the photooxidation reactions of the binder, while the second one has a well-known photocatalytic action that can cause the degradation of paint upon UV light exposure [65]. This example explains why a detailed identification of the materials constituting the paints used in Street Art is always important, in order to understand the possible degradation processes that are occurring and the future prevention and protection practices to be implemented.

Table 1. List of binders and pigments identified in commercial formulations of modern spray paints used for street artworks.

Number of Analysed Commercial Spray Paints	Trademark and Commercial Brands of the Analysed Spray Paints	Polymeric Binding Media	Pigments and Colour Index (C.I.)	References
51 red spray paints	Altona, Hammerite, Trimetal, cuworks, Levis, Air Crafts, Dupli Colour, De Keyn, Colourworks, Gamma, Motip, Auto-K.	Alkyd styrene Acrylic alkyd Acrylic Polyvinyl acetate Styrene	Monoazo red, PR112–PR254 Quinacridone red, PR122 Monoazo yellow, PY74	Govaert et al. (2004) [47]
20 spray paints	Brico, Dupli, Colourworks, Montana, Motip, SparVar, Tuttocolour, Colourpol	Alkyd Acrylic Styrene Silicone	n.a.	Zieba-Palus et al. (2005) [48]
40 spray paints	Montana Colours	Alkyd Styrene alkyd Polyvinyl acetate	Quinacridone red, PR122 Monoazo red, PR170 Quinacridone violet, PV19 Phthalocyanine green, PG7 Phthalocyanine blue, PB15	Cortea et al. (2021) [25]
45 spray paints	Dupli-Colour, Fly Colour, Molotow, Montana colours, Arexons, Fantastica Ver-O, Saratoga, Keen–Vantage, Capec, Tecnoral, Spraycar	Alkyd Acrylic styrene Acrylic	Titanium white, PW6 Monoazo yellow, PY74 Lead chromate, PY34 Monoazo red, PR170 Disazo diarylide, PY83 Disazo pyrazolone, PO13 Phthalocyanine green, PG7 Phthalocyanine blue, PB15	Germinario et al. (2015) [33]
20 spray paints	Flame, Montana Black, Loop Colours, Montana Gold	Alkyd nitrocellulose Acrylic Acrylic nitrocellulose styrene	Titanium white, PW6 Phthalocyanine blue, PB15:3 Monoazo red, PR112–PR254 Phthalocyanine green, PG7 Monoazo yellow, PY74	Marazioti et al. (2022) [49]

Table 2. List of binders and pigments identified in paint samples from contemporary murals and divided according to different artists, time of realisation, binders, and pigments characterised. They are reported in the relevant literature.

Title	Artist	Year of Production	Binders	Pigments	Reference
Cinema Airone	G. Capogrossi	1953 (Rome, Italy)	Alkyd resin	PW6, PY34, PB29, PB15	La Nasa et al. (2021) [50]
Polyforum Cultural Siqueiros	D.A. Siqueiros	1964 (Mexico City, Mexico)	Polystyrene, alkyd resin	PR101, PR112, PR122, PY1, PY3	La Nasa et al. (2021) [50]
Collingwood	K. Haring	1984 (Melbourne, Australia)	Alkyd resin, 2-EHA acrylic resin	PR3	Dickens et al. (2016); Carlesi et al. (2016); La Nasa et al. (2016) [51–53]
XXXKH8	K. Haring	1986 (Amsterdam, Netherlands)	Alkyd resin	PW6	La Nasa et al. (2021) [50]
Necker Hospital	K. Haring	1987 (Paris, France)	Polyvinyl acetate (PVAc)	PB15, PG7, PR112, PY74, PY73	La Nasa et al. (2016); Magrini et al. (2017) [51,54]
Tuttomondo	K. Haring	1989 (Pisa, Italy)	n(butilacetate (BA))/styrene resin	PW6, red ochre, PB15:x, arylide yellow pigments, PR122, PV23	Dickens et al. (2016); La Nasa et al. (2016); Cucci et al. (2016) [51,52,55]
Writing	Peeta and Deban + Ment	2006 (Verona, Italy)	Alkyd resin, PVAc, ethyl acetate (EA) acrylic resin, nitrate cellulose	PW6, PBk7, PB15:6, PR101, PY83	La Nasa et al. (2021); Fenzi et al. (2018) [50,56]
The Big Mother	Gola Hundun	2010 (Reggio Emilia, Italy)	n.a.	PB15, PV23, PW6	Cimino et al. (2022); Rousaki et al. (2022) [19,57]
Big Sacral Bird	Kenor	2010 (Reggio Emilia, Italy)	n.a.	PR254, PY74, PO34, PV23, PW6, PB15, PR112, PY83	Cimino et al. (2022); Rousaki et al. (2022) [19,57]
Oriental Carpet	H101	2010 (Reggio Emilia, Italy)	n.a.	PO34, PW6	Cimino et al. (2022); Rousaki et al. (2022) [19,57]
The Economy Subdues You	Zosen	2010 (Reggio Emilia, Italy)	n.a.	PY74, PO34, PW6, PB15	Cimino et al. (2022); Rousaki et al. (2022) [19,57]
La strada la trovi da te	A. Pasquini	2011 (Rome, Italy)	Acrylic resin, alkyd	PW6, PBk7, PR101, PB15, PG7, PR48, PR110, PY74	Bosi et al. (2020) [58]
No Title	Rojo Roma	2012 (Turin, Italy)	Alkyd resin	PW6, PY42, PB15	Pellis et al. (2022) [32]
Frontier	Etnik	2012 (Bologna, Italy)	nBA/ methyl methacrylcate (MMA), nBA/styrene, alkyd resin	PW6, PBk7, PY184, PB15:x, PG7, PV23, PY74	La Nasa et al. (2021) [50]
No Title	BLU	2014 (Rome, Italy)	MMA/EA, nBA/MMA, 2-EHA, and 6-MHA acrylic resins nBA/styrene resin	PW6, PBk7, burnt umber, PB15:x, PR112, PR122, PY1	La Nasa et al. (2021) [50]
Straniera	A. Luchko	2014 (Rome, Italy)	Styrene/acrylic, alkyd resin	PW6, PR101, PR48	Bosi et al. (2020) [58]
The Trial of Joseph K.	SEPE and Chazme	2016 (Fondi, Italy)	PVAc	PW6, PBk7, PR112	Bosi et al. (2020) [58]
ORME	OrticaNoodle	2016 (Milan, Italy)	Acrylic resin	Organic pigments	Pagnin et al. (2022) [66]
Necesse	SMOE Studio	2021 (Milan, Italy)	Acrylic, alkyd resin	Organic pigments	Pagnin et al. (2022) [66]

4. Effects of Outdoor Exposure on Street Artworks

As previously mentioned, Street Art has been gaining popularity also thanks to its inherent nature of being accessible and enjoyable by the public at any time. However, while the exposure to outdoor and urban environments has favoured its development and diffusion, it is also one of the key aspects related to the short durability of street artworks. Urban outdoor exposure is one of the main sources of deterioration problems of heritage materials. Attention and studies concerning the degradation of these murals are arising in literature only in the last years and are specifically case studies oriented. This is because only during the last year contemporary muralism started to be considered worthy of preservation, while previously it was simply repainted or substituted [52]. Figure 3 is proposed as an example of the state of conservation of a street artwork due to the outdoor environmental exposure, after a short period of time.

Figure 3. Effects of outdoor exposure on contemporary mural "*Emigranti*" by SMOE Studio in Catanzaro (Italy). (**a**) The artwork in 2017 when it was realised; (**b**) the state of conservation after four years in 2021. Images courtesy of SMOE Studio.

The comparison between the photo taken immediately after the realisation of "*Emigranti*" by SMOE Studio in 2017 (Figure 3a) and four years later (Figure 3b), makes it clear what kinds of deterioration phenomena can affect these artworks and the span of time in which they occur. After only 4 years, cracks and detachments of the painting layer from the support, diffused losses of painting materials, discolouration and fading of the yellow background, deposits and washouts, destroyed completely the impactful appearance and the message of the mural. It is reasonable to attribute these degradation patterns to the peculiar location of the mural. It is located on a portion of the wall where there are numerous water drains which can cause severe water infiltrations. Moreover, it is close to a very busy road with a south-west exposure. The prolonged pollutants and sunlight exposure played a crucial role in the severe deterioration of the mural. This example shows how the location, orientation, and exposure of these kinds of artworks are crucial for their durability.

It has also been reported in the study of Pozo-Antonio et al. [67] that the degradation of contemporary murals occurs at a significantly higher rate than other types of Cultural Heritage objects. The main causes are related to the more aggressive urban environment where they are placed; the combination of simultaneous and multiple degradation factors (as paint layer degradation, substrate instability, and anthropogenic factors); the lower resistance of modern paints to the environmental agents (especially to sunlight) compared to traditional paints; the fact that most of them are not applied on a preparation layer [67]. The convergence of the truly wide variety of factors makes it often confusing to understand, which is the main mechanism of degradation of these kinds of artworks.

Thus, the investigation of the deterioration causes and the definition of the state of conservation is very complex, above all because these processes occur simultaneously, and their synergistic action leads to fast and significant changes in the physical–chemical properties of materials. A robust, but not exhaustive, list of the various degradation patterns of Street Art and, particularly contemporary muralism, was realised by the CAPuS Project in 2020 [18].

Figure 4 proposes different images from the contemporary mural "*Musica Popolare*" by Orticanoodles (Milan, Italy), a case study of the Prin 2020 Superstar project [20], where it is possible to identify some of the most typical and frequent degradation patterns according to CAPuS glossary [68].

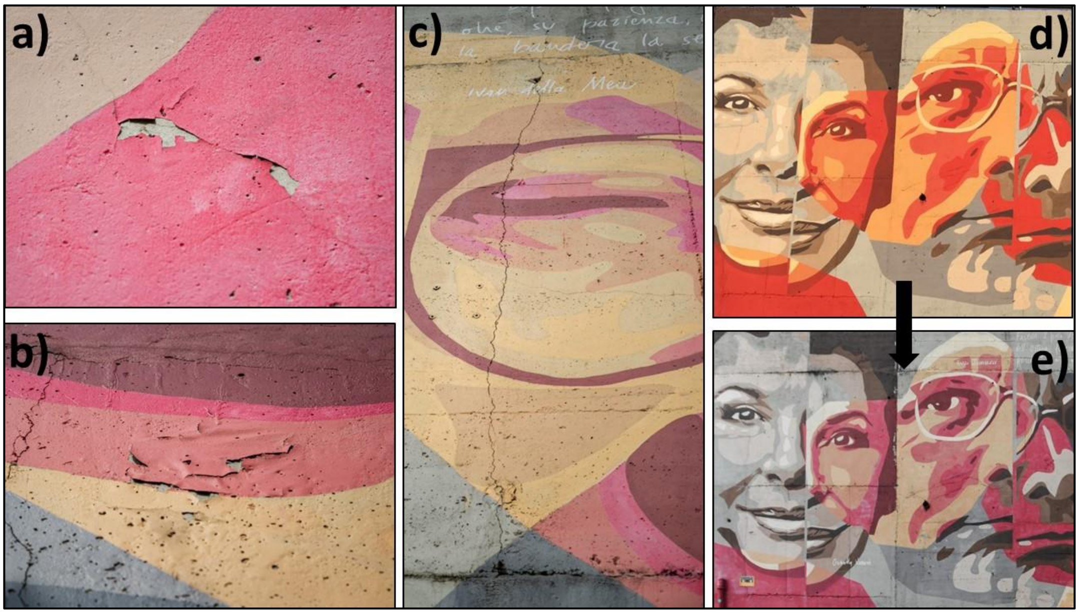

Figure 4. Images from the contemporary mural "*Musica Popolare*" by Orticanoodles (Milan, Italy): examples of deterioration patterns that can be observed on contemporary murals. (**a**) Flaking; (**b**) scaling; (**c**) fracture of the substrate; (**d**) original colour of the artwork realised in 2016 and (**e**) colour fading observed.

The main physical and mechanical degradations of the paintings include phenomena like embrittlement, cracking, morphology alteration, craquelure formation, and paint loss. All these processes are influenced by several factors, such as the nature of the substrate, the paint characteristics, the aggressiveness of the environment to which it is exposed (e.g., thermal excursions, pollutants), the mechanical action of rain drops, the wet and dry cycles and condensation, and the related water movement within the porous system. These different factors are, actually, acting simultaneously on the painted surfaces.

Some of the examples of physical damages are paint losses with a crack pattern that follows the bricks underneath [57]; craquelure formation (involving only the paint layer), associated with increased porosity of the substrate and higher roughness of the paint surface [67,69]; wrinkling related to the presence of plasticisers sensitive to temperature variations during the day [50,51]; shrinkage caused by photodegradation [70]; incompatibility problems due to non or incorrect preparation of the substrate [52,69].

All these mechanisms lead to mechanical tensions of the paint film and the consequent deformation up to the development of surface cracks and detachment of painting film [67,71]. In addition, thermal stresses tend to expand and shrink paint layers, inducing the mechanical failure. In drastic outdoor conditions and sunlight exposure, additives (such as surfactants and plasticisers) can migrate towards the surface following the cracks network and then be removed by rain, leading to a more brittle and fragile paint film, devoid of the plasticisers [32,45,50]. Equally, studies described the migration to the surface of the paint layer of inorganic additives of the paint itself or from background layers (as preparatory layers or underlying paints) [52], in particular, it has been observed that thinner paint layers (as the one produced by spray paints) are more susceptible to this phenomenon [50].

Discolouration, comprising total or partial colour variation, usually manifested as chroma and gloss change, results from direct exposure to sunlight, photo-chemical reactions, and additive migration [57,67,70]. The mechanisms leading to colour change are very different, not fully understood, and dramatically influenced by vulnerabilities of the specific case study (Figure 5). Colour fading has been related to the composition of the paint, because it can be caused by the formation of a white surface veil (called the chalking effect); by local enrichment of white additives of the paints [19,37,52]; by a darkening due to interactions between the organic binder and aluminium particles [67]; by yellowing of the binder [32,50]; by biological colonisation [67–69]. The chalking effect is a phenomenon whose mechanism requires further investigations [19,58]; as previously mentioned, it has been linked to the superficial accumulation of white additives [57] due to a photodecomposition of the binder of the paint [67]. During this process, the binding medium starts to break down and lose its integrity by the formation of volatiles, low molecular weight species that are lost due to photocleavage reactions in the binder. Therefore, it causes a relative superficial enrichment of white additives (such as TiO_2, $CaCO_3$, and $BaSO_4$) that are loosely bound and can easily detach from the painted surface. This results in the formation of a powdery, white residue that accumulates on top of the paint [72].

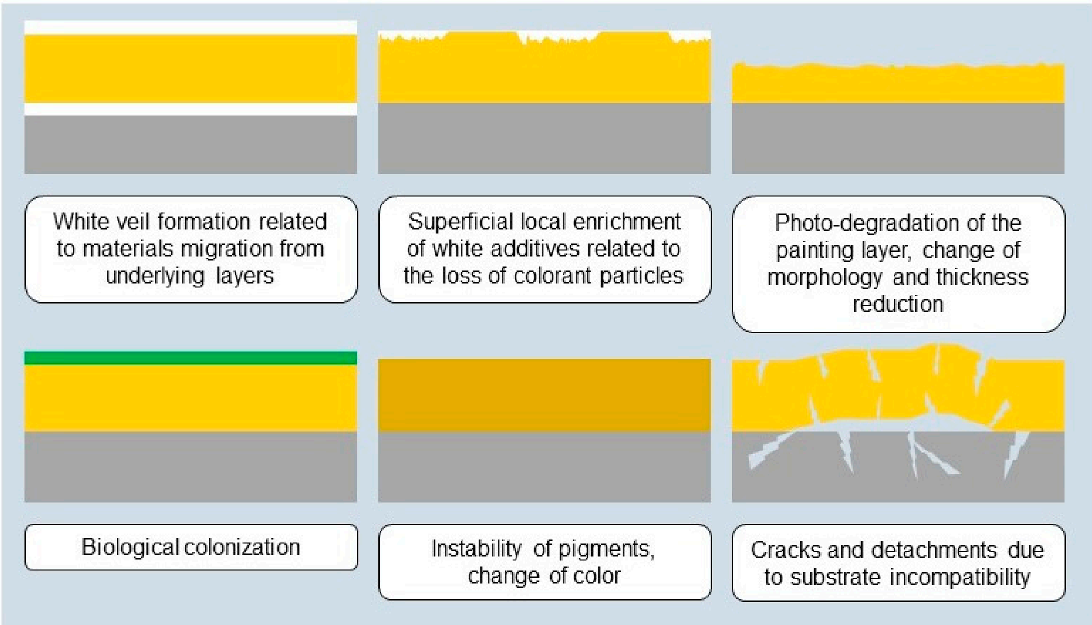

Figure 5. Scheme summarising the main chemical–physical phenomena related to colour instability.

As already reported, sometimes, artists obtain the desired tone of a paint by mixing different paints. Hence, the sensitivity to colour fading of a specific paint of the mixture could generate a total colour change in the mural. This is the case reported in Figure 6 (showing the contemporary mural "*20 Years of Freedom and Democracy*" in Milan, Italy, by Orticanoodles, currently investigated by the authors), where the different shades of brown were obtained by mixing various paints, leading to a surprising and colour-selective discolouration in less than two years. The theme of colour appearance is very complex. The orientation of the mural seems to be crucial in colour fastness [57] since the most relevant cause of fading can be ascribed to UV irradiation of the painting materials. It has been shown that also the nature of substrate influences the colour change in the paints. In fact, loss of adherence between the paint and substrate (due to low roughness of the substrate or to inherent vulnerability of the paint formulation) may also cause changes in the perceived colour [73]. In addition, some studies showed how the intensity of fading is more related to the nature and stability of the chromophore than to the type of substrate and type of exposure of the mural [69,74].

Figure 6. Images from the contemporary mural "*20 Years of Freedom and Democracy*" by Orticanoodles, Pao, Ivan, and Nais (Milan, Italy): example of colour fading. (**a**) Original brown tones of Mandela's face were obtained by mixing different paints. (**b**) After the probable colour degradation of a component used in the mixture, the aspect is completely changed and the black vault of Mandela is barely recognisable.

Chemical degradation is mainly induced by the interaction of the binder matrix with gaseous pollutants in combination with atmospheric oxygen, water, and UV radiation [75]. Sunlight initiates photodegradation reactions producing radical fragments that react rapidly with oxygen, leading to polymer deterioration, mainly via scission and cross-linking reactions [36,67,76]. In general, photo-oxidation begins at the very superficial layer of the paints and moves inward through the layer depending on several factors such as radiation, oxygen diffusion, time of exposure, properties of the materials, environment, and presence of additives or pigments [32,37,77,78]. The aromatic groups and conjugated double bonds in the molecular structure of binder polymers (i.e., the carbonyl group in acrylics and the benzene ring in polystyrene) are very sensitive to this kind of reaction, while the presence of transition metal compounds (present in pigments and additives) catalyses it by absorbing UV rays [36]. Moreover, studies confirmed that the presence of synthetic organic pigments influences the degradation processes, even if their effective action is still unclear; pigments may either have a protective effect by absorbing and/or screening the UV light or they may be photo-active, and therefore catalyse or accelerate the photodegradation of the polymer (TiO_2, azo pigments) [19,34,36,38,58,70,72,79]. This topic underlines again the fact that deterioration seems to be specific to the paint formulation since different combinations of binders, pigments, and additives could have different behaviours, stabilities, and interactions. Once again, it becomes clear how necessary it is to characterise paints in order to predict their degradation mechanisms and to determine restoration interventions.

Exposure to solar radiation also involves thermal degradation processes. In fact, it is known that solar radiation includes a visible (VIS) and an infrared (IR) spectral band. These frequencies increase the temperature of the exposed surface by means of thermal energy causing the degradation of the polymer and its properties [76,80].

Environmental relative humidity induces reactions of hydrolysis on the polymeric structure of the paint (especially for acrylic) which coincides also with a further absorption of water by the presence of hygroscopic materials inside the paint (such as non-ionic surfactants) [81], and the breaking of the saturated aliphatic chains (in alkyd paints) [82]. Moreover, rain washes away the surface causing solubilisation, loss of additives, and entrance of polluting agents, such as nitrogen oxides and sulphur dioxide which lower the pH and catalyse the activation of further chemical reactions [83]. Specifically, the corrosive agents present in the air (such as NO_X, CO_2, and SO_2) can be hydrolysed with a series of equilibrium reactions in rainwater droplets, leading to rain acidification. Although in recent years the level of acid rain is well below alert levels [84], these acidic compounds can get in contact with outdoor building materials or paints, promoting their aesthetic, physical, chemical, and mechanical decay. In addition, the presence of SO_2 in the paint favours interactions in the coating–substrate interface leading to the formation of hydrated sulphur compounds (as gypsum and barite) that could alter the chemical stability of the painting material [85]. Finally, it should be highlighted that warm and humid environments may create ideal micro-environments for the colonisation of biodeteriogens, such as fungi and bacteria [69]. The presence of micro-organisms infestation has been cited in multiple case study evaluations but their action, the colonisation mechanism, and bio-deterioration has not been investigated to date. It should be clarified if they only cause an aesthetic damage or they contribute actively to a more severe decay pattern affecting the painting layers.

To summarise, the degradation mechanisms of contemporary muralism reveal that various factors contribute to the deterioration of street artworks. These factors encompass natural elements like sunlight radiation, temperature fluctuations, rain wash, and humidity, as well as gaseous pollutants such as CO_2, NOx, SO_2, oxygen, and ozone and fine particulate matters like PM10, but the intrinsic susceptibility of paint formulation to degradation has proven to be a crucial aspect. Additionally, the location and orientation themselves could further aggravate the degradation process. All these features make each evaluation extremely specific to single case studies. These artworks, in addition to the problems mentioned above and to their normal deterioration, are exposed to potential acts of vandalism. In fact, overwriting poses a further important problem, which is independent of the degradation mechanism of the paint, but which sometimes leads to the total loss of the artwork; since the chemical nature of the materials used in these vandal actions is very similar to those of the artwork, selective cleaning operations are often complicated. For this reason, a strategy of applying anti-graffiti products is often adopted. Considering the complex nature of all these deterioration mechanisms, it becomes evident that gaining a profound comprehension of the degradation factors affecting contemporary muralism artworks is highly challenging but fundamental, to allow experts and conservators an effective evaluation and choice of intervention [58,86]. To ensure the long-term preservation, it is crucial to conduct wider research and broaden the investigation. By encompassing a wider range of experiences and cases, we can gain a deeper comprehension of the unique degradation susceptibilities associated with each future case study. By expanding our research in this manner, we can develop more complete and specialised protective strategies tailored to the specific needs of each individual mural.

5. Protective Strategies for Outdoor Exposed Contemporary Mural Paintings

As reported in Section 4, in outdoor conditions, street artworks are subjected to fast deterioration and fading, due to their intrinsic organic chemical nature which is not stable when exposed to atmospheric agents (UV light, humidity, temperature, rain, and pollutants). For this reason, preservation and protection strategies are necessary to grant a sustainable maintenance and reasonable durability to these artworks. The research, carried out through the examination of the available literature, case studies, and through interviews with experts in the field and street artists, revealed that the protection of contemporary murals is an emerging issue, with several problematic aspects.

The main one is the limited availability on the market of commercial protective products specifically developed and/or formulated for street artworks. For this reason, commercial protective products available for other Cultural Heritage substrates, are being tested on Street Art painted surfaces, in the last years. However, they show some limitations in terms of applicability, compatibility, and durability. The following sections explore these arguments in more detail, focusing on requirements, properties, and the behaviour of protective coatings, as well as results and observations from specific case studies.

5.1. Protective Coating Requirements and Methods

Protective barriers and coatings applied on Cultural Heritage surfaces in outdoor conditions should satisfy specific requirements [87–89] schematised in Figure 7, that can be summarised as follows: compatibility (no changes in optical properties, aesthetic characteristics of the surfaces and perception); protection effectiveness (protective efficacy against water and humidity, UV irradiation, etc.); chemical inertness (no chemical reactions with the surrounding environment); maintenance of the original water vapour permeability (also called breathability, material's ability to allow water vapor to pass through it); long-term durability (5–10 years); reversibility and/or re-treatability (capability to be easily removed from a surface allowing the re-applicability of the same or different products after restoration practices); low cost for large surfaces application.

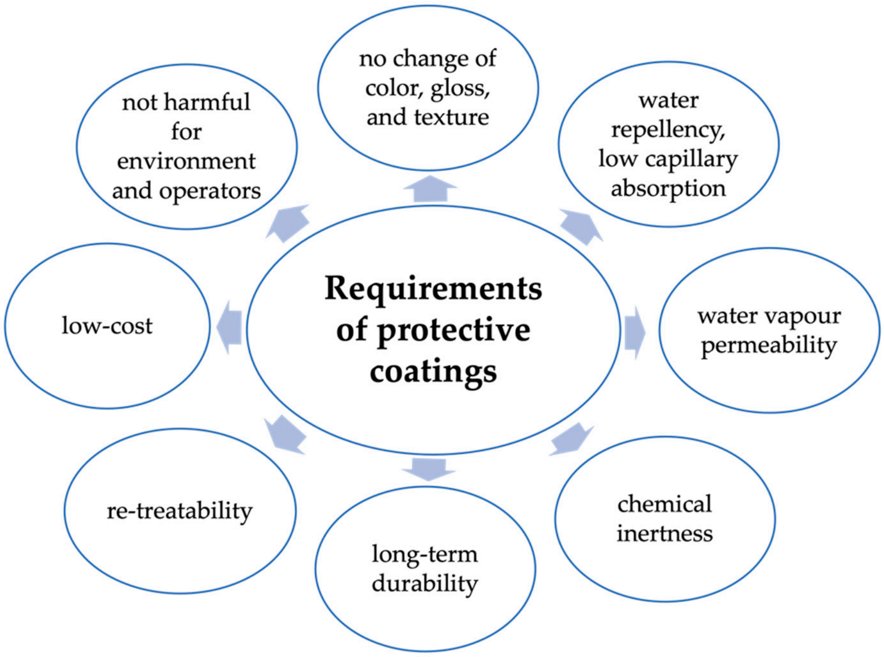

Figure 7. Scheme of the properties and requirements that protective coatings should satisfy to be applied on Cultural Heritage.

Finally, the use of green and non-toxic coatings for the operators and for the environment is an important additional requirement for the selection of the most suitable protective systems.

To select the most appropriate protective coating for the artwork, it is also necessary to choose between two types of protection methods. They can be divided into indirect and direct (Figure 8).

- The first type refers to transparent barriers, usually plastic (polycarbonate, plexiglass, etc.) or glass, applied in the extreme proximity but not in contact with the work of art, having the main function of limiting the mechanical or vandalic action of anthropogenic origin.
- On the other hand, in the case of the direct protective method, a liquid and transparent protective coating of various chemical natures is applied directly to the pictorial surface by brush, roller, or spray. This is usually the most used method, mainly for economic reasons, but also because these products can satisfy many, if not all, of the requirements mentioned above. As it will be explained later, some examples of protective coatings are represented by acrylic-based or silicon-based resins. Another category, recently considered as a protective coating, is represented by anti-graffiti products. Anti-graffiti systems have been created with the intent to limit vandalism phenomena [90] such as the illegal writing acts that fall into the category of "graffiti" and "tags", i.e., identification drawings and marks that writers use to communicate with each other. In order to remove these unwanted paintings and facilitate the cleaning operations, anti-graffiti systems have been introduced in the market. After various studies [91–94], it was observed that these systems do not only protect building and painted surfaces, preventing inks and paints from penetrating the pictorial support, but also have a protective role against atmospheric agents. Specifically, these

coatings are capable of not altering the aesthetic appearance of the artworks as they are transparent, resist ultraviolet light (preventing yellowing), and limit physical or chemical damage [95]. For this reason, some examples of anti-graffiti tested on painted surfaces, were included in this review with the intention of widening the selection and knowledge of eligible coatings for the protection of street artworks.

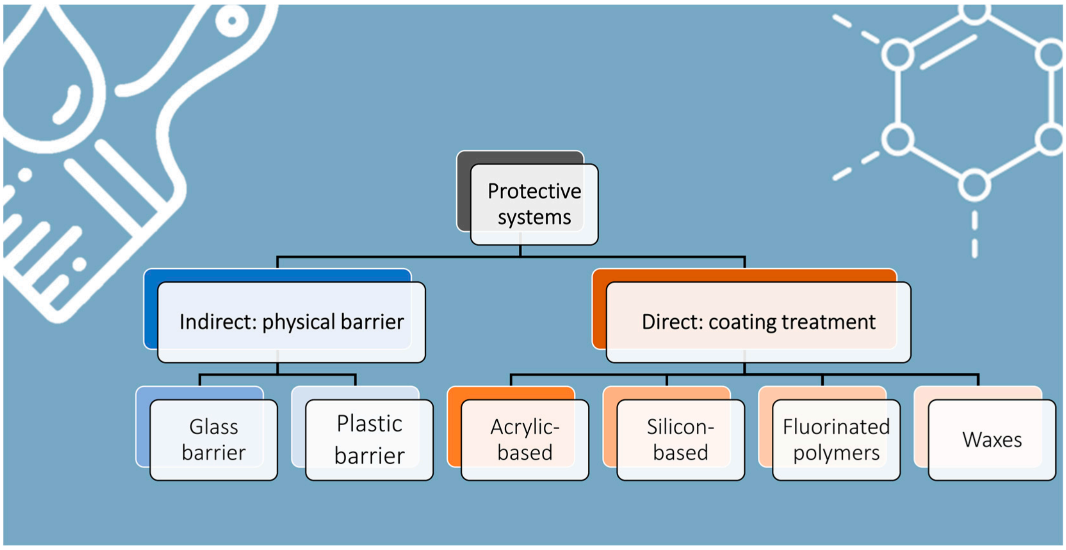

Figure 8. Schematic representation of protective systems described.

Compared to the other protective coatings previously listed, anti-graffiti are classified into three different categories: permanent, semi-permanent, and sacrificial [90,96,97].

Permanent coatings can endure repeated cleaning cycles preventing graffiti from adhering to the substrate and can include siloxanes and acrylic-siloxane copolymers, fluorinated hydrocarbons and perfluoro polyethers, as well as nanocomposites. The second category of anti-graffiti is represented by the *semi-permanents*, which are able to undergo two or three cleaning cycles before being reapplied on the artworks. They are transparent and comprise one- or two-layer systems. And finally, the *sacrificial coatings*. As the name suggests, they are removed during the cleaning phase and need to be reapplied afterwards [98]. The most popular product is based on waxes. In the following chapters, the mentioned product classes, their application on real case studies, and considerations on their advantages and disadvantages related to the protection of Street Art will be explored.

5.2. In Situ Indirect Protective Systems

A possible approach for the protection of Street Art is the use of plastic or glass barriers in order to avoid any approach of pedestrians to the artwork and the affixing of vandalism writings, especially in the urban environment. This is the case, for example, of the artwork "*Madonna con la Pistola*" by Banksy that appeared in Naples between 2003 and 2004 (Figure 9) [99]. The artwork had immediately a large success both for the city of Naples and at international level (with a further flow of visitors). However, it was realised on a critical masonry support with raising dump phenomena, and in a very crowded urban environment easily accessible for vandalic acts. For this reason, the citizens of the area, decided to protect the artwork by implementing a physical barrier, i.e., a plexiglass transparent panel, with the intention of preserving it and trying to prolong its durability.

From a social point of view, this solution represents a turning point, as the citizens themselves took on the burden of protecting Cultural Heritage by extending it also to Street Art. Nevertheless, the role of public administrations with this popular initiative remains unclear. The effectiveness of the implemented solution should be discussed and understood. In fact, from a conservative point of view, this solution presents several problems. The application of polymethylmethacrylate or glass panels can have harmful consequences for the rising dump and cause problems of transpiration of the wall support, creating an unsuitable microclimatic condition between the wall and the painting layers. It may cause alteration and deterioration processes and, at the same time, alter the visual perception of the artwork [1].

Figure 9. Protective system (plastic panel) applied on la "*Madonna con la Pistola*", Banksy (2004).

Another example of the indirect protection system is represented by the latest contemporary mural "*Tuttomondo*" by Keith Haring, painted in Pisa in 1989. In contrast to his other artworks, it was created with the intention of being permanent, and therefore the public administration started to immediately try to preserve its artistic integrity by installing glass balustrades [100]. They are arranged at the base of the mural with the intention of limiting accessibility and avoiding intentional contacts and vandalism. Unfortunately, as previously discussed, vandalism and pedestrian contact are not the only forms of deterioration and already 10 years after its realisation, the artwork showed clear signs of deterioration, such as discolouration of the pictorial film, followed by some detachments, paint loss, and black staining from biological attack [101]. The artwork was therefore restored after an important campaign of scientific investigations [52,55,101] and a careful selection of materials and methods for conservation, including the application of a protective coating.

These examples of indirect protection show the evident limitations in terms of aesthetic compatibility with the pictorial substrate (being a physical barrier, it limits the visual accessibility of the artwork); protective efficacy (not reducing degradation processes and in some cases accelerating them); the low reversibility represented by this protection methodology. For this reason, direct protective systems are usually preferred both for the protection of Street Art and other Cultural Heritage materials.

5.3. In Situ Direct Protective Systems

Compared to indirect, direct protective systems can better satisfy the key requirements for an adequate and effective protective practice, listed in Section 5.1. Examples of protective coatings fall in the classes of acrylic-based, silicon-based, fluorinated, and waxes. However, literature and experiences about the application on real Street Art case studies, are only few. They represent a starting point for further investigations; more research and experimental work are needed to assess the compatibility, stability, and durability of materials for the protection of contemporary muralism (Figure 10).

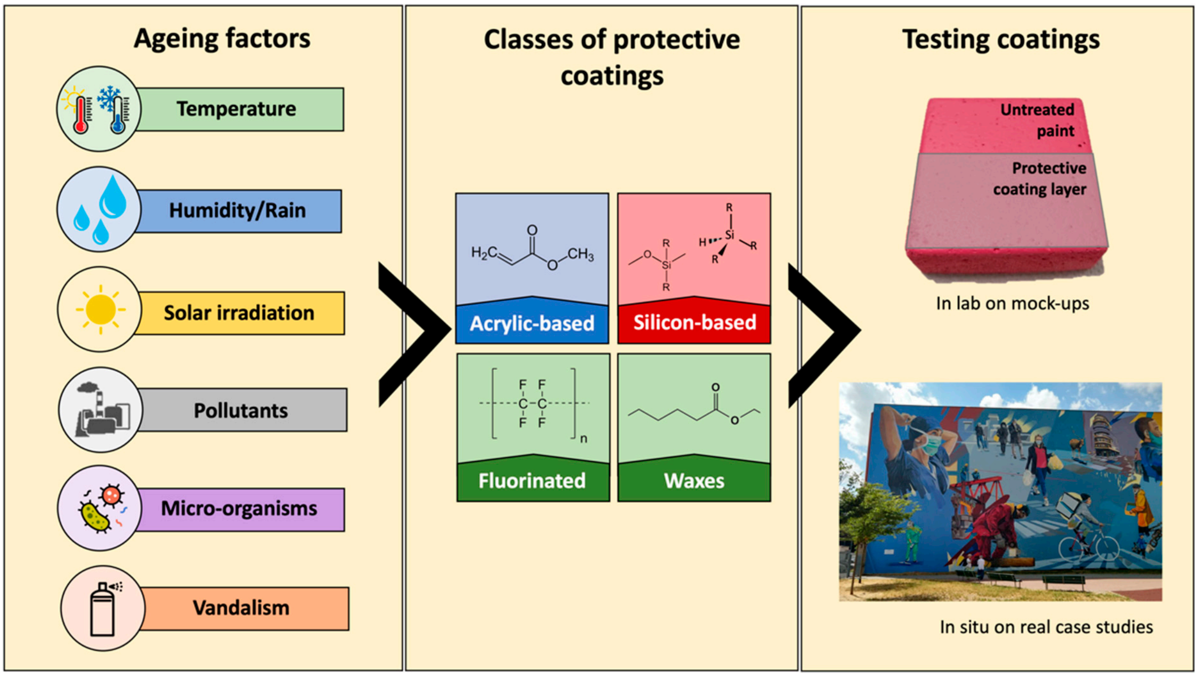

Figure 10. Schematic representation of main atmospheric agents and pollutants involved in the degradation of Street Art painting layers, main class of direct protective systems available, and example of samples where their protective efficacy was tested during PRIN 2020 SuPerStar.

5.3.1. Acrylic-Based Coatings

One of the first cases of the protection of Street artworks was in 1992, during the restoration of the artwork "*Occupazione delle terre e lotta per lo sviluppo*" by Ernesto Treccani and Carlo Levi [102]. According to the authors, the mural showed a significant chromatic alteration, mainly related to a bleaching of the red paint and visible cracks and detachments of the paint film due to the solar irradiation. For the restoration action, it was decided to select a product with a double function: (i) consolidate the detachments of the paint layers from the substrate and (ii) protect the artwork from future environmental threats. Paraloid® B72, an acrylic-based resin obtained from a free radical polymerisation reaction between ethyl methacrylate (EMA) and methyl acrylate (MA), was used as a protective coating. Microscopic observations showed that the resin was applied in large quantities on the damaged surface of the mural, resulting in the penetration of the product under the paint (with consequent re-adhesion to the substrate). After 10 years of outdoor exposure, a chromatic alteration was evident due to this resin's instability to oxidative photodegradation. The same study also showed that the knowledge related to the degradation processes of modern paintings is still incomplete. This is because such paints have been typically used for works of art preserved in museums, a condition and environment that is easier to monitor. Furthermore, it was evident that it was not only important to understand the stability of these paints to environmental atmospheric agents, but it was also necessary to dig deeper into the interaction that these materials had with the substrate (such as cement) and the consequent effects of degradation. The cited study highlights the need to focus research studies on the understanding of the chemical stability of the acrylic-based protective products used to protect the artwork.

Some studies [103,104] highlight how ParaloidB72®, if compared to other types such as Paraloid B66®, B67®, and B87®, shows good stability towards oxidation, thanks to the presence of the methacrylic short side-chain units EMA and MMA. Oxidative activity primarily affects the acrylic units (i.e., MA and EA), resulting in the formation of γ-lactones. From the experiments of artificial UV exposure [105], it is clear that its use has the additional advantage of creating a balance between scission reactions and macromolecular couplings allowing the polymer not to become insoluble, guaranteeing its durability over time and re-treatability using solvents, but it shows the disadvantage of turning yellow quickly [106].

A recent experimental study tested an acrylic-based protective coating (Proa BV000-Barniz, Spain) on acrylic-based painting mock ups realised on different substrates. On these samples, accelerated artificial UV light ageing experiments were carried out, in order to understand their protective efficacy after ageing by investigating the morphological and chemical–physical changes observed on the paint layers [107]. The study highlighted that the different types of substrate alter the overall stability of the paints (in fact they degraded more quickly on concrete than on bricks). The application of the protective coatings showed a slowdown in the colour change, even though, after the application, they changed the original aesthetic appearance. Moreover, after the complete drying phase of the protective coating, it shows some cracks all over the painted surface, making the painting layer susceptible to the action of atmospheric agents.

From the mentioned studies, it is evident that the use of this class of protectives in the protection of Street Art has limited real case study applications and that their chemical stability is not completely suitable for the outdoor exposure to which these artworks are subjected. For this reason, some research studies [19,73,96,108] began to test the addition of UV stabilisers to acrylic formulations to improve their chemical, optical, and weather resistance performance (see Section 3). However, the results show problems related to the chemical composition of the protectives, the chemical affinity between protectives and paints, the complexity of substrates (sometimes prepared for painting and sometimes raw) and application methods, and the different durabilities of these materials.

5.3.2. Silicon-Based Coatings

Silicon-based conservation treatments used in Cultural Heritage are alkyl-alkoxy silanes (organosilicon charge-neutral compounds) and siloxanes (polymeric and/or oligomeric compounds containing the siloxane functional group Si-O-Si that forms the backbone of silicones, the main example of which is polydimethylsiloxane (PDMS)) [97]. In turn, these inorganic/organic units can be chemically modified by adding different functional groups or monomers; an example of this modification is the organofunctional alkoxysilane. This class of compounds is commonly used in the field of consolidation/protective coatings in Cultural Heritage [109,110], in which the silane groups are mainly linked to acrylic, methacrylic, and epoxy-functional units. They result from photochemical crosslinking reactions or induced thermal polymerisation before, during, or after the formation of the silica network. This additional crosslinking of organic groups increases the crosslink density, and consequently the surface mechanical properties of the organofunctional alkoxysilanes [111]. In the following paragraph, some Street Art case studies, where this class of coating was tested, are presented.

An interesting case study is represented by the "*Untitled*" mural by Blu and Ericailcane, created as a temporary artwork in 2007 on the facade of the Contemporary Art Pavilion in Milan [112]. The preliminary analyses highlighted several compromised areas of the mural mainly due to environmental exposure that caused the detachment of painting layers from the support. The choice of the restoration techniques and specific products for the protection of the paint layer was debated for a long time until the decision to test two oligomeric organosiloxane protective coatings commercialised by CTS s.r.l., namely, Silo 112, 10% diluted in water and Silo 111, in white spirit. According to the authors, they were selected both for their compatibility with the mural support and to avoid the possible interaction with the alkyd-based resin constituting the paint films [112]. The monitoring of their stability over time is still ongoing, and no conclusive results have been published regarding the behaviour of these materials.

Other case studies have emerged as the conservation of the "*Writings*" of Deban and Ment, and the problems of pictorial integration on Peeta's mural in Verona [56]. Also in this case, a transparent silane-based water-repellent protective coating was applied (commercial product name not mentioned). Another case study concerns some street artworks created by American writers during the exhibition *Arte in Frontiera* in Quattordio, (Italy), in 1984. For the *Quattordio Urban Art* event in 2017, it was decided to carry out conservation interventions, and apply a nano-silane protective coating in order to increase the durability of the paint layers without pictorial integrations [113].

Another example of the protection practice of contemporary murals is represented by "*Tuttomondo*" by Keith Haring (1989), located on the external wall of the 14th-century convent annexed to the Church of Sant'Antonio Abate in Pisa (Italy). It was restored between 2011 and 2013 involving the Municipality of Pisa, the Keith Haring Foundation, the University of Pisa, and two restorers, Will Shank and Antonio Rava, following a conservation project that was intended to maintain the authenticity of the artist's execution, despite a strong chromatic alteration after twenty-two years [51,52,55,114].

For the protection phase, an alkyl-alkoxysilane protective material (Hydrophase® Acqua, Phase Restauro s.r.l., Florence, Italy) was selected by the restorers [101]. For this important case study, experimental research was carried out also in the laboratory [115], from which it was possible to evaluate the protective behaviour after outdoor natural ageing for two years. It was observed that Hydrophase Acqua® undergoes thermal degradation by means of a homolytic scission reaction of the Si-CH_3 bond [115]. Even if a not significant chromatic alteration was observed after application, the testing carried out to monitor the performance of the coating after two years of natural ageing, showed that Hydrophase Acqua® is not stable. A repeated application over time was suggested to maintain the aesthetic appearance and the active protection of the painting layers from atmospheric agents. Several factors emerge from these studies: the use of this coating meets many of the requirements necessary for the protection of Street Art; important Italian restorers love this kind of material for ease of application; this class of products was shown to be reversible over time and possesses dual functionality, adhesive/cohesive, and protective nature. Nevertheless, monitoring studies of the stability are really limited, and the need for re-treatability/maintenance represents a large cost for administrations.

5.3.3. Fluorinated Coatings

This class of protective materials is part of the so-called *permanent anti-graffiti*. Several classes of fluorinated polymers are available on the market with properties adaptable to different materials and needs (fluoroalkyl polysiloxane, fluorinated polyacrylates, and fluorine containing PUs) [97]. As reported in the literature [116], the introduction of fluorine atoms in the polymeric structures decreases the surface free energy, increasing the value of contact angle and improving the water repellent properties. The strong bond between the fluorine and carbon atoms (C–F) provides good chemical, thermal, and photochemical stability [117]. These properties can also be enhanced by fluorinated chain length, copolymer composition, and overall fluorine content. Increasing the latter also increases the cohesive energies of the C–F covalent bonds and significantly improves thermal, oxidative, chemical, and surface dirt accumulation resistance [118]. Surface contamination resistance is linked to the ability of the fluorine atom to migrate towards the upper part of the surface which, together with its low polarizability and electronegativity, prevents the adhesion of graffiti to the coating system. Thus, fluorinated coatings are considered excellent anti-graffiti and protective systems against pollution [94,119]. However, the ability to create a surface barrier on polymeric films has also some disadvantages. Indeed, the walls on which contemporary murals are created need to breathe and allow the water to evaporate, while with these systems, water vapour permeability can be severely compromised, leading also to the acceleration of other deterioration mechanisms, such as salt crystallisation and freeze-thaw action [120].

Various experimental studies were carried out by testing products already on the market, evaluating their protective properties. One of them is an experimental study on the application on painted mock ups of Prostone® (Pelicoat® Italia s.r.l., Rome, Italy), a fluorinated acrylic polymer specifically developed for the protection of stone and building materials from the penetration of water, grease (pollution), and graffiti [121]. The product was evaluated in a comparative experimental study where, together with other anti-graffiti products, it was tested on acrylic and styrene paints applied on a cement mortar substrate. The results obtained after its application showed a low chromatic alteration. In addition to the aesthetic compatibility tests, reversibility tests were carried out by performing different cleaning procedures. They showed a good resistance to the selected cleaning operations and, in the areas where the protective layer was removed, a colour difference was observed compared to the original paint layer. However, this study has limitations as no ageing tests were performed to assess the stability of the protective coating and no applications on the real case study were performed.

In a study developed in recent years, a fluorinated acrylic-based system was tested as an anti-graffiti coating [122]. The protective coating was called PRO-ART (YOCOCU/Pelicoat®), which compared to other commercial formulations, was modified to increase its chemical–physical properties for application on exterior contemporary murals. In addition to being evaluated in the laboratory, it was applied to the artworks of the GRAArt project. The murals are still monitored today through colourimetric measurements at various natural ageing times to observe and document any changes. In any case, the results in the laboratory have shown that the application on the specimens does not substantially alter the colour (although attention must be paid to the number of applications chosen) and is one of the coating systems with the best hydrophobic performance [13].

The results of the presented studies confirm the good protective properties of fluorinated coatings in compliance with the requirements such as good aesthetic compatibility, reversibility, and high surface water repellence. However, it is also necessary to underline a limitation of these products due to the possible toxicity of this class of materials. Further research is needed to extend the knowledge of their physical and mechanical durability.

5.3.4. Wax Coatings

This category is part of the *sacrificial anti-graffiti*. As the name suggests, they are removed during the cleaning phase and must be reapplied afterwards [98]. Sacrificial systems based on water-based microcrystalline waxes are among the most popular because they are transparent or translucent and can be easily cleaned with hot high-pressure water to remove unwanted graffiti. They have the main characteristic of creating a barrier between the pictorial substrate and the surrounding environment, but at the same time not being able to form a strong bond with the substrate making the future removal easier. Being very versatile, reversible, and inexpensive, they are preferred by restorers and professionals. However, from the experience gathered on stone surfaces, it was found that the higher the porosity of the substrate, the more the vandal paint tends to penetrate the anti-graffiti through cracks and fractures, making difficult its complete removal [123]. In addition, wax-based anti-graffiti was proven to have poor durability when exposed to natural environmental conditions, above all to UV radiation [124].

Macchia et al. [13] tested the product Antigraffiti I.M.A.R. (IMAR Italia® s.r.l., Rome, Italy), a microcrystalline wax with fluorinate polymers on paint mock ups simulating a real contemporary mural. The presented results are encouraging for the technological development of this product (no chromatic alteration after application and good water repellence); however, the evaluations on the intrinsic stability of this product and its behaviour when exposed to polluting agents are still limited. Many shortcomings in its physicochemical stability (especially against UV rays), protective efficacy, re-treatability after the wax removal, and durability over time are factors that need to be further investigated.

6. Future Perspectives

In the last twenty years, the rapid public attention towards street artworks and the consequent interest of professionals and research groups, expanded the common knowledge related to conservation practices. An important debate about the most suitable protection solutions for these artworks, has commenced. From the recent literature, the formulation of paint materials and the techniques adopted by contemporary artists have emerged and are in constant development.

Although the polymeric classes chosen by the industry remain unchanged (acrylic, alkyd, styrene, vinyl polymers), the proportions of the various chemical compounds in the formulation, the new additives available, and the pigments added make the final paint a complex and constantly changing chemical system. This aspect may play an important role in the degradation processes of these materials when exposed to atmospheric pollutants, emphasising the need for an effective and specific protection system.

Restoration and conservation practices are still inherited from other Cultural Heritage sectors; it is clear that these practices (materials and methods) need to be updated specifically for street artworks. The issue of Street Art protection remains complex because there are no specific materials on the market purposely developed for such applications, i.e., to be used to overcoat modern paints. The problem of the compatibility and stability of different paints and protective materials remains a challenge for conservators.

The missing aspect, which is also fundamental, resulting from the previous considerations is the definition of a specific methodology to improve the conservation practices of street artworks and to allow for a better and more specific selection of protective systems. This methodology should include a better definition of the state of conservation of artworks, and a valid procedure for testing the protective performances and durability of coatings in laboratory and in situ conditions. This protocol should enable experts in the field to select the correct protective system according to the different painting materials, predict its chemical–physical behaviour, and therefore safeguard street artworks for future generations.

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References

1. Cadetti, A. *Conservare La Street Art. Le Problematiche Del Muralismo Contemporaneo in Italia*; Edifir: Florence, Italy, 2020.
2. Lewisohn, C. *Street Art: The Graffiti Revolution*; Tate Publishing: London, UK, 2008.
3. Hughes, M. Street Art & Graffiti Art: Developing an Understanding. Master's Thesis, Georgia State University, Atlanta, GA, USA, 2009; pp. 1–70.
4. Gómez, M. The Writing on Our Walls: Finding Solutions Through Distinguishing Graffiti Art from Graffiti Vandalism. *Univ. Mich. J. Law Reform* **1993**, *26*, 697.
5. Mezzadri, P. Contemporary Murals in the Street and Urban Art Field: Critical Reflections between Preventive Conservation and Restoration of Public Art. *Heritage* **2021**, *4*, 2515–2525. [CrossRef]
6. Forte, F.; de Paola, P. How Can Street Art Have Economic Value? *Sustainability* **2019**, *11*, 580. [CrossRef]
7. Brajer, I. Values and the Prevention of Contemporary Outdoor Murals. In *Conservation Issues in Modern and Contemporary Murals*; Cambridge Scholars Publishing: Cambridge, UK, 2015; pp. 39–59.
8. Rainer, L.; Paul, T.J.; Trust, G. The Conservation of Outdoor Contemporary Murals. In *Conservation*; The Getty Conservation Institute: Los Angeles, CA, USA, 2003; Volume 18, pp. 4–9.
9. Shank, W.; Norris, D.H. Giving Contemporary Murals a Longer Life: The Challenges for Muralists and Conservators. *Stud. Conserv.* **2008**, *53*, 12–16. [CrossRef]
10. Folgarait, L.; Garfinkle, A.; Healy, W.; Shank, W.; Rainer, L.; Levin, J. Preserving Art in Public Places: A Discussion about Mural Painting and Conservation. *Conserv. GCI Newsl.* **2003**, *18*, 1–7.

11. Sawicki, T. The Conservation of Murals—A New Trend in Protecting Works of Art. *Acta Univ. Lodz. Folia Philos. Ethica-Aesthetica-Practica* **2022**, *40*, 81–95. [CrossRef]
12. Sanchez Pons, M.; Shank, W.; Fuster-Lòpez, L. *Conservation Issues in Modern and Contemporary Murals*; Cambridge Scholars Publishing: Cambridge, UK, 2015.
13. Macchia, A.; Castro, M.; Curbelo, C.; Rivaroli, L.; Capriotti, S.; Vieira, E.; Moreira, P.; Ruffolo, S.A.; La Russa, M.F. Methods and Products for the Conservation of Vandalized Urban Art Murals. *Coatings* **2021**, *11*, 1304. [CrossRef]
14. Gayo, E.; Gayo, E. From Post-Graffiti to Contemporary Mural Art. *SAUC-Str. Art Urban Creat.* **2017**, *3*, 26–28. [CrossRef]
15. Macchia, A.; Rivaroli, L.; Rivaroli, M. Your Art: Yococu Urban ART. In *Action/Reaction: Arte Urbana e Street Art a Roma*; Palombi: Rome, Italy, 2020; pp. 255–264.
16. GRAArt. Urban Contemporary Art Project. Available online: https://www.graart.it/ (accessed on 6 September 2023).
17. Rivaroli, L.; Moretti, P.; Caricchio, A.; Macchia, A. Mural Art Conservation Data Recording (Scima): The Graart Project. *Heritage* **2021**, *4*, 4222–4232. [CrossRef]
18. CAPuS. Conservation of Art in Public Spaces. Available online: https://www.capusproject.eu/ (accessed on 6 September 2023).
19. Cimino, D.; Lamuraglia, R.; Saccani, I.; Berzioli, M.; Izzo, F.C. Assessing the (In)Stability of Urban Art Paints: From Real Case Studies to Laboratory Investigations of Degradation Processes and Preservation Possibilities. *Heritage* **2022**, *5*, 581–609. [CrossRef]
20. PRIN 2020 SUPERSTAR. Sustainable Preservation Strategies for Street Art. Available online: https://prin2020superstar.dcci.unipi.it/ (accessed on 6 September 2023).
21. Miranda, T.J. The Future of the Coatings Industry. In *Surface Coatings*; Springer: Oil and Colour Chemists' Association: Dordrecht, The Netherlands, 2012; pp. 1–10.
22. Shashoua, Y. *Conservation of Plastics—Materials Science, Degradation and Preservation*; Elsevier: Amsterdam, The Netherlands, 2008.
23. La Nasa, J.; Biale, G.; Sabatini, F.; Degano, I.; Colombini, M.P.; Modugno, F. Synthetic Materials in Art: A New Comprehensive Approach for the Characterization of Multi-Material Artworks by Analytical Pyrolysis. *Herit. Sci.* **2019**, *7*, 8. [CrossRef]
24. Chiantore, O.; Rava, A. *Conserving Contemporary Art:Issues, Methods, Materials, and Research*; Getty Conservation Institute: Los Angeles, CA, USA, 2005.
25. Cortea, I.M.; Ratoiu, L.; Radvan, R. Characterization of Spray Paints Used in Street Art Graffiti by a Non-destructive Multi-analytical Approach. *Color Res. Appl.* **2021**, *46*, 183–194. [CrossRef]
26. Macchia, A.; Rivaroli, L.; Damiani, F.; Ruffolo, S.A.; La Russa, M.F. Protezione Delle Opere Di Street Art: Materiali e Metodi. *Kermes Restauro Conserv. Tutela Patrim. Cult.* **2018**, *109*, 86–89.
27. Learner, T. *Analysis of Modern Paints*; The Getty Conservation Institute: Los Angeles, CA, USA, 2004.
28. Bentley, J.; Turner, G.P.A. *Introduction to Paint Chemistry and Principles of Paint Technology*, 4th ed.; Chapman & Hall: London, UK, 1998.
29. Sackler, A.M. *Scientific Examination of Art: Modern Techniques in Conservation and Analysis*; The National Academic Press: Washington, DC, USA, 2003.
30. Learner, T.; Smithen, P.; Krueger, J.; Schilling, M. *Modern Paints Uncovered*; Getty Conservation Institute: Los Angeles, CA, USA, 2006.
31. Wiesinger, R.; Pagnin, L.; Anghelone, M.; Moretto, L.M.; Orsega, E.F.; Schreiner, M. Pigment and Binder Concentrations in Modern Paint Samples Determined by IR and Raman Spectroscopy. *Angew. Chem.-Int. Ed.* **2018**, *57*, 7401–7407. [CrossRef] [PubMed]
32. Pellis, G.; Bertasa, M.; Ricci, C.; Scarcella, A.; Croveri, P.; Poli, T.; Scalarone, D. 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* **2022**, *165*, 105576. [CrossRef]
33. Germinario, G.; van der Werf, I.D.; Sabbatini, L. Chemical Characterisation of Spray Paints by a Multi-Analytical (Py/GC–MS, FTIR, μ-Raman) Approach. *Microchem. J.* **2016**, *124*, 929–939. [CrossRef]
34. Melchiorre Di Crescenzo, M.; Zendri, E.; Sánchez-Pons, M.; Fuster-López, L.; Yusá-Marco, D.J. The Use of Waterborne Paints in Contemporary Murals: Comparing the Stability of Vinyl, Acrylic and Styrene-Acrylic Formulations to Outdoor Weathering Conditions. *Polym. Degrad. Stab.* **2014**, *107*, 285–293. [CrossRef]
35. Fardi, T.; Pintus, V.; Kampasakali, E.; Pavlidou, E.; Schreiner, M.; Kyriacou, G. Analytical Characterization of Artist's Paint Systems Based on Emulsion Polymers and Synthetic Organic Pigments. *J. Anal. Appl. Pyrolysis* **2018**, *135*, 231–241. [CrossRef]
36. Pintus, V.; Wei, S.; Schreiner, M. Accelerated UV Ageing Studies of Acrylic, Alkyd, and Polyvinyl Acetate Paints: Influence of Inorganic Pigments. *Microchem. J.* **2016**, *124*, 949–961. [CrossRef]
37. Anghelone, M.; Jembrih-Simbürger, D.; Pintus, V.; Schreiner, M. Photostability and Influence of Phthalocyanine Pigments on the Photodegradation of Acrylic Paints under Accelerated Solar Radiation. *Polym. Degrad. Stab.* **2017**, *146*, 13–23. [CrossRef]
38. Pagnin, L.; Calvini, R.; Wiesinger, R.; Weber, J.; Schreiner, M. Photodegradation Kinetics of Alkyd Paints: The Influence of Varying Amounts of Inorganic Pigments on the Stability of the Synthetic Binder. *Front. Mater.* **2020**, *7*, 600887. [CrossRef]
39. Stoye, D.; Freitag, W. *Paints, Coatings and Solvents*; Wiley-VCH: Hoboken, NJ, USA, 1998.
40. Marcilla, A.; Beltrán, M. Mechanism of Plasticizers Action. In *Handbook of Plasticizers*, 4th ed.; ChemTec Publishing: Scarborough, ON, Canada, 2023; pp. 139–158. ISBN 978-1-77467-022-4.
41. Silva, M.F.; Doménech-Carbó, M.T.; Fuster-Lopéz, L.; Martín-Rey, S.; Mecklenburg, M.F. Determination of the Plasticizer Content in Poly(Vinyl Acetate) Paint Medium by Pyrolysis–Silylation–Gas Chromatography–Mass Spectrometry. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 487–491. [CrossRef]

42. Vash, R. *Pigment Wetting and Dispersinig Additives for Water-Based Coatings and Inks BT—Surface Phenomena and Additives in Water-Based Coatings and Printing Technology*; Sharma, M.K., Ed.; Springer: Boston, MA, USA, 1991; pp. 139–149. ISBN 978-1-4899-2361-5.
43. Beaugendre, A.; Degoutin, S.; Bellayer, S.; Pierlot, C.; Duquesne, S.; Casetta, M.; Jimenez, M. Self-Stratifying Coatings: A Review. *Prog. Org. Coat.* **2017**, *110*, 210–241. [CrossRef]
44. Sundberg, B.N.; Lagalante, A.F. Characterization of Non-Ionic Surfactants in Winsor & Newton's Water-Mixable Oil Paints. *J. Cult. Herit.* **2021**, *48*, 54–64. [CrossRef]
45. Pagnin, L.; Wiesinger, R.; Koyun, A.N.; Schreiner, M. The Effect of Pollutant Gases on Surfactant Migration in Acrylic Emulsion Films: A Comparative Study and Preliminary Evaluation of Surface Cleaning. *Polymers* **2021**, *13*, 1941. [CrossRef]
46. Valet, A.; Braig, A. *Light Stabilizers for Coatings*; Vincentz Network: Hannover, Germany, 2017.
47. Govaert, F.; Bernard, M. Discriminating Red Spray Paints by Optical Microscopy, Fourier Transform Infrared Spectroscopy and X-Ray Fluorescence. *Forensic Sci. Int.* **2004**, *140*, 61–70. [CrossRef]
48. Zieba-Palus, J. Examination of Spray Paints by the Use of Reflection Technique of Microinfrared Spectroscopy. *J. Mol. Struct.* **2005**, *744–747*, 229–234. [CrossRef]
49. Marazioti, V.; Douvas, A.M.; Katsaros, F.; Koralli, P.; Chochos, C.; Gregoriou, V.G.; Boyatzis, S.; Facorellis, Y. Chemical Characterisation of Artists' Spray-Paints: A diagnostic tool for urban art conservation. *Spectr. Acta Part A Molec. Bio Spectr.* **2022**, *291*, 122375. [CrossRef] [PubMed]
50. La Nasa, J.; Campanella, B.; Sabatini, F.; Rava, A.; Shank, W.; Lucero-Gomez, P.; De Luca, D.; Legnaioli, S.; Palleschi, V.; Colombini, M.P.; et al. 60 Years of Street Art: A Comparative Study of the Artists' Materials through Spectroscopic and Mass Spectrometric Approaches. *J. Cult. Herit.* **2021**, *48*, 129–140. [CrossRef]
51. La Nasa, J.; Orsini, S.; Degano, I.; Rava, A.; Modugno, F.; Colombini, M.P. A Chemical Study of Organic Materials in Three Murals by Keith Haring: A Comparison of Painting Techniques. *Microchem. J.* **2016**, *124*, 940–948. [CrossRef]
52. Dickens, J.; Rava, A.; Colombini, M.P.; Picollo, M.; Shank, W. Keith Haring in Pisa and Melbourne: Controversy and Conservation. *Stud. Conserv.* **2016**, *61*, 29–37. [CrossRef]
53. Carlesi, S.; Bartolozzi, G.; Cucci, C.; Marchiafava, V.; Picollo, M.; La Nasa, J.; Di Girolamo, F.; Dilillo, M.; Modugno, F.; Degano, I.; et al. Discovering "The Italian Flag" by Fernando Melani (1907–1985). *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2016**, *168*, 52–59. [CrossRef]
54. Magrini, D.; Bracci, S.; Cantisani, E.; Conti, C.; Rava, A.; Sansonetti, A.; Shank, W.; Colombini, M. A Multi-Analytical Approach for the Characterization of Wall Painting Materials on Contemporary Buildings. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2017**, *173*, 39–45. [CrossRef]
55. Cucci, C.; Bartolozzi, G.; De Vita, M.; Marchiafava, V.; Picollo, M.; Casadio, F. The Colors of Keith Haring: A Spectroscopic Study on the Materials of the Mural Painting Tuttomondo and on Reference Contemporary Outdoor Paints. *Appl. Spectrosc.* **2016**, *70*, 186–196. [CrossRef] [PubMed]
56. Fenzi, F.; Gasperini, R.; La Nasa, J.; Di Carlo, S.; Michelotto, C.; Modugno, F.; Scalvi, M.; Todaro, C. I Writing Di Peeta, Deban e Ment a Verona. Los Tudio e Il Restauro Di Due Opere Di Street Art. *Kermes Doss. Str. Art* **2018**, *109*, 71–80.
57. Rousaki, A.; Vandenabeele, P.; Berzioli, M.; Saccani, I.; Fornasini, L.; Bersani, D. An In-and-out-the-Lab Raman Spectroscopy Study on Street Art Murals from Reggio Emilia in Italy. *Eur. Phys. J. Plus* **2022**, *137*, 252. [CrossRef]
58. Bosi, A.; Ciccola, A.; Serafini, I.; Guiso, M.; Ripanti, F.; Postorino, P.; Curini, R.; Bianco, A. Street Art Graffiti: Discovering Their Composition and Alteration by FTIR and Micro-Raman Spectroscopy. *Spectrochim. Acta-Part A Mol. Biomol. Spectrosc.* **2020**, *225*, 117474. [CrossRef] [PubMed]
59. Murillo, E.A.; Percino, J.; López, B.L. Colloidal, Morphological, Thermal, Rheological, and Film Properties of Waterborne Hyperbranched Alkyd–Acrylic Resins. *J. Coat. Technol. Res.* **2019**, *16*, 1223–1232. [CrossRef]
60. Chardon, F.; Denis, M.; Negrell, C.; Caillol, S. Hybrid Alkyds, the Glowing Route to Reach Cutting-Edge Properties? *Prog. Org. Coat.* **2021**, *151*, 106025. [CrossRef]
61. Lomax, S.Q.; Learner, T. A Review of the Classes, Structures, and Methods of Analysis of Synthetic Organic Pigments. *J. Am. Inst. Conserv.* **2006**, *45*, 107–125. [CrossRef]
62. Ghelardi, E.; Degano, I.; Colombini, M.P.; Mazurek, J.; Schilling, M.; Learner, T. Py-GC/MS Applied to the Analysis of Synthetic Organic Pigments: Characterization and Identification in Paint Samples. *Anal. Bioanal. Chem.* **2015**, *407*, 1415–1431. [CrossRef]
63. Rosi, F.; Daveri, A.; Moretti, P.; Brunetti, B.G.; Miliani, C. Interpretation of Mid and Near-Infrared Reflection Properties of Synthetic Polymer Paints for the Non-Invasive Assessment of Binding Media in Twentieth-Century Pictorial Artworks. *Microchem. J.* **2016**, *124*, 898–908. [CrossRef]
64. Lettieri, M.; Calia, A.; Licciulli, A.; Marquardt, A.E.; Phaneuf, R.J. Nanostructured TiO_2 for Stone Coating: Assessing Compatibility with Basic Stone's Properties and Photocatalytic Effectiveness. *Bull. Eng. Geol. Environ.* **2017**, *76*, 101–114. [CrossRef]
65. van Driel, B.A.; van der Meer, S.R.; van den Berg, K.J.; Dik, J. Determining The Presence of Photocatalytic Titanium White Pigments via Embedded Paint Sample Staining: A Proof of Principle. *Stud. Conserv.* **2019**, *64*, 261–272. [CrossRef]
66. Pagnin, L.; Izzo, F.C.; Goidanich, S.; Toniolo, L. Interview with the Artists SMOE and OrticaNoodle about the Paint Material Used for their Murals "*Necesse*" and "*ORME*" in Milan. 27 September 2022; *unpublished*.
67. Pozo-Antonio, J.S.; Rivas, T.; González, N.; Alonso-Villar, E.M. Deterioration of Graffiti Spray Paints Applied on Granite after a Decade of Natural Environment. *Sci. Total Environ.* **2022**, *826*, 154169. [CrossRef] [PubMed]

68. Conservation of Art in Public Spaces (CAPuS)-Illustrated Glossary. Available online: https://www.capusproject.eu/glossary/ (accessed on 21 March 2023).
69. Rivas, T.; Alonso-Villar, E.M.; Pozo-Antonio, J.S. Forms and Factors of Deterioration of Urban Art Murals under Humid Temperate Climate; Influence of Environment and Material Properties. *Eur. Phys. J. Plus* **2022**, *137*, 1257. [CrossRef]
70. Sanmartín, P.; Pozo-Antonio, J.S. Weathering of Graffiti Spray Paint on Building Stones Exposed to Different Types of UV Radiation. *Constr. Build. Mater.* **2020**, *236*, 117736. [CrossRef]
71. Croll, S.G. Stress and Embrittlement in Organic Coatings during General Weathering Exposure: A Review. *Prog. Org. Coat.* **2022**, *172*, 107085. [CrossRef]
72. Krmpotić, M.; Jembrih-Simbürger, D.; Siketić, Z.; Anghelone, M.; Radović, I.B. Study of UV Ageing Effects in Modern Artists' Paints with MeV-SIMS. *Polym. Degrad. Stab.* **2022**, *195*, 109769. [CrossRef]
73. Alonso-Villar, E.M.; Rivas, T.; Pozo-Antonio, J.S. Resistance to Artificial Daylight of Paints Used in Urban Artworks. Influence of Paint Composition and Substrate. *Prog. Org. Coat.* **2021**, *154*, 106180. [CrossRef]
74. Alonso-Villar, E.M.; Rivas, T.; Pozo-Antonio, J.S. Sol-Silicate versus Organic Paints: Durability after Outdoor and Ultraviolet Radiation Exposures. *Prog. Org. Coat.* **2022**, *168*, 106843. [CrossRef]
75. Feller, R. *Accelerated Aging, Photochemical and Thermal Aspects*; The Getty Conservation Institute: Los Angeles, CA, USA, 1994.
76. Chiantore, O.; Trossarelli, L.; Lazzari, M. Photooxidative Degradation of Acrylic and Methacrylic Polymers. *Polymer* **2000**, *41*, 1657–1668. [CrossRef]
77. Izzo, F.C.; Balliana, E.; Perra, E.; Zendri, E. Accelerated Ageing Procedures to Assess the Stability of an Unconventional Acrylic-Wax Polymeric Emulsion for Contemporary Art. *Polymers* **2020**, *12*, 1925. [CrossRef]
78. Pintus, V.; Wei, S.; Schreiner, M. UV Ageing Studies: Evaluation of Lightfastness Declarations of Commercial Acrylic Paints. *Anal. Bioanal. Chem.* **2012**, *402*, 1567–1584. [CrossRef]
79. Ciccola, A.; Serafini, I.; Guiso, M.; Ripanti, F.; Domenici, F.; Sciubba, F.; Postorino, P.; Bianco, A. Spectroscopy for Contemporary Art: Discovering the Effect of Synthetic Organic Pigments on UVB Degradation of Acrylic Binder. *Polym. Degrad. Stab.* **2019**, *159*, 224–228. [CrossRef]
80. Pintus, V.; Schreiner, M. Characterization and Identification of Acrylic Binding Media: Influence of UV Light on the Ageing Process. *Anal. Bioanal. Chem.* **2011**, *399*, 2961–2976. [CrossRef]
81. Ormsby, B.; Foster, G.; Learner, T.; Ritchie, S.; Schilling, M. Improved Controlled Relative Humidity Dynamic Mechanical Analysis of Artists' Acrylic Emulsion Paints: Part II. General Properties and Accelerated Ageing. *J. Therm. Anal. Calorim.* **2007**, *90*, 503–508. [CrossRef]
82. Pagnin, L.; Calvini, R.; Sterflinger, K.; Izzo, F.C. Data Fusion Approach to Simultaneously Evaluate the Degradation Process Caused by Ozone and Humidity on Modern Paint Materials. *Polymers* **2022**, *14*, 1787. [CrossRef] [PubMed]
83. Pagnin, L.; Calvini, R.; Wiesinger, R.; Schreiner, M. SO2- and NOx- Initiated Atmospheric Degradation of Polymeric Films: Morphological and Chemical Changes, Influence of Relative Humidity and Inorganic Pigments. *Microchem. J.* **2021**, *164*, 106087. [CrossRef]
84. Timoncini, A.; Brattich, E.; Bernardi, E.; Chiavari, C.; Tositti, L. Safeguarding Outdoor Cultural Heritage Materials in an Ever-Changing Troposphere: Challenges and New Guidelines for Artificial Ageing Test. *J. Cult. Herit.* **2023**, *59*, 190–201. [CrossRef]
85. Gomes, V.; Dionísio, A.; Santiago Pozo-Antonio, J. The Influence of the SO2 Ageing on the Graffiti Cleaning Effectiveness with Chemical Procedures on a Granite Substrate. *Sci. Total Environ.* **2018**, *625*, 233–245. [CrossRef] [PubMed]
86. Pagnin, L.; Izzo, F.C.; Goidanich, S.; Toniolo, L. Preliminary Approach to Protect Street Art from Environmental Agents and Gaseous Pollutants. In Proceedings of the 2022 IMEKO TC4 International Conference on Metrology for Archaeology and Cultural Heritage, IMEKO, Calabria, Italy, 19–21 October 2022; pp. 80–83.
87. Artesani, A.; di Turo, F.; Zucchelli, M.; Traviglia, A. Recent Advances in Protective Coatings for Cultural Heritage. *Coatings* **2020**, *10*, 217. [CrossRef]
88. Doehne, E.; Price, C. *Stone Conservation*; Getty Conservation Institute: Los Angeles, CA, USA, 2010.
89. Snethlage, R. Stone Conservation. In *Stone in Architecture*; Springer: Berlin/Heidelberg, Germany, 2015; pp. 516–528.
90. Sanmartín, P.; Cappitelli, F.; Mitchell, R. Current Methods of Graffiti Removal: A Review. *Constr. Build. Mater.* **2014**, *71*, 363–374. [CrossRef]
91. Bertasa, M.; Ricci, C.; Scarcella, A.; Zenucchini, F.; Pellis, G.; Croveri, P.; Scalarone, D. Overcoming Challenges in Street Art Murals Conservation: A Comparative Study on Cleaning Approach and Methodology. *Coatings* **2020**, *10*, 1019. [CrossRef]
92. Carmona-Quiroga, P.M.; Panas, I.; Svensson, J.E.; Johansson, L.G.; Blanco-Varela, M.T.; Martínez-Ramírez, S. Protective Performances of Two Anti-Graffiti Treatments towards Sulfite and Sulfate Formation in SO_2 Polluted Model Environment. *Appl. Surf. Sci.* **2010**, *257*, 852–856. [CrossRef]
93. Gomes, V.; Dionísio, A.; Pozo-Antonio, J.S. Conservation Strategies against Graffiti Vandalism on Cultural Heritage Stones: Protective Coatings and Cleaning Methods. *Prog. Org. Coatings* **2017**, *113*, 90–109. [CrossRef]
94. García, O.; Malaga, K. 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.* **2012**, *13*, 77–82. [CrossRef]

95. Norbutus, A. Common Threads, Common Goals: Protective Coatings for Outdoor Public Murals. In *Conservation Issues in Modern and Contemporary Murals*; Cambridge Scholars Publishing: Cambridge, UK, 2015; pp. 218–237.
96. Lamuraglia, R. Evaluation of Anti UV and Anti Graffiti Coatings for Contemporary Paints in Urban Art. Master's Thesis, Ca' Foscari University of Venice, Venice, Italy, 2020.
97. Amrutkar, S.; More, A.; Mestry, S.; Mhaske, S.T. Recent Developments in the Anti-Graffiti Coatings: An Attentive Review. *J. Coatings Technol. Res.* **2022**, *19*, 717–739. [CrossRef]
98. Gagne, L. Evaluation of Two Sacrificial Anti-Graffiti Polysaccharide Coatings for the Conservation of Outdoor Contemporary Murals. Ph.D. Thesis, Queen's University, Kingston, ON, Canada, 2014. [CrossRef]
99. Podagrosi, M. Street Art: Conseguenze Giuridiche Della Realizzazione Di Opere Su Superfici Altrui. *Riv. Dirit. Arti Spett.* **2018**, *1*, 109–126.
100. McDonald, E. *Keith Haring a Pisa*; Cronaca Di Un Murales: Pisa, Italy, 2013.
101. Rava, A.; Shank, W.; Colombini, M.P.; Chiantore, O.; Picollo, M.; Palleschi, V. Keith Haring in Pisa: Cleaning and Protection of an Acrylic Painting in an Outdoor Environment. In *Conservation Issues in Modern and Contemporary Murals*; Cambridge Scholars Publishing: Cambridge, UK, 2014; pp. 184–201.
102. Gurgone, P.; Iazurlo, U.; Santamaria, M.G. Problematiche Conservative Dei Murales Contemporanei Acrilico-Vinilici. In *Proceedings of Sulle Pitture Murali: Riflessioni, Conoscenze, Interventi in Atti del XXI Convegno Internazionale Scienze dei Beni Culturali*; Arcadia Ricerche: Venice, Italy, 2005; pp. 860–868.
103. Chiantore, O.; Lazzari, M. Photo-Oxidative Stability of Paraloid Acrylic Protective Polymers. *Polymer* **2001**, *42*, 17–27. [CrossRef]
104. Lazzari, M.; Chiantore, O. Thermal-Ageing of Paraloid Acrylic Protective Polymers. *Polymer* **2000**, *41*, 6447–6455. [CrossRef]
105. Bracci, S.; Melo, M.J. Correlating Natural Ageing and Xenon Irradiation of Paraloid® B72 Applied on Stone. *Polym. Degrad. Stab.* **2003**, *80*, 533–541. [CrossRef]
106. Melo, M.J.; Bracci, S.; Camaiti, M.; Chiantore, O.; Piacenti, F. Photodegradation of Acrylic Resins Used in the Conservation of Stone. *Polym. Degrad. Stab.* **1999**, *66*, 23–30. [CrossRef]
107. Pozo-Antonio, J.S.; Alonso-Villar, E.M.; Rivas, T.; Márquez, I. Evaluation of a Protective Acrylic Finish Applied to Surfaces Painted with Acrylic Paints for Outdoor or Indoor Uses. *Dye. Pigment.* **2023**, *212*, 111141. [CrossRef]
108. Alonso-Villar, E.M.; Rivas, T.; Pozo-Antonio, J.S.; Pellis, G.; Scalarone, D. Efficacy of Colour Protectors in Urban Art Paintings under Different Conditions: From a Real Mural to the Laboratory. *Heritage* **2023**, *6*, 3475–3498. [CrossRef]
109. Wheeler, G. Alkoxysilanes and the Consolidation of Stone. In *Research on Conservation*; Getty Conservation Institute: Los Angeles, CA, USA, 2005; pp. 1–11.
110. Cappelletti, G.; Fermo, P. Hydrophobic and Superhydrophobic Coatings for Limestone and Marble Conservation. In *Smart Composite Coatings and Membranes*; Montemor, M.F., Ed.; Woodhead Publishing Series in Composites Science and Engineering; Woodhead Publishing: Sawston, UK, 2016; pp. 421–452. ISBN 978-1-78242-283-9.
111. Hofacker, S.; Mechtel, M.; Mager, M.; Kraus, H. Sol-Gel: A New Tool for Coatings Chemistry. *Prog. Org. Coat.* **2002**, *45*, 159–164. [CrossRef]
112. Rauseo, A. Il Restauro Negato. Senza Titolo Di Blu Ed Ericailcane Al Padiglione d'Arte Contemporanea Di Milano. *Kermes Doss. Str. Art* **2018**, *109*, 20–25.
113. Carrieri, A. Perchè Restaurare Questo Graffito. In *Quattordio Urban Art. Nessuna Frontiera*; Mantovani, K., Ed.; Milan, Italy, 2018; pp. 159–172.
114. Colombini, M.P.; Modugno, F.; Di Girolamo, F.; La Nasa, J.; Duce, C.; Al, E. Keith Haring and the City of the Leaning Tower: Preservation of the Mural "Tuttomondo". In *Conservation Issues in Modern and Contemporary Murals*; Cambridge Scholars Publishing: Cambridge, UK, 2014; pp. 274–284.
115. Spepi, A.; Pizzimenti, S.; Duce, C.; Vozzi, G.; De Maria, C.; Tiné, M.R. Chemico-Physical Characterization and Evaluation of Coating Properties of Two Commercial Organosilicons: Hydrophase® and Disboxan 450®. *J. Therm. Anal. Calorim.* **2019**, *138*, 3277–3285. [CrossRef]
116. Chiantore, O.; Lazzari, M.; Aglietto, M.; Castelvetro, V.; Ciardelli, F. Photochemical Stability of Partially Fluorinated Acrylic Protective Coatings. *Polym. Degrad.* **2000**, *67*, 461–467. [CrossRef]
117. Scheerder, J.; Visscher, N.; Nabuurs, T.; Overbeek, A. Novel, Water-Based Fluorinated Polymers with Excellent Antigraffiti Properties. *J. Coatings Technol. Res.* **2005**, *2*, 617–625. [CrossRef]
118. Rossi, S.; Fedel, M.; Petrolli, S.; Deflorian, F. Behaviour of Different Removers on Permanent Anti-Graffiti Organic Coatings. *J. Build. Eng.* **2016**, *5*, 104–113. [CrossRef]
119. Licchelli, M.; Marzolla, S.J.; Poggi, A.; Zanchi, C. Crosslinked Fluorinated Polyurethanes for the Protection of Stone Surfaces from Graffiti. *J. Cult. Herit.* **2011**, *12*, 34–43. [CrossRef]
120. Carmona-Quiroga, P.M.; Jacobs, R.M.J.; Martínez-Ramírez, S.; Viles, H.A. Durability of Anti-Graffiti Coatings on Stone: Natural vs Accelerated Weathering. *PLoS ONE* **2017**, *12*, e0172347. [CrossRef] [PubMed]
121. Macchia, A.; Ruffolo, S.A.; Rivaroli, L.; Malagodi, M.; Licchelli, M.; Rovella, N.; Randazzo, L.; La Russa, M.F. Comparative Study of Protective Coatings for the Conservation of Urban Art. *J. Cult. Herit.* **2020**, *41*, 232–237. [CrossRef]
122. Macchia, A.; Capriotti, S.; Rivaroli, L.; Ruffolo, S.A.; La Russa, M.F. Protection of Urban Art Painting: A Laboratory Study. *Polymers* **2022**, *14*, 162. [CrossRef]

123. Pozo-Antonio, J.S.; Rivas, T.; Jacobs, R.M.J.; Viles, H.A.; Carmona-Quiroga, P.M. Effectiveness of Commercial Anti-Graffiti Treatments in Two Granites of Different Texture and Mineralogy. *Prog. Org. Coat.* **2018**, *116*, 70–82. [CrossRef]
124. Moura, A.; Flores-Colen, I.; De Brito, J. Study of the Effect of Three Anti-Graffiti Products on the Physical Properties of Different Substrates. *Constr. Build. Mater.* **2016**, *107*, 157–164. [CrossRef]