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Article

Compatibility and Efficacy Evaluations of Organic Protective Coatings for Contemporary Muralism

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Abstract: Contemporary muralism is a constantly expanding form of urban art, whose preservation is highly debated and for which no specific preventive conservation measures have been defined. The degradation of painting materials remains a dramatic issue as mural paintings undergo rapid and inevitable chemical–physical reactions, leading to their aesthetic decay and chemical–mechanical disintegration. This work started with interviews with, and questionnaires given to experts in the field from which various needs emerged, including defining a testing protocol for the study of the compatibility and effectiveness of organic coatings to protect street art painted surfaces. Five protective formulations available on the market were selected and applied on mock-ups realized with three different types of paintings (alkyd, acrylic, and styrenic). The efficacy and affinity of the five protective treatments in relation to the different underlying painting layers were investigated. The adopted testing protocol enabled understanding the protection efficacy and compatibility of the different tested formulations in relation to the type of painting and wall preparation. The typology of the underlying paint mainly influences the final aesthetic result, while the application of the primer may play a relevant role in terms of the protection effectiveness, confirming the importance of pre-treating the substrate before painting. The results clearly show that there is still no specific and effective protection system that is appropriate for all commercial paints used by street artists.

Keywords: contemporary muralism; testing protocols; protective coatings; compatibility and efficacy; protective performance

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1. Introduction

Contemporary muralism is an artistic expression that is gaining importance across the world in different urban contexts. Important and well-renowned artists, such as Keith Haring, Basquiat, Lady Pink, Blu, Banksy, etc., created often very large artworks that are exposed in outdoor polluted urban conditions and therefore subject to fast weathering and deterioration [1,2]. Beyond this group of well-established artists, there is growing interest in attracting young artists who can work in urban contexts, essentially for their ability to combine art and relevant social messages. Through their large-scale works they can transform neglected neighborhoods and revitalize depressed urban areas. In this regard, the urgency of setting up preventive conservation practices is becoming a necessity for institutions, organizations, and entities that commission these artworks and for professionals in the restoration and heritage conservation fields [1].

It is well known that the degradation of contemporary murals is a very rapid process (taking place over a few years) [2–9] due, essentially, to the synergistic effects of the following: the intrinsic weakness of the polymeric painting materials used by artists, the frequent lack of preparation of walls and substrates, and the aggressive outdoor conditions of exposure (thermal excursions, solar irradiation, humidity, atmospheric pollutants, and rain).

Regarding painting materials, cans and spray paints composed of organic binding media, organic dyes and pigments, additives, and solvents have been investigated in different important case studies [2,10,11] to reveal the artist's palette and to understand the nature of the materials. Only limited research has focused on the evaluation of paint durability [3,12].

Optical alterations (fading, whitening, color changes), craquelure formation, painting detachment, cracking, powdering and disintegration, exfoliation, and salt efflorescence are among the most common deterioration patterns that can be identified on aged mural painted surfaces [2,13,14]. These phenomena and degradation processes can rapidly lead to the partial or complete loss of the readability of painted surfaces. Additionally, vandalism often occurs, since these paintings are easily accessed from the street.

Conservators and restorers are particularly concerned about the conservation of contemporary murals, especially iconic works, for example, those by Keith Haring and other murals. Only limited studies are available in the literature concerning the possibility of protecting contemporary murals from environmental and anthropic threats [2,15,16].

The application of protective coatings to these artistic surfaces, indeed, is not a common practice, as revealed through interviews that were conducted when preparing this study, with both street artists and conservators in Italy. These interviews highlighted concerns regarding the inadequate suitability of current protective coatings for modern street art materials. Several commonly used products offer the great advantage of reversibility but require frequent re-application (in some cases, in less than 5 years). Experts recommend testing siloxane products and, for acrylic-based murals, traditional coatings, such as Paraloid B72. It is also clear that, despite the growing interest in preventive conservation, the market for appropriate coating remains limited, and advice from paint dealers is often unsuitable. Artists typically choose materials based on cost and aesthetics, with an increasing awareness of the impact of the paint's chemistry on the long-term resistance to environmental factors.

A recent comprehensive literature review [2] highlights the following: (i) protective materials are normally borrowed from other application fields and substrates (such as architectural surfaces made of natural stones, bricks, plasters, etc.); (ii) the water repellency achieved with these treatments is moderate; (iii) the adhesion of the coating depends both on the type of substrate and on the chemical nature of the painting materials; and (iv) coatings are often applied to stabilize deteriorated paint layers by re-adhering lifted flakes and exfoliations to the surface.

The aim of the present study was therefore twofold: (i) to set up a reliable laboratory evaluation methodology to assess the compatibility and effectiveness of protective coatings for contemporary muralism and (ii) to verify the effectiveness and compatibility of a selection of commercial products applied on a set of suitable specimens, prepared with paints of different chemical natures.

The first challenge in this study was selecting a significant array of commercial protective materials for contemporary mural artworks. As already mentioned, to achieve this goal, a series of interviews and questionnaires, addressed to professionals (restorers, conservators, scientists, technicians, and artists), were conducted and collected to better understand their experiences about treatments and protective coatings. The collected answers and in-depth bibliographic research enabled the creation of a list of different classes of commonly used commercial materials, among which five different products were selected for laboratory experimentation. The selection criteria included the chemical class as declared on the technical data sheet and the popularity of the product among restorers and artists.

2. Materials and Methods

2.1. Preparation of Mock-Up Samples

Mock-up samples were prepared based on previous research [17], specifically based on the survey campaign conducted by the CAPuS project team from 2018 to 2021. This campaign examined over 50 murals located in various European cities [14], from which it emerged that one of the most widespread supports for contemporary murals are walls finished with cement mortar. Although there is some variety in the composition and morphological characteristics of the mortars, the one reproduced in the present study can be considered representative of many case studies from the CAPuS project as well as the SuperStar project, of which this work is a part [16]. Accordingly, a total of 72 cement mortar mock-ups were prepared by using i. work TECNOCEM® B-LL 32,5 R (Italcementi, Milan, Italy), a Portland cement with limestone type II having a high initial strength. According to the UNI EN 197-1 standard [18], it contains between 65% and 79% of clinker, while the remaining fraction consists of limestone (TOC $\leq$ 0.20% in mass (LL)) with other minor constituents. The mixture used for the mock-ups had the following volume ratios: 2.5 parts of mixed sand, of which there were 2 parts of fine natural sand (fine AXTON natural river sand) and 1 part of mixed sieved coarse sand (sieved AXTON sand); 1 part of cement; 0.65–1 parts of water. Silicone molds (5 cm $\times$ 5 cm $\times$ 2.5 cm) were used to shape the mock-ups. Subsequently, they hardened in the laboratory (20 $\pm$ 2 °C, 50 $\pm$ 10% RH) for approximately one month before paint application. After the complete hardening, the surfaces of the mortar samples were treated with 180 grit sandpaper to remove the shiny superficial effect of the mold, simulating the texture of real outdoor surfaces. On half of the prepared mock-ups (36 samples), one layer of primer was applied by brush. Specifically, the selected primer was an acrylic impregnating agent (Sikkens, Novara, Italy). Following the technical data sheet, the product was diluted to 400% by volume with distilled water and applied by brush on the side of interest. Once dried, different painting layers were applied. Samples with primer were labeled with the abbreviation "Pr".

According to the literature [19], the paints used to create the mock-ups are among the most used by street artists. Three types of paint were selected, produced by different manufacturers and representing distinct chemical classes according to the nature of the binder. By carefully analyzing the information provided in the technical data sheets, product lines without secondary binders were selected. These were Flame Orange acrylic spray paints (Molotow, Lahr/Schwarzwald, Germany) (Acr), Montana 94 alkyd spray paints (Montana Colors, Barcelona, Spain) (Alk), and the styrene-acrylic water-based Alpha Acrilmat paints (Sikkens, Novara, Italy) (Sty), the latter being representative of paints applied by brush or roller. For this study, magenta was chosen for all three products, as it is typically one of the most sensitive to chromatic alteration. Therefore, it is particularly suitable for highlighting the protective efficacy of the coatings in screening solar light and other sources of degradation (Table 1).

Table 1. Summary of the selected paints and protective treatments, with specific information regarding the abbreviations, class of product, and declared chemical composition (from the technical datasheet of the suppliers).

Paint Abbreviation	Chemical Composition from Technical Datasheet		Chemical Identification *
Acr	Acrylic emulsion		Acrylic emulsion + PR122 + PR254 + PW6
Alk	Alkyd resin		Alkyd resin + PR122 + PW6 + Talc (filler)
Sty	Styrene-acrylic emulsion		Styrene-acrylic emulsion + Eosin B + $CaCO_3$ (filler)
Protective Treatment Abbreviation	**Product Class from Technical Data Sheet**	**Chemical Composition from Technical Datasheet**	**Chemical Characterization by ATR-FTIR**
A1	Acrylic	Water-based Acrylic	Acrylic polymer, polyurethane, Si-containing filler
A2	Acrylic	Acrylic resin copolymer MA-EMA	Copolymer MA-EMA
S1	Silane	Alkyl alkoxy silane with catalyst	Silane/acrylic polymer
S2	Silane/Siloxane	Micromolecular silane/siloxane	Dimethyl-siloxane/silane
SF3	Fluoro-silane	Water dispersion of fluoro-silane at nano scale	Not resolved formulation

* Complete information will be reported in the SuperStar project report [20] and in papers under preparation.

The spray paints were applied from approximately 15–20 cm of distance, following the producer's instructions. The nozzles used were fine type (super skinny, 0.5–2 mm). To ensure homogeneous and complete coverage, three spray layers were applied in succession. Meanwhile, the styrene-acrylic emulsion (Sikkens, Novara, Italy) was applied by brush. Following the technical data sheets' instructions, the paint was diluted by volume by 20% in water and then applied with a 38 mm brush in two orthogonal layers.

2.2. Protective Coatings: Choice and Application Methodologies

Five commercial protective coatings were selected based on the results of the interviews and questionnaires mentioned in Section 1, the experiences of professionals in conservation, and the most recent literature. They are listed in Table 1 and classified into two main chemical classes according to the technical datasheets: acrylic-based products (labelled as "A") and silane/fluoro-silane-based formulations (labelled as "S" and "SF").

The specified protective products were applied to $5 \times 5 \times 2.5$ cm^3 cement mortar mock-ups, purposely prepared for this study and painted with commercial paints: an acrylic emulsion (Acr), an alkyd resin (Alk), and a styrene–acrylic emulsion (see Table 1 and Section 2.1).

According to the technical datasheets and manufacturers' instructions, the coatings were applied pure, except for A2 and S1, which required dilution. The S1 coating was diluted at 10% in distilled water. Initially, half the dose of water was added to the product and stirred for 5–7 min; then, the remaining water was added and mixed for another 2 min.

A2 needs to be diluted in toluene or acetone; however, these solvents also cause the dissolution of acrylic-based paints used for murals. For this reason, the solubility triangle [21] was considered to prepare the correct dilution. The MA-EMA copolymer has a dispersion force value (f_d) between 41 and 87. After several tests on acrylic paint specimens, the A2 coating was diluted initially at 30% in ethyl acetate (f_d = 51) to ensure the complete dissolution of the coating and then further diluted by 15% in isopropanol (f_d = 40), to lower the polarity factor and avoid the solubilization of the acrylic paint during treatment.

To ensure a uniform coating application, the specifications indicated in the technical data sheets were followed. The amount of product required to obtain an optimal final yield was calculated by considering the mock-up area (25 cm^2). On each mock-up, the calculated amount of coating (Table 2) was applied using a pipette and then spread with a soft bristle brush (20 mm). Subsequently, the coatings were left to dry under the hood at laboratory temperature (around 20–25 °C) for 15 days.

Table 2. Application and specific amount of protective coating applied on mock-ups.

Coating	Application Modalities	Recommended amount of Product per Surface Unit (L/m^2)	Amount of Product on Mock-Ups, After Curing (g)
A1	Pure	0.10–0.15	0.34 ± 0.03
A2	30% in ethyl acetate; 15% in isopropanol	0.1–0.3	0.14 ± 0.02
S1	10% diluted in distilled water	0.1–0.2	0.15 ± 0.05
S2	Pure	0.4	0.30 ± 0.05
SF3	Pure	0.1–0.2	0.15 ± 0.05

2.3. Investigation Techniques and Testing Methodologies

For an adequate and reliable evaluation of the compatibility and effectiveness of the protective coatings, specific analytical techniques and measurements were selected. For the aesthetic compatibility evaluation, optical microscopic observations, and colorimetric and gloss measurements were conducted. On the other hand, the evaluation of protective efficacy included measurements of the static contact angle and water absorption by capillarity. The instrumental parameters are listed below.

Microscopy. The morphological characterization of protective coatings and morphological changes observed after the coating application were examined using a Leica M205C stereomicroscope (Leica Microsystems, Milan, Italy). On the acquired images, a hole size and frequency analysis was performed using image processing software (ImageJ) [22]. The images were initially converted to 8-bit grayscale image resulting in 256 intensity graduations (according to the shade of grey, starting from 0 = black to 256 = white), assigned to each pixel. The pixels were then separated by intensity graduation intervals using the "threshold grayscale" function, forming a unique subset of the image. The grayscale images obtained were then converted into a binary image by defining a grayscale breakpoint. Values below the limit become black (superficial holes), and those above become white (painting layer). From this processing, the area and the diameter for each hole were calculated to generate histograms of the hole frequency.

Subsequently, the mock-ups were observed with a Leica DM6 3D optical microscope (Leica Microsystems, Milan, Italy) with a 20× objective. LASX software v5.1. was used for roughness evaluation on the acquired 3D images. For each image (average of 10 photos per sample), 10 lines (~1 mm each) were selected. The Ra values were calculated as the arithmetic average of the absolute profile height deviations from the mean line, recorded within the evaluation length. The roughness values (Ra) were calculated using the formula [23]:

$$\mathrm{Ra} = \frac{1}{L}\int_0^L |f(x)||dx|$$

Roughness measurements were performed only on the untreated painted samples, characterized by a colored opaque surface, as the presence of a transparent protective coating layer, would have made the acquisition of the profiles difficult and the calculated Ra data unreliable [24].

Scanning Electron Microscopy. SEM analyses were performed with a Zeiss EVO 50 EP (Carl Zeiss, Jena, Germany) environmental scanning electron microscope, equipped with an EDS Bruker Quantax 200 spectrometer (Bruker, Ettlingen, Germany). Small fragments were collected from the treated samples and coated with Au using a gold sputter coater S150B. Measurements were carried out in a high vacuum with an accelerating voltage of 15 kV and a working distance of 9.5 mm. The acquired images were used to study the morphology of the painted surfaces after coating application.

Colorimetry. The aesthetic compatibility evaluation of the treatments was assessed using a portable Spectro-colorimeter CM-2600d (Konica Minolta, Tokyo, Japan). Following the standard protocol [25], the measurements were carried out with a D65 light source at 10° and a spot size of around 8 mm. The system was calibrated using an internal white reference. For each sample, 15 spots were measured and averaged. The measurements were acquired in SCE (specular reflectance excluded) mode, excluding the specular reflected light, which is the most suitable mode for evaluating the color of the analyzed samples, correlating the visual perception to surface conditions (such as roughness), and measuring the actual color of the sample as perceived by the human eye [26]. To determine the color changes between the untreated and treated samples, CIELAB coordinates (L*, a*, b*), chroma C*, and ΔE values were evaluated following the indications of the Commission Internationale de l' Èclairage 2000 (CIE 2000). To evaluate the significance of the ΔE values, the Student's *t* test was calculated [27]. A significance level (*p* value) was set at 5%, as reported in a previous study [28]: if the *p* value is below the significance level, the measurements are considered invalid. Otherwise, if the *p* value is greater than 5%, then the set of measurements can be considered reliable and significant. The ΔE calculations showed good agreement, with the significance levels reaching 95%.

Glossmetry. The aesthetic compatibility was also assessed through gloss evaluation. Gloss measurements were conducted using a multi-gloss 268 glossmeter (Konica Minolta, Tokyo, Japan), capable of working with incidence angles of 20°, 60°, and 85°. For each sample, 15 spots were measured, and the averaged values were expressed in gloss units (GU). Measurements were carried out on the planar sample surfaces according to the standard protocol UNI EN ISO 2813 [29]. Since the gloss values obtained in this study did not exceed 30 GU, the gloss results obtained at 60° (angle of incidence) were considered. In fact, generally, surfaces that show a high gloss are evaluated at 20°, while those with a low gloss are evaluated at 85° [30]. By calculating the difference in the gloss before and after treatments, positive or negative changes in the gloss were obtained. A positive change indicates an increase in the surface gloss, while a negative change indicates a decrease. According to ASTM D 523 [31], a tolerance level of 7.2 gloss units was set as the maximum acceptable difference.

Static contact angle. Wettability measurements were performed according to the standard protocol EN15802:2009 [32] to determine the effectiveness of the applied protective treatments. Static contact angle measurements were carried out by using a prototype equipped with a planar stage (able to be moved according to the XY axis), a light source parallel to the stage, and a syringe vertical to the stage, equipped with a 23G needle of 0.6 mm diameter. The photos were acquired 10 s after distilled water drop deposition, with a drop volume of 5 µL, on 20 spots per sample. The contact angle value (θ), resulting from the interfacial tension between the paint surface and water phase, was acquired according to Laplace-Young theory [33] using ImageJ software. The contact angle is measured to determine the wettability of a surface, defined as the angle formed by the tangent to the liquid–vapor interface and the tangent to the liquid–solid interface. A low contact angle (θ < 90°) describes a situation in which the solid is partially wetted by the liquid (hydrophilicity), while a high contact angle (θ > 90°) describes the behavior of the solid to be slightly wetted (hydrophobicity) [34]. According to the European standard protocol for the evaluation of water-repellent treatments EN 16581 [35], a protective treatment (whether coating or painting) can be defined a good barrier to water when it exceeds or equals a θ value of 120°.

Water absorption by capillarity. These tests were carried out on $5 \times 5 \times 2.5$ cm^3 samples following the standard protocol UNI 10859 [36]. According to the norm, the dried samples were initially weighed and then placed on a stack of 1 cm high filter paper sheets, inserted into a container. In the latter, distilled water was poured until it reached half the total level of the filter papers. The samples were weighed at time intervals of 10 min, 20 min, 30 min, 60 min, 4 h, 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Before each weighing, the samples were swabbed with a damp deerskin cloth. The amount of water absorbed per area unit after each time interval was calculated according to the Q_i values (mg/cm^2). The relative capillary index (IC_{rel}), i.e., the ratio of the integrals from 0 to 168 h of the absorption curves of treated and untreated samples, is expressed by the formula:

$$\mathrm{IC_{rel}} = \int_{t0}^{tf} f(Q_i)_{tr} \cdot dt / \int_{t0}^{tf} f(Q_i)_{ntr} \cdot dt,$$

where t_0 is the test starting time; t_f is the test end time; Q_i is the amount of absorbed water per unit surface area; tr indicates the treated mock-up; and ntr indicates the untreated mock-up. This equation describes the long-term water absorption behavior by capillarity, which enables a determination of which coating performed better, reducing the amount of absorbed water in the paint layers.

3. Results and Discussion

3.1. Compatibility Evaluation

Based on the microscopic observations, it can be observed that the three untreated painted mock-ups showed similar surface morphologies (Figure 1). In the case of spray paints (Acr and Alk), the paint covered the mortar substrate with frequent holes spread across the entire surface. The Sty paint also presented a rather uniform surface with fewer surfaces, large holes and visible brushstroke signs (Figure 1). At higher magnification, the Acr and Alk paints showed similar surface morphologies and roughness profiles (Figure 1c–e), while the Sty paint showed a rougher surface.

The microscopic observations were in good agreement with the roughness profiles and the holes' size and frequency. The results (Table 3) show that Acr paint presented the lowest Ra value, followed by Alk and Sty; Acr and Alk paints had the largest holes' size and frequency, while Sty paints had smaller and less frequent holes on the surface (Table 3). These holes ranged in size from 0.4 to 0.2 μm. This is probably connected to the application modalities, i.e., Acr and Alk by spray and Sty by brush.

According to Fisher [37], from spray cans, the liquid particles coalesce together as soon as they leave the spray nozzle, especially in the center of the spray cone. In this way, by deposition of successive droplets next to each other, they form rather regular paint layers with an average thickness of 74 μm ± 15.4 for Alk and 66 μm ± 12.2 for Acr. The presence of frequent medium–large sized holes on the entire surface can be due to the fast-drying process of the spray paint layer (Table 3 and Figure 1).

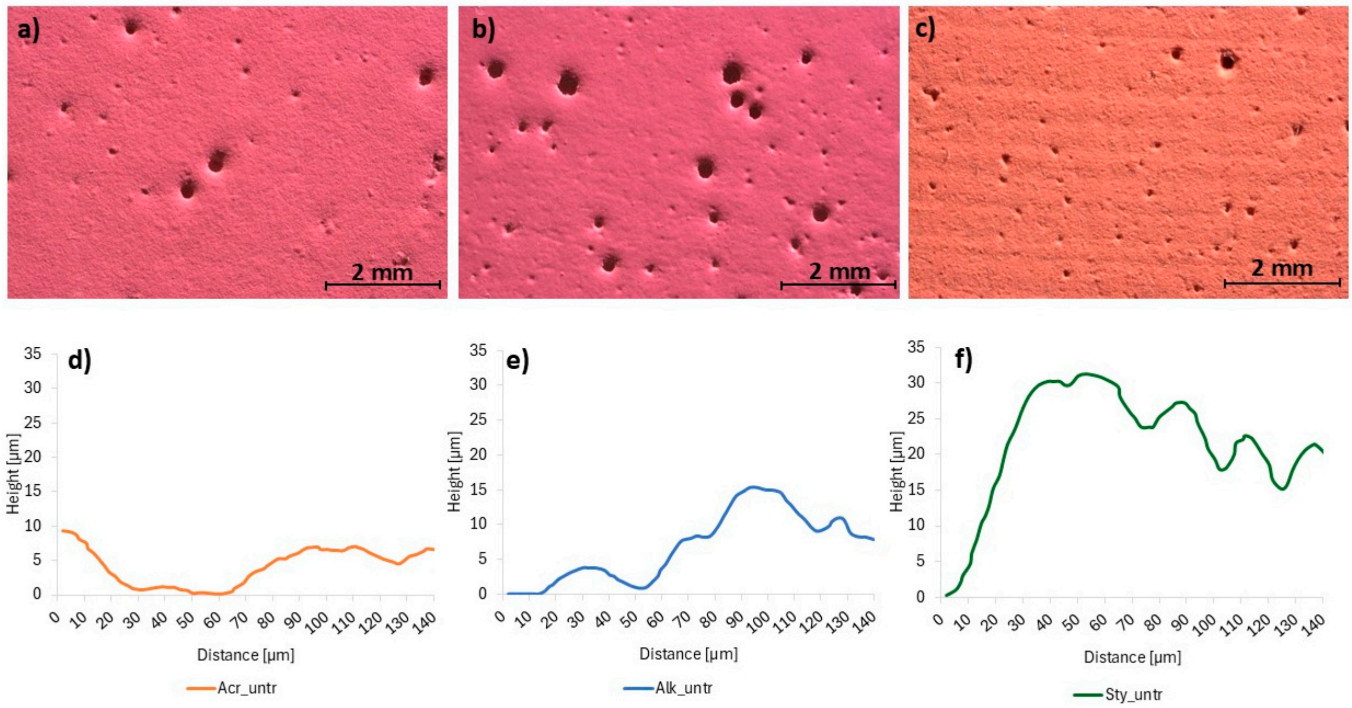


Figure 1. Stereomicroscopic images of (**a**) Acr, (**b**) Alk, and (**c**) Sty paints and the roughness profile of the (**d**) Acr, (**e**) Alk, and (**f**) Sty surfaces.

Table 3. Roughness (Ra) and hole diameter and frequency values (and SD) of all paints with and without primer (Pr).

Paint	Ra Value [µm]	Average Hole Diameter [µm]	Total Hole Frequency [a.u.]
Acr	13.4 ± 0.7	0.34 ± 0.04	76.5 ± 0.13
Alk	15.6 ± 0.4	0.27 ± 0.02	51.3 ± 0.11
Sty	21.0 ± 0.2	0.23 ± 0.03	24.5 ± 0.07
PrAcr	12.3 ± 0.5	0.40 ± 0.01	31.5 ± 0.15
PrAlk	13.7 ± 0.5	0.29 ± 0.03	40.1 ± 0.1
PrSty	19.4 ± 0.4	0.17 ± 0.02	15.5 ± 0.03

On the other hand, for Sty paint, after the brush leaves the superficial paint layer, several competing processes begin: the paint layer starts to dry, and the dispersed pigment particles tend to reconstruct the original thixotropic structure. If this phenomenon occurs too quickly, brush marks are formed, and a rougher surface is observed, the so-called "orange-peel" surface. Therefore, the developed paint layer will be thicker (mean thickness value of 131 µm ± 6.4 was observed) and rougher. In addition, the paint evaporates at a slower rate than spray paints, enabling a paint film with less frequent and smaller surface holes.

The application of a primer between the mortar and paint layers slightly reduces, on average, the roughness of the painted surfaces (Table 3). The cross sections show that the primer, a transparent uncolored product, filling the surface porosity, improved paint adhesion and promoted the formation of a layer with a constant thickness (Figure 2). The primer may also reduce the paint roughness compared to samples without primer. On the other hand, the presence of the primer did not significantly affect the average hole size, but it did decrease the hole frequency (Table 1).

After coating application, several morphological changes were observed, and the applied protectives can sometimes be visually perceived on the surfaces (Figure 3). It should be noted that the coatings are transparent, making them difficult to observe over the colored painting layers using optical microscopy; furthermore, it is also not possible to measure the roughness by laser profilometry or microscopy with visible light.

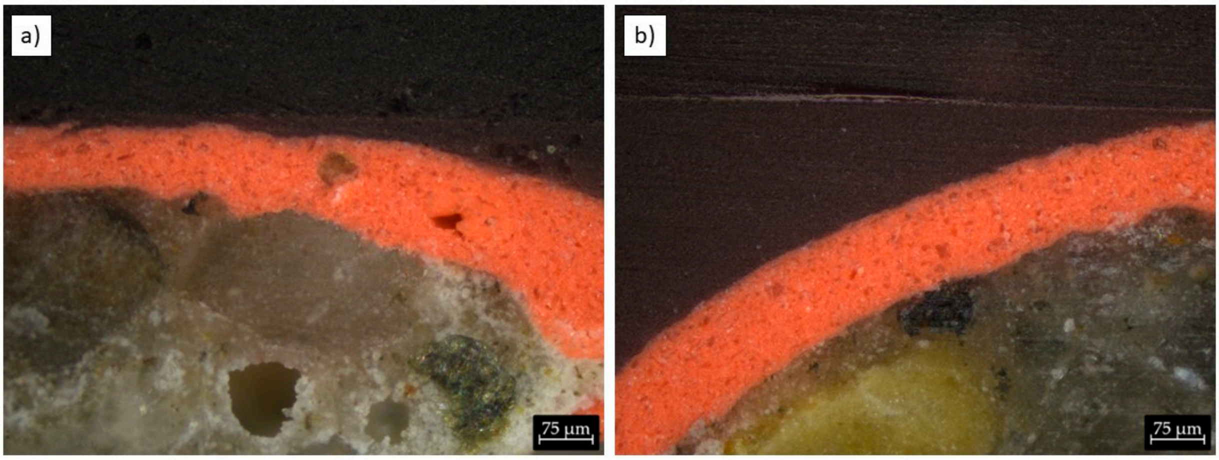


Figure 2. Cross sections of untreated styrene paint: (**a**) without and (**b**) with primer.

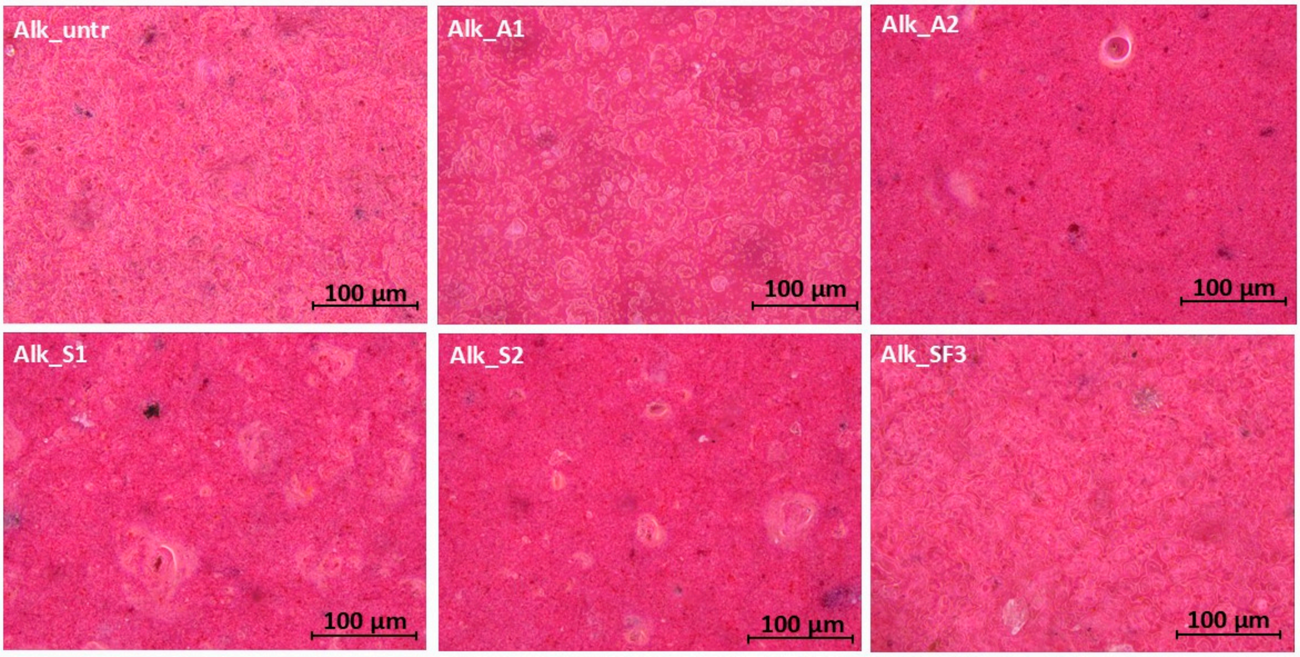


Figure 3. Optical microscopy images on the morphological changes observed on Alk paint before and after protective treatments.

To overcome this limitation, SEM observations were carried out. Generally, once the protective is applied on the paints, the resulting superficial morphology is not strongly affected by the type of underlying paint, as observed for the A1 coating spread on Alk (Figure 4a) and on Acr paint (Figure 4b); in both images, filler grains are visible, embedded in the polymeric layer (EDX analysis confirmed the presence of Si, corresponding to the clearer grains). The most evident differences among the three types of protectives (acrylics, silane, fluoro-silane) were as follows: A1 provided a homogeneous coverage with evident roughness due to the presence of the inorganic filler (Figure 4a); A2 and S2 also appeared homogeneous but with smoother surfaces compared to the other coatings (Figure 4c,e); S1 appeared homogeneous but showed accumulation of atmospheric particulates (Figure 4d); and SF3 displayed a different type and higher roughness with small scales and resin accumulation, probably due to the SiO_2-based filler in the formulation (Figure 4f).

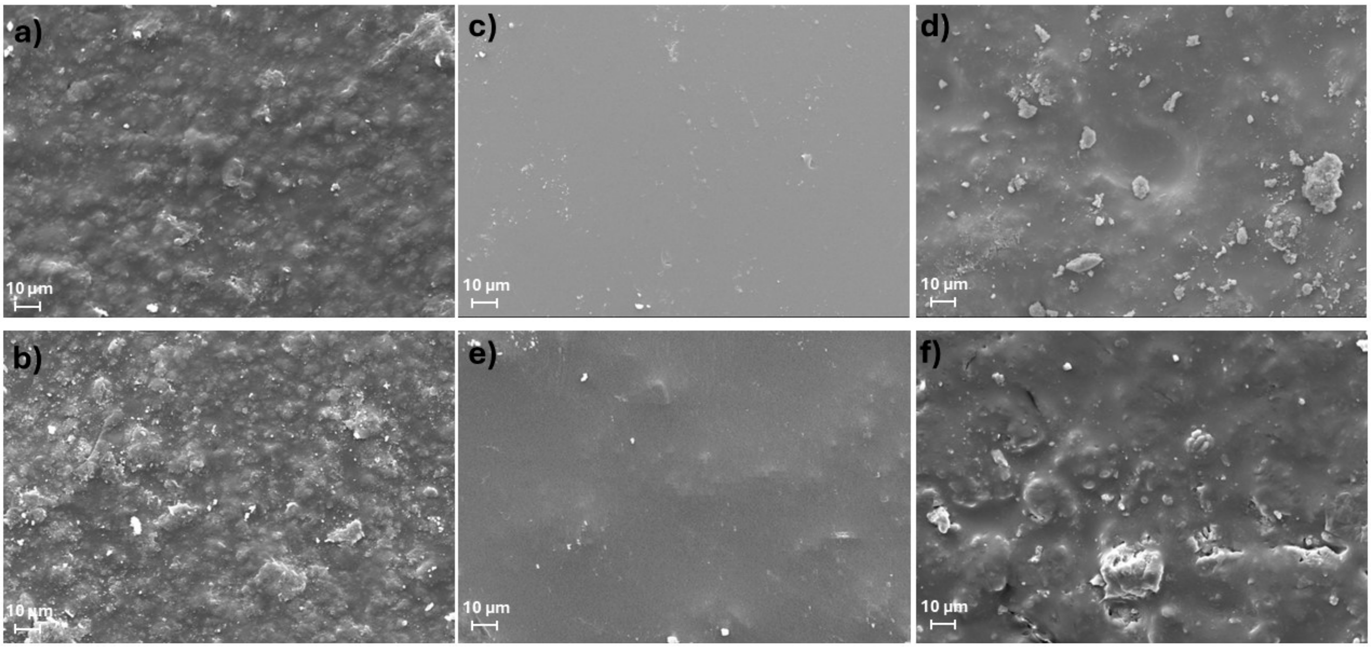


Figure 4. SEM images of alkyd paint treated with (**a**) A1, (**c**) A2, (**d**) S1, (**e**) S2, and (**f**) SF3 coatings. Moreover, the comparison between a) Alk and (**b**) Acr paints treated with A1 coating is displayed.

Figure 5 shows that all the coatings reduced the average hole diameter, filling and covering the surface irregularities; in addition, the holes' frequency was also slightly reduced. A1 produces the most significant reduction, followed by A2, SF3, S2, and S1.

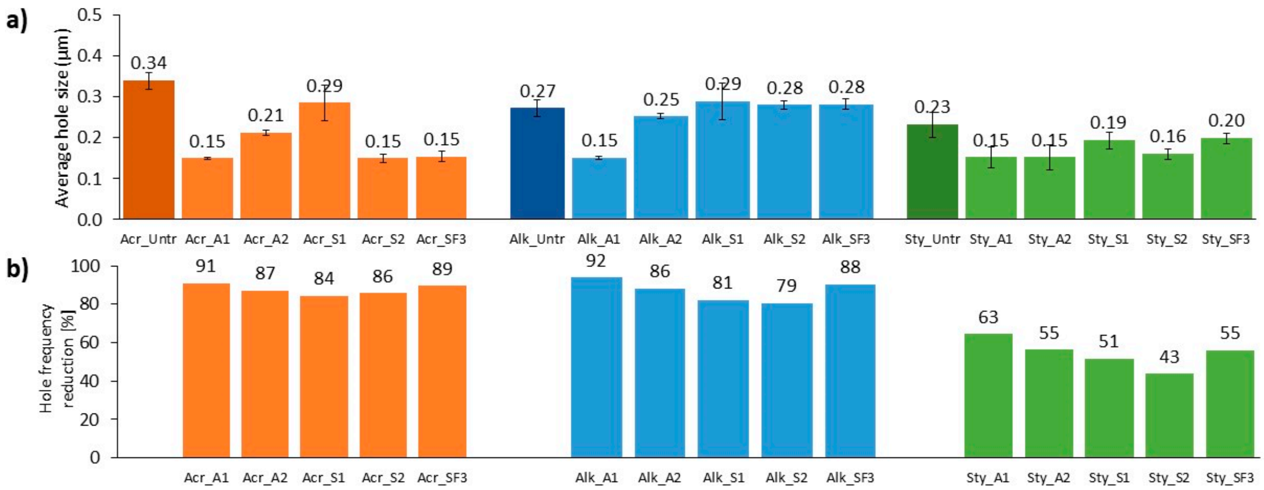


Figure 5. Bar graphs obtained from the image processing analysis before and after protective treatments on Acr (orange columns), Alk (blue columns), and Sty (green columns) paints. The image indicates: (**a**) average hole size measurements and (**b**) hole frequency evaluation.

Colorimetric and glossmetric measurements were conducted before and after the application of the protective coatings. According to ΔE values, no significant differences were observed between the painted surfaces with and without primer (Table 4). The greatest color changes were observed on Alk paint, particularly with silicone-based protectives and the A2 acrylic protective coating dispersed in organic solvents (ΔE values exceeding 4.0).

A similar trend was also observed for Acr and Sty paints, although with color differences below the tolerance threshold (<3.5) [38,39].

Table 4. Colorimetric results: total color variation (ΔE) and total gloss unit variation (ΔGU) after coating application for each paint, with and without primer.

	ΔE	ΔGU		ΔE	ΔGU
Acr_A1	1.8 ± 0.2	−0.37 ± 0.2	Pr-Acr_A1	1.7 ± 0.2	−0.42 ± 0.1
Acr_A2	3.3 ± 0.7	0.48 ± 0.4	Pr-Acr_A2	4.7 ± 0.7	0.53 ± 0.2
Acr_S1	2.0 ± 0.4	−0.18 ± 0.3	Pr-Acr_S1	1.5 ± 0.2	−0.14 ± 0.2
Acr_S2	4.4 ± 0.5	1.91 ± 0.1	Pr-Acr_S2	4.8 ± 0.5	1.79 ± 0.3
Acr_SF3	2.3 ± 0.8	−0.14 ± 0.7	Pr-Acr_SF3	1.9 ± 0.3	−0.10 ± 0.5
Alk_A1	3.3 ± 0.2	1.02 ± 0.3	Pr-Alk_A1	2.7 ± 0.1	0.94 ± 0.2
Alk_A2	4.4 ± 0.2	2.29 ± 0.1	Pr-Alk_A2	4.7 ± 0.3	2.04 ± 0.2
Alk_S1	5.4 ± 0.5	1.53 ± 0.4	Pr-Alk_S1	6.2 ± 0.5	1.47 ± 0.4
Alk_S2	6.6 ± 0.9	4.98 ± 0.5	Pr-Alk_S2	4.5 ± 0.3	4.97 ± 0.2
Alk_SF3	4.0 ± 0.8	0.60 ± 0.3	Pr-Alk_SF3	3.9 ± 0.7	0.56 ± 0.2
Sty_A1	1.3 ± 0.2	3.03 ± 0.2	Pr-Sty_A1	1.1 ± 0.2	2.95 ± 0.1
Sty_A2	1.8 ± 0.9	3.47 ± 0.6	Pr-Sty_A2	1.0 ± 0.3	3.37 ± 0.3
Sty_S1	3.3 ± 0.7	3.56 ± 0.4	Pr-Sty_S1	3.2 ± 0.8	3.48 ± 0.3
Sty_S2	3.5 ± 0.8	9.49 ± 0.7	Pr-Sty_S2	2.4 ± 0.4	9.35 ± 0.3
Sty_SF3	2.9 ± 0.5	1.07 ± 0.3	Pr-Sty_SF3	2.3 ± 0.4	0.96 ± 0.2

In general, the color changes were associated with increased color saturation (a rise in a* values), with a slight yellowing (higher b* values), and, especially on Alk and Sty paints, with a brightness reduction (slight decrease in L* values) (Figure 6). This behavior has been reported in previous studies [40–43].

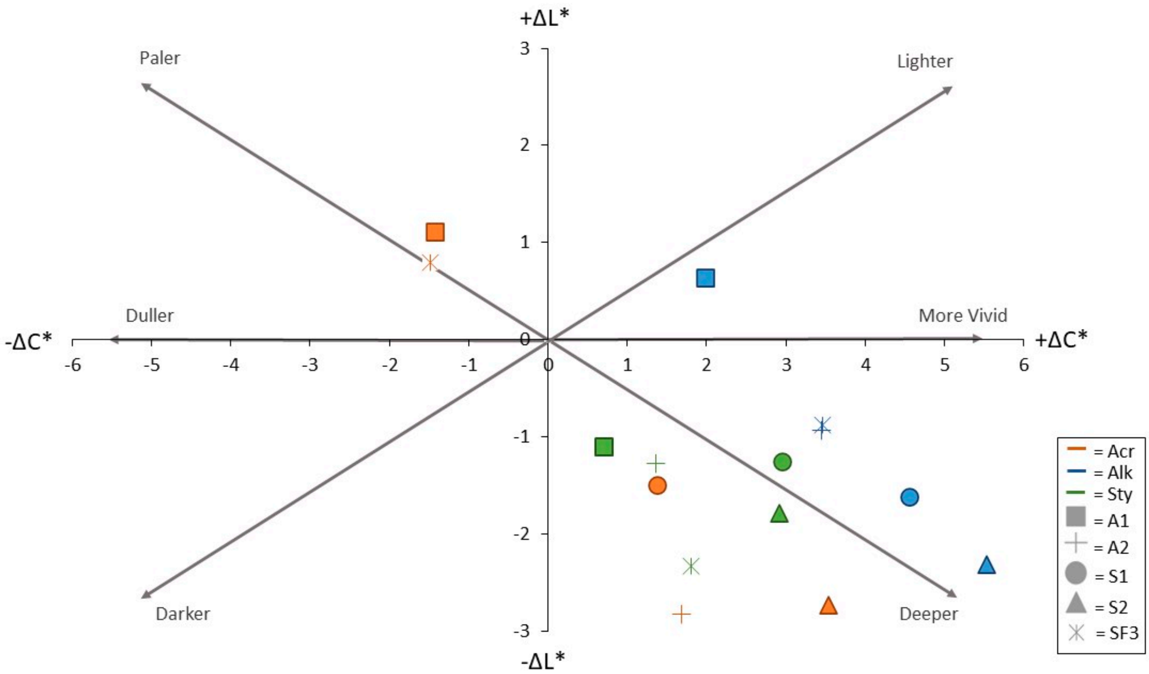


Figure 6. Colorimetric evaluation expressed as an ΔL*/ΔC* graph. ΔL and ΔC values are calculated for each paint, after the application of each protective coating. The grey lines in the graph represent the interpretation of the color variations observed after protective treatments, according to [44].

Interestingly, SF3 did not cause color variations on Acr (Figure 6). A1 produced three different effects depending on the paint: it deepened the color on Sty, made it paler on

Acr, and made it lighter and more vivid on Alk paint. This variation could result from the differences in adhesion to the different painted surfaces.

The gloss measurements provided information regarding the gloss value of the untreated and treated mock-ups (Figure 7). According to the technical data sheets of the paints used, the declared gloss level was matte for all three paints. The GU (gloss unit) for Alk and Sty was 2.6 and 1.4 respectively, confirming their matte appearance, while that of Acr was 8.4, classifying it as a low sheen paint [45]. Similar to the colorimetric measurements, the presence of the primer did not alter the aesthetic appearance in terms of gloss (Table 4).

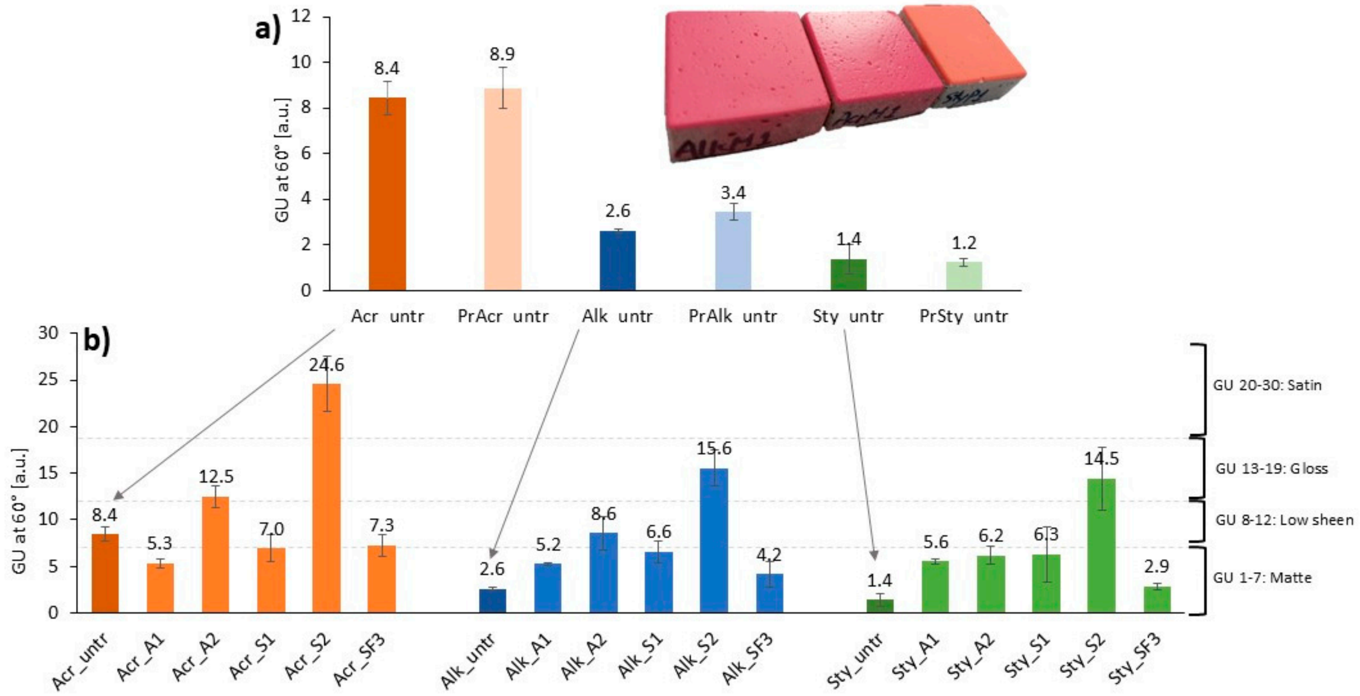


Figure 7. Gloss units (GU) acquired at 60° before and after the application of each protective coating: (**a**) GU values of untreated samples with and without primer and (**b**) GU values of all protective coatings divided for each paint. GU classification (satin, gloss, low sheen, and matte) according to [31].

After the application of the protective coatings, an increase in the GU values was observed for all treatments, particularly for S2 and A2, exceeding the tolerance level (>7.2) [46,47]. The other three coatings (SF3, S1, and A1) produced acceptable values expressed as the difference in GU units before and after coating application (i.e., ΔGU). Interestingly, on Acr samples, SF3, S1, and A1 showed lower GU values compared to the untreated surface, indicating that these coatings create an opaquer surface when applied on Acr paint.

3.2. Evaluation of Protective Efficacy

The water contact angle (WCA) measurements of the untreated painted surfaces (Figure 8) indicated that Acr and Alk paints had wettable surfaces with θ of 69.0° and 68.3°, respectively, while Sty paint was at the limit of water repellency with θ equal to 92° [48]. The presence of the primer slightly increased the WCA values of Acr and Alk paints (though within the standard deviation error), while the Sty WCA value remained almost unchanged.

As well known, WCA values are strongly influenced by the surface roughness [49,50]. Thus, the lower wettability of the Sty paint can be explained by its higher roughness (Ra = 21.0). Considering the five pure coatings spread on glass, it can be observed that most did not show high WCA values. Most of the tested coatings showed hydrophilic behavior with WCA values below 90° (Figure 8). S2 and SF3 were the exception, with hydrophobic WCA values of 92 and 115, respectively.

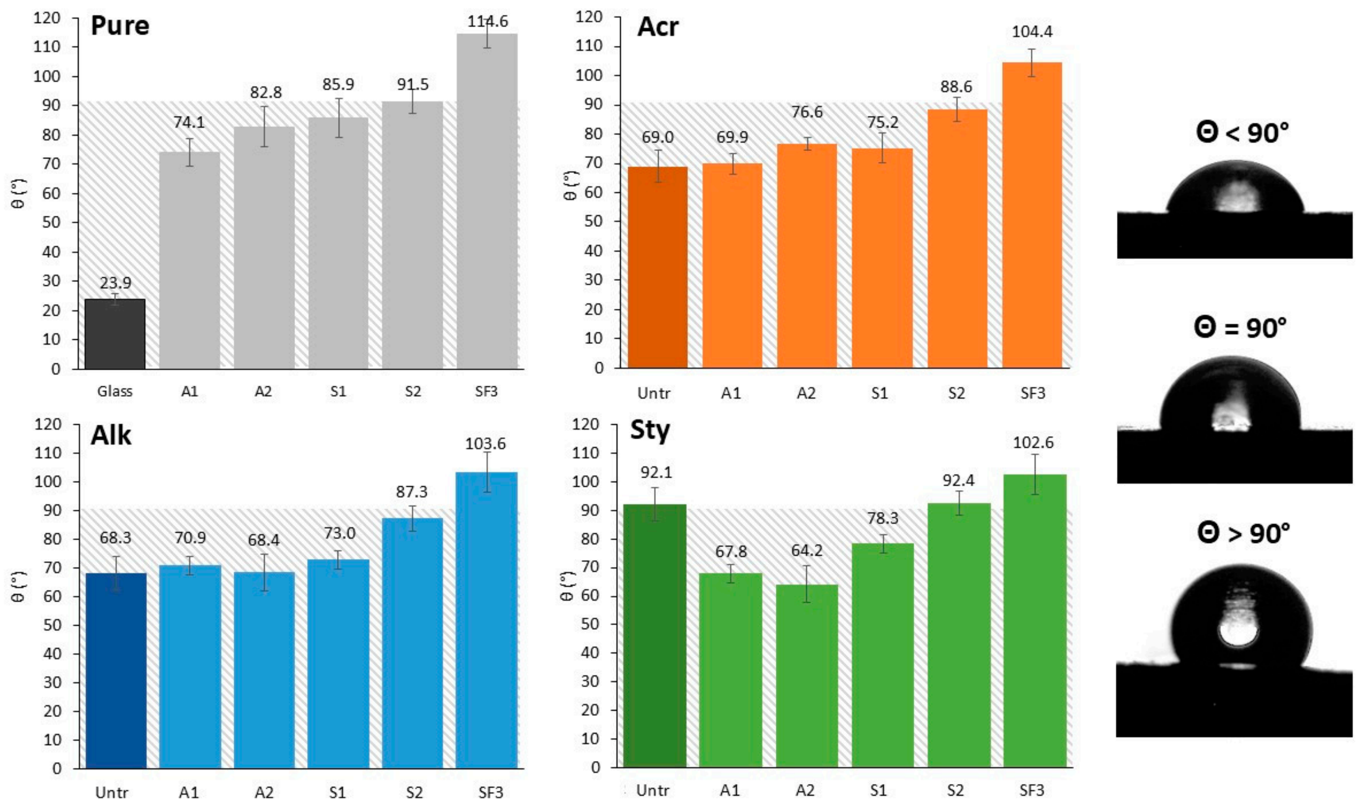


Figure 8. Contact angle values (θ) of pure coatings spread on glass (grey columns) and on the three paints: Acr (orange columns), Alk (blue columns), and Sty (green columns), before and after the application of each protective coating. On the right, some images of the measurements are reported.

After the coating application, the acrylic protectives (A1 and A2) did not significantly vary the wettability of Acr and Alk paints, and, moreover, tended to reduce the WCA of Sty (Figure 8). The silicone-based coatings, S1 and S2, slightly improved the water repellency of the Acr and Alk painted surfaces but had minimal impact on Sty. S2, containing dimethylsiloxane, provided acceptable water repellency levels (WCA around 90°) [51]. In contrast, S1, a silane–acrylic blend, was difficult to apply, resulting in a film with low WCA values [52].

Finally, SF3 showed consistent behavior across all three types of mock-ups, with WCA values around 100°. The primer effect was modest, remaining within the standard deviation. SF3 was the only coating that granted a sort of hydrophobicity to the treated surfaces: this is clearly related to the fluorine-containing declared composition. As is well known, the hydrophobicity of fluorinated coatings arises from the fact that fluorocarbon polymers tend to cluster on the surface, with polarized C-F functional groups toward the exterior [53–55].

The effectiveness of protective coating was also assessed by measuring water absorption by capillarity, as this evaluates the coatings' behavior during prolonged exposure to liquid water. As shown in Figure 9, the primer alone had a modest effect (IC_{rel} = 0.9, Table 5), while the application of the painting layers resulted in a notable reduction in water absorption. As observed, none of the three paints reached a plateau of water absorption (i.e., a steady amount of absorbed water at the end of the testing time). Sty paint, however, showed a slower absorption trend than the other two paints.

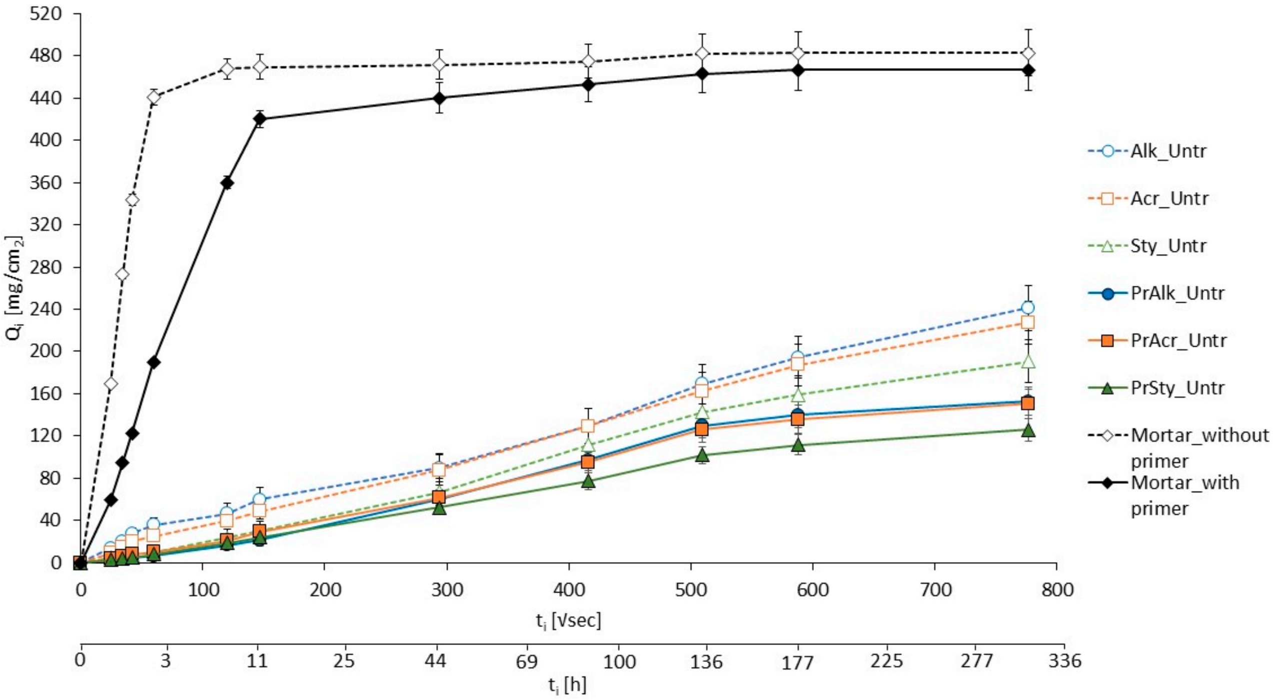


Figure 9. Water absorption curves as a function of the water absorbed (Q_i) versus the exposure time (t_i) of Acr (orange line), Alk (blue line), and Sty (green lines) paints, with (solid lines) and without (dashed lines) the presence of the primer.

Table 5. IC_{rel} values calculated over the treated with primer/untreated sample of the three paints and on the mortar mock-up (before the application of the protective coating).

Sample	IC_{rel}
Mortar	0.90 ± 0.02
Alk	0.66 ± 0.02
Acr	0.69 ± 0.01
Sty	0.69 ± 0.02

This may be linked to the lower frequency and smaller size of the surface holes observed in Sty paint compared to the other two paints (Table 3). The primer's effect was more pronounced on the mortar samples without painting, while it appeared to only have a limited impact on the long-term water absorption. For the painted surfaces, the absorption curves showed only a slight reduction in water absorption with the primer; however, it has to be noted that the final slope of the absorption curve suggested that a plateau would eventually be reached.

After the coating applications, the absorption curves showed a further reduction in water absorption (Figure 10) for all protective products and paints. The difference, in terms of water absorption, between specimens with and without primer, became even less significant. One exception was A1, which, without the primer, did not significantly reduce the water absorption but showed a similar performance to the other coatings when the primer was used.

The IC_{rel} values (Figure 11) were relatively high for all the tested coatings. As observed, the treatments neither drastically reduced the water absorption nor provided an additional barrier effect against water. Apparently, most of the water resistance came from the paint layer itself, while the coating only added a further modest reduction (40%–65%). It is interesting to observe that even the fluorinated material, despite having the highest contact angle values, did not significantly improve the protection against prolonged water contact. Overall, the protective effect was greater on Acr- and Alk-painted mock-ups, while all the coatings showed lower protective efficacy on Sty paints.

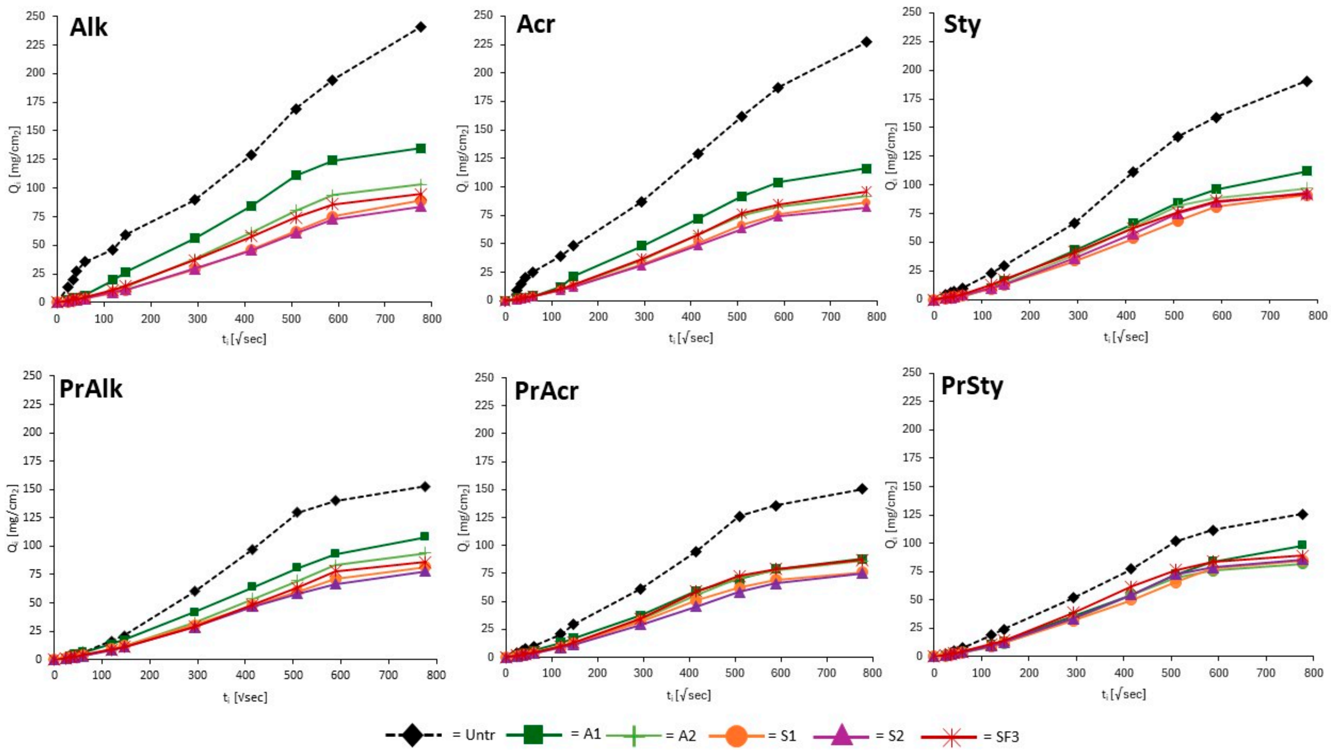


Figure 10. Water absorption curves before and after protective treatments on samples without (on **top**) and with (**bottom**) primer.

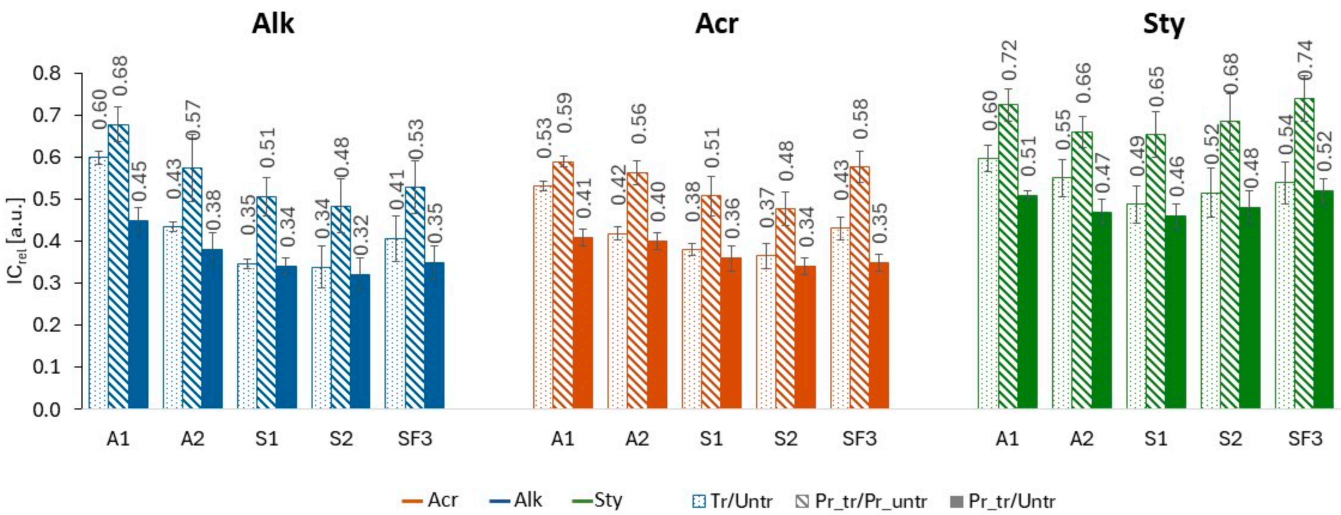


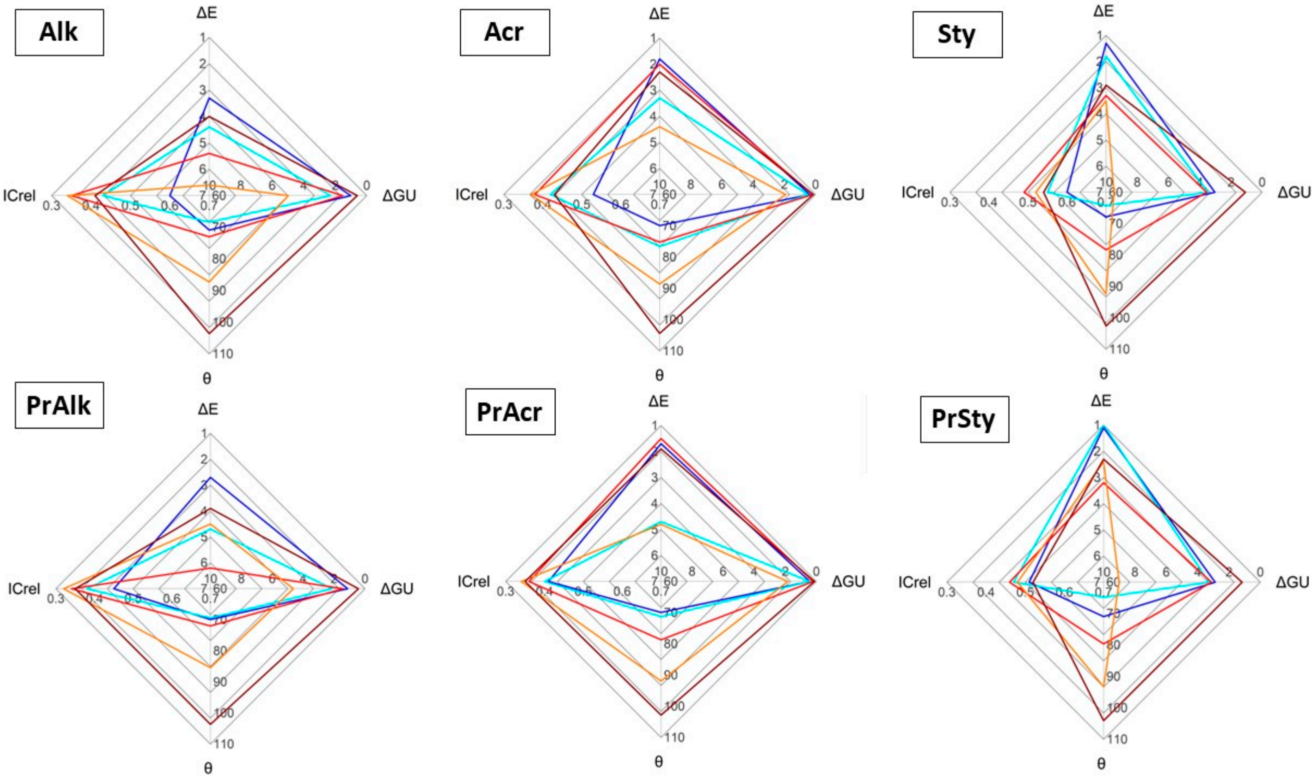
Figure 11. IC_{rel} values calculated over the treated/untreated sample (Tr/Untr, dotted columns), treated with primer/untreated with primer (Pr_Tr/Pr_Untr, dashed columns), and treated with primer/untreated sample (Pr_Tr/Untr, solid columns) of the three paints.

The silane-based materials (S1 and S2) provided the best protective performance, among the tested products, with very similar absorption curves. In contrast, SF3 performed poorly. This is likely because it forms a rigid layer with high water repellence but does not adhere well to the paint, particularly for Sty paint.

3.3. Testing Protocol and Discussion of the Results

The testing protocol and methods used in this study were derived from the vast literature on protective treatments for cultural heritage surfaces. Such consolidated experience in protecting porous ceramic substrates, particularly historical buildings facades, and some specific European standard protocols to which this study referred, provided valuable insight for the definition of testing procedures. The set-up of the protocol included mock-up preparation, morphological analysis of the surfaces, and the adaptation of the capillary water absorption test to obtain reproducible and reliable values.

Based on the results, Alk paint showed the most significant aesthetic changes after coating application in terms of the ΔE. Among the tested protectives, silicone-based ones caused the greatest aesthetic variations and altered the gloss appearance of the surface, particularly S2. On the other hand, silane-based protective coatings showed the best results in terms of water protection efficacy but were not entirely satisfactory. Spider graphs (Figure 12) clearly show that none of the coatings performed optimally, and Alk-and Sty-based paints were more difficult to protect than Acr-based ones. The presence of the primer, between the paint layer and the mortar substrate, improved the protective performance, particularly for the resistance to water absorption. Finally given the difficulty of determining the product formulations and their chemical characteristics, an in-depth product testing appears essential to ensure "good" or "acceptable" performance on the considered surfaces.



	ΔE	ΔGU	θ	ICrel
Excellent	1 – 2	1-2	> 125	< 0.25
Good	2 – 3.5	2.5 - 3.5	110 - 125	0.25 – 0.40
Acceptable	3.5 – 4.5	4 - 7	90 - 110	0.40 – 0.55
Poor	> 5	> 7	< 90	> 0.55

Figure 12. Comparison of compatibility (according to ΔE and ΔGU) and effectiveness (according to θ and IC_{rel}) factors among different coatings expressed as spider plots, divided by treated paints with and without primer.

As reported in other studies [42,56,57], adequate preparation of the substrate before painting is essential for the future protective performance of the coatings.

Selecting the right primer and the optimal preparation methods of the wall surface are key preventive conservation measures to enhance the durability of murals. In this study, the selected primer was an impregnating material, i.e., a product that penetrates the porosity of the mortar, whose properties were not investigated. The ability of the primer to create a protective barrier between the paint and mortar and to improve the adhesion between the primer and the paint can be crucial aspects to prevent the degradation effects of atmospheric weathering [58].

4. Conclusions

The adopted testing protocol provided valuable insights into the protection efficacy and compatibility of the different tested formulations in relation to the type of paint and wall preparation. The type of underlying paint mainly influences the final aesthetic result, while the application of the primer may play a significant role in terms of protection effectiveness, confirming the importance of pre-treating the substrate before painting. Despite the research into selecting protective materials, none of the tested products achieved optimal compatibility and effectiveness when applied on the paints, indicating that further studies and research are necessary. These results provide a starting point for future investigations into protective materials for contemporary muralism, particularly to evaluate their durability in outdoor conditions (such as exposure to rain and solar irradiation) and their ability to protect the underlying paints.

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