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Porcelain Enamel Coatings for Building Façades

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Abstract: Materials used for building façades should combine aesthetics with functionality and durability. Vitreous enamels are a class of inorganic coatings, with a glossy and brilliant aspect, as well as high chemical resistance and protective properties. This study aimed to investigate the potentiality of enamel coatings for use in the architectural field. Different accelerated tests were carried out on enamel steel panels to test their durability and resistance to natural aggressive conditions (corrosive atmosphere and basic pH conditions, UV radiation, and pollution) and to mechanical damages. Two colors were chosen, red and white, to determine the effect of the addition of diverse pigments. Paints were employed as reference coating protection systems, as they currently serve as the standard for building façade design. Compared to paints, the enamel panels presented better corrosion protection, with higher adhesion to the steel substrate and stable aesthetic properties during the conducted tests, both in terms of color and gloss. Nevertheless, the white coating exhibited superior color stability, likely attributable to the presence of Se- and Cd-based pigments in the red coating. These pigments are known to be more prone to degradation. Overall, this work showed that porcelain enamels display good functional and aesthetic qualities, which make them suitable for use in the cladding of buildings and as transport infrastructure elements.

Keywords: porcelain enamel coatings; building façades; coatings adhesion properties; layer aesthetic features; enamel durability

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1. Introduction

One of the main issues in the sector of façade engineering is the selection of materials able to guarantee long-term structural durability [1]. Within the realm of architecture, the primary role of cladding is undeniably to shield the building from environmental elements, yet its significance extends beyond mere protection. Indeed, the exterior coating also shapes the building's visual impression, a crucial factor given that buildings influence the value of their surrounding urban landscape. Hence, aside from representing a protective barrier, architectural cladding must present pleasing hues that harmonize with the external surroundings, along with aesthetic qualities. Moreover, it should possess the flexibility to accommodate diverse architectural structures, enabling architects to explore varied design strategies. Changes in the exterior appearance of buildings are an obvious consequence of natural exposure, with a negative impact both on their functional and aesthetic properties. In addition to the construction costs, a large economic outlay is thus needed to preserve the building exterior, and a large fraction of all the money invested in the construction sector is spent on maintenance [2,3]. The goal is thus to exploit durable materials resistant to aggressive conditions to extend the service life of buildings, reducing the need for intervention for maintenance. Another aspect to consider for materials selection in the architectural field is the ease of cleaning. Indeed, a significant fraction of the total maintenance costs is attributed to the removal of soiling caused by environmental pollutants and contaminants [4] and graffiti [5,6].

Ultimately, panels designed for the exterior of buildings should meet two specific requirements. First, they should prove long-term durability and resistance, withstand

potentially damaging environmental conditions, and be easily cleanable. Secondly, they ought to exhibit favorable aesthetic qualities, as the visual appeal of a structure is significant and should not be overlooked. Currently, the predominant materials employed for the realization of building façades are coil coatings, painted panels and components, anodized aluminum, and stainless steel. While these materials offer viable solutions, they also possess inherent drawbacks and limitations.

Coil coatings and painted panels are largely applied in the architectural sector, mainly thanks to the low cost of construction. These coatings may, however, undergo degradation after UV exposure, which is dependent on their composition [7]. The resistance of coil coatings was found to be reduced after natural exposure, as well as after the accelerated laboratory salt spray test [8]. Furthermore, to maintain low usage costs and facilitate the bending of components, the protective thickness of coil coatings must remain relatively low. The construction of façades made of stainless steel, including colored stainless steel, is cost-effective in the long run and allows combining the brightness of the surface with high resistance to corrosion and to aggressive conditions, such as acid rain [9,10]. Some issues are, however, related to the heavy weight of this material, which may be mitigated by the use of composite materials [11]. Moreover, anodized aluminum finds application in façade engineering, mainly for its long-term durability and the protection from corrosion conferred by the oxide layer. It has been recently shown that the anti-corrosive properties of anodized aluminum remain intact even when the material is mechanically deformed [12]. However, there is an increasing demand for a wide range of color options, and this represents a limitation for the use of anodized aluminum, which is generally available only in a limited color palette. Among the organic coatings, paints are the most commonly used for the cladding of buildings. Self-cleaning paints with a superhydrophobic surface are available and employed to prevent the excessive accumulation of air pollutants and dust [13]. Nonetheless, paints may be damaged upon exposure to a series of atmospheric conditions, with a negative impact both on the functionality of the coating and also on its aesthetic, particularly color integrity [14–16].

Therefore, the different materials that are currently available as choices for the design of building claddings are possible and valid alternatives, but they also display some limitations. Some of these materials offer a limited number of colors and patterns, and this has a negative impact on their aesthetic properties. On the other side, more varying materials, such as paints, are more advantageous in terms of aesthetics, offering a broader spectrum of solutions, but they are less valid for what concerns long-term durability. Poor durability goes in parallel with a higher demand for maintenance and consequent economic expenditures. A more suitable material for building façades should thus display high durability and resistance over time, reduce maintenance procedures, and have good aesthetic qualities. In this way, it could be possible to achieve a reduction in maintenance costs without, however, compromising the exterior appearance.

Enameled steel and aluminum are valid alternatives for the engineering of building façades, which combine material durability and resistance with pleasing aesthetic properties. Enamels are inorganic coatings with a long history of decorative usage [17]. During the industrial revolution, enamels started to be used for technical applications, thanks to their good engineering properties [17]. The glassy nature of enamel contributes to its high resistance to chemicals and abrasion. Moreover, they guarantee good protection against corrosion when deposited on a steel substrate [18–20], thanks to the strong adhesion between the coating and the same substrate [21,22]. Enamel coatings have a glossy appearance, and several brilliant colors are now available, enabling the creation of surfaces with diverse and appealing visual characteristics [23,24].

Nowadays, the enamel market finds application mainly in household items and in industry [25]. However, the utilization of enameled steel and aluminum in the field of architecture remains limited due to the associated higher costs in comparison with other solutions. Furthermore, there is a lack of knowledge regarding the characteristics and excellent performance of this type of material, which is why designers overlook enameled

panels as a viable option for building construction. In addition to the high durability of these coatings, the use of enameled panels is environmentally sustainable. Indeed, they require minimal maintenance, thereby reducing the waste associated with maintenance procedures. At the same time, enameled panels are recyclable due to the glassy nature of this material, further enhancing their environmental appeal.

The purpose of this study is to test the durability of porcelain enamel, with a focus on its possible application in the architectural sector. A comparative analysis is also performed to evaluate the performance of enamel coatings in comparison to paints. Indeed, even if the potentiality of enamel coatings has already been proven, a study that directly compares the properties of enamel and paints is missing. This research gap correlates with a lack of knowledge in the sector of materials for architecture. Indeed:

- Since there is a lack of knowledge, architects possess limited awareness concerning the potential material solutions accessible for crafting exterior panels of buildings.
- Enabling the choice of the optimal material necessitates conducting performance comparisons among various materials. If comparisons are missing, it may be challenging to evaluate which one of the possible solutions performs better, for example, in terms of protection for the substrate, color stability, and resistance to abrasion.
- Often, architects lack scientific data to underpin their material selection, relying solely on commercial information, which can make it challenging to guide the choice of the most suitable material.

Different laboratory-accelerated tests were thus performed to simulate aggressive conditions that may damage the coatings during their service life. These tests include exposure to UV-B radiation and pollutants to simulate outdoor conditions, a salt spray test to evaluate the protective properties, and a test of resistance to concrete products to study the behavior in a basic pH environment. Considering the possible aesthetic damage to which buildings could be subjected, a graffiti resistance test was conducted to test both the ease of cleaning and the resistance of these coatings to aggressive solvents used for façade cleaning. Eventually, the mechanical damage caused by abrasion was studied through the Taber and PEI tests. The tests were conducted on two different colors, red and white, to determine the potential impact of different pigments on coating performance. White and red are indeed two widely utilized colors for the design of exterior claddings.

2. Materials and Methods

2.1. Materials

The carbon steel substrates (Q-panel type R (0.15 wt.% C—Fe bal.)—75 mm × 150 mm × 2 mm and 100 mm × 100 mm × 2 mm) were purchased from Q-lab (Westlake, OH, USA). The acrylic-based paint was Adler Samtalkyd (Schwaz, Austria) with two colors, RAL 9016 and 3004. Samples were produced by Vibrantz Technologies (Fiorano Modenese, MO, Italy). Table 1 reports the composition of the employed frit. Na_2O was used as a balancer. The main difference between the red and white enamel layers is the presence of a higher quantity of TiO_2 in the white frit (16%), while the red color is given by Se and CdO pigments. The enamels present the same colors (RAL) as the paints.

Table 1. Composition of the frit.

Component	Ground Layer [wt.%]	Red (Final Layer) [wt.%]	White (Final Layer) [wt.%]
SiO_2	53.5	52.5	47
K_2O	2.6	0.5	6
Na_2O	9.2	15.5	7.9
F	1.0	3.0	2.0
Al_2O_3	5.0	2.0	0.7
B_2O_3	12.2	12.5	15.5
TiO_2	2.5	6.5	16
MnO_2	0.8	/	/

Table 1. *Cont.*

Component	Ground Layer [wt.%]	Red (Final Layer) [wt.%]	White (Final Layer) [wt.%]
LiO_2	1.7	/	/
BaO	1.6	/	/
Fe_2O_3	2.0	/	/
CuO	0.4	/	/
CaO	1.3	2.0	/
Co_3O_4	1.2	/	0.02
ZrO_2	5.0	/	1.2
CdO	/	2.5	/
Se	/	0.5	/
SO_3	/	0.5	/
MgO	/	2.0	1.2
P_2O_5	/	/	2.5

Acetone, citric acid, methyl ethyl ketone (MEK), xylene, Fe_2O_3, NaCl, $CaSO_4$, and humic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. The $NaNO_3$ reagent was purchased from J.T Baker (Phillipsburg, NJ, USA), while $Ca(OH)_2$ was provided by Carlo Erba Reagents (Cornaredo, MI, Italy), and they were used as received.

2.2. Coatings Deposition

Steel panels were pre-washed with hot water at 60 °C for 2 min. Then, an alkaline degreasing was effectuated for 6 min, with a solution of 7.5 wt.% NaOH at a temperature of 50 °C. The samples were rinsed with hot water at 50 °C and then with cold water at 20 °C for 2 min and an acid pickling was conducted with a 5 wt.% H_2SO_4 solution for 2 min. Two 2 min-long washing steps were performed with water at 50 °C and 20 °C. As ground enamel, two layers were applied: a first ground layer, with the composition reported in Table 1, and an intermediate recovered layer, applied to the still-wet ground. This choice is frequent for the preparation of enamel panels for the architectural sector, to reduce the thickness of the ground layer and thus the associated costs. After the application of the ground, the samples were subjected to drying and firing. For the white panels, one layer of enamel coating was then applied, with a subsequent drying and firing step. The red coating—due to the particularities of the pigments—required the application of two enamel coats. Indeed, Cd and Se-based red pigments are not stable, and they are especially critical in "ground" enamels, which tend to break them down due to high chemical reactivity and aggressiveness. Thus, a white enamel layer was introduced between the ground and the red coating to create a barrier to avoid the negative reaction between ground and red enamel and to obtain a more vivid color. After the application of the two enamel layers, the red panels were also dried and fired. For the drying phase, the convection dryer was set at 140 °C, while a continuous industrial kiln was used for the firing, which provides a stationary time of 330 s at temperatures above 800 °C, with a maximum peak at 860 °C.

For the preparation of the painted sample, the low-carbon steel substrates were degreased with acetone. Paints were applied using the spray technique. A first layer of antitrust primer was applied, and after two hours, the coating layer was uniformly sprayed.

The four samples are summarized in Table 2, with the corresponding nomenclature.

Table 2. Nomenclature of samples.

RAL	Coating Typology	Sample Nomenclature
3004	Enamel	Red enamel
	Spray paint	Red paint
9016	Enamel	White enamel
	Spray paint	White paint

2.3. Characterization

The thickness of the coating was measured using a Phynix Surfix FN thickness gauge (Phynix, Neuss, Germany). The roughness of the surface was measured through the MAHR Marsurf PS1 roughness tester (Mahr, Göttingen, Germany), with an evaluation length of 5.6 mm and a sampling length of 0.8 mm, according to the ISO 21920-2 standard [26]. Five measurements were conducted to find the surface average roughness values. The surface and a cross-section of enamel samples were observed at the scanning electron microscope SEM JEOL IT300 (JEOL, Akishima, Tokyo, Japan). Various accelerated tests were carried out, carefully selected to replicate the harsh conditions that building façades could potentially face. In fact, façades should ensure protection during a long service life, during which they can be worn and damaged due to environmental and atmospheric conditions. In this context, conventional assessments for gauging material deterioration were employed. Furthermore, adhesion tests were executed, as a robust adhesion between the metal substrate and the coating is pivotal in ensuring the elevated level of protection provided by the coating layer. Lastly, the capacity to resist abrasion was tested, given that this represents a conceivable form of mechanical damage that building claddings might encounter.

The adhesion between the coatings and the substrate was evaluated through a direct impact test, following the ASTM B916 standard [27]. Despite this standard being the reference for the evaluation of the adherence of the porcelain enamel coatings to metals, the same parameters were also used to evaluate the adherence of the paints to the metallic substrate, so that there could be a direct comparison. Accordingly, after conditioning the samples at a temperature of (23 $\pm$ 2) °C with a humidity of (50 $\pm$ 5)% for 16 h in the Angelantoni climatic chamber DM340 C (Angelantoni DM340 C, Angelantoni Test Technologies, Perugia, Italy), a 1 kg weight was impacted on the sample surface with an energy of 9.03 J.

Durability tests specific to enamel coatings are often lacking. Thus, the tests conducted in this study are inspired by a series of standards generally used to study the durability of paints. Given the probable coating-concrete contact in the architectural sector, the resistance of enamel coatings to the chemical attack by concrete products was investigated considering the EN 12206-1 standard [28]. Three spots of mortar (15 g $Ca(OH)_2$, 41 g of concrete, and 244 g of sand with water) were applied to the sample surfaces. The samples were maintained for 24 h at a temperature of (38 $\pm$ 3) °C and humidity of (95 $\pm$ 5)% in an Erichsen Hygrotherm 519 SA humidostatic chamber (Erichsen, Hemer, Germany). The mortar was removed, and surfaces were cleaned with water. Eventually, variations in the aesthetic properties were evaluated through the gloss and color change measurements. The gloss was measured with a Glossmeter Erichsen NL34 (Erichsen, Milan, Italy), for an angle of 60° [29], taking 5 measurements per spot, while color measurements were performed with the Konica Minolta CM-2600d spectrophotometer (Konica Minolta, Tokyo, Japan), with a D65/10° illuminator/observer, according to the CIELab color space method [30]. The entire procedure was repeated three times. The reported values of gloss and color changes are the average values of the three measurements for each sample.

To evaluate the resistance to corrosion of the coated metals and to highlight eventual problems of loss of adhesion, samples were continuously exposed to the salt spray chamber (Ascott Analytical Equipment, Tamworth, UK) with a 5 wt.% NaCl solution at 35 °C, following the procedure of the ASTM B117 standard [31]. At the test endpoint, delamination around the scribe was evaluated as per UNI EN ISO 4628-8 [32]. The test was conducted on two samples per typology.

The resistance to UV radiation was tested in accordance with the ASTM G154 standard [33], with an irradiation of 0.71 W/m^2 and a temperature of 60 °C, employing a UV173 Box Co.Fo.Me.Gra (Co.Fo.Me.Gra, Milan, Italy), with a wavelength of 313 nm. Changes in the aesthetic properties were evaluated through gloss and color measurements. The test was conducted on two samples per typology, taking three measurements of gloss and color

per sample. The reported values of gloss and color changes are the average values of the two samples.

Another potential damaging factor for coatings is the presence of dust and pollutants in the natural environment. The resistance of enamel coatings to air pollution and soiling was tested following the ASTM D7897 standard [34]. The soiling solution simulating the average conditions of three US cities (Phoenix, Arizona; Miami, Florida; and Youngstown, Ohio) was prepared by mixing equal volumes of (1) a dust suspension (2.3 g/L); (2) a salt solution (1.0 g/L); (3) a particulate organic matter (POM) solution (1.4 g/L); and (4) a soot suspension (0.26 g/L). The dust suspension was prepared with 0.3 g/L of Fe_2O_3 powder, 1.0 g/L montmorillonite, and 1.0 g/L of bentonite. The salt solution was prepared with 0.3 g/L of NaCl, 0.3 g/L of $NaNO_3$, and 0.4 g/L of $CaSO_4$ $2H_2O$. The POM solution was prepared by dissolving 1.4 g of humic acid into 1 L of distilled water, while the soot suspension was obtained by diluting 0.26 g of carbon black (Vulcan XC-72) into 1 L of distilled water [34]. In total, three test cycles were performed, each composed of three phases:

- Weathering-apparatus exposure before soiling, involving 2 cycles, each one with 8 h of UV-A (UV173 Box Co.Fo.Me.Gra—Co.Fo.Me.Gra, Milan, Italy) and 4 h of condensation at 50 °C. Then, samples were dried under an infrared heat lamp for 5 min at 150 W (Philips IR150R R125, Philips, Eindhoven, Netherlands).
- Soiling, consisting of spraying the samples with the soiling solution and drying under an IR lamp for 5 min.
- Weathering-apparatus exposure after soiling involves 2 cycles, each with 8 h of UV-A exposure and 4 h of condensation at 50 °C. Then, the samples were dried under an IR heat lamp for 5 min.

The UV-A lamp (UVA-340) had a wavelength of 340 nm and an irradiance of 0.89 W/(m^2 nm). Changes in aesthetic properties were evaluated through measurements of gloss and color.

The ASTM D6578 standard was followed to test the resistance of coated samples to graffiti [35]. A homogenous layer of a solvent-based alkyd spray (Dupli Color, Milano, Italy, red RAL 3000) was applied to the samples, which were then cured at room temperature for 24 h [6,35]. Graffiti was removed with a typical organic solvent such as methyl ethyl ketone (MEK) and xylene, and color and gloss were measured.

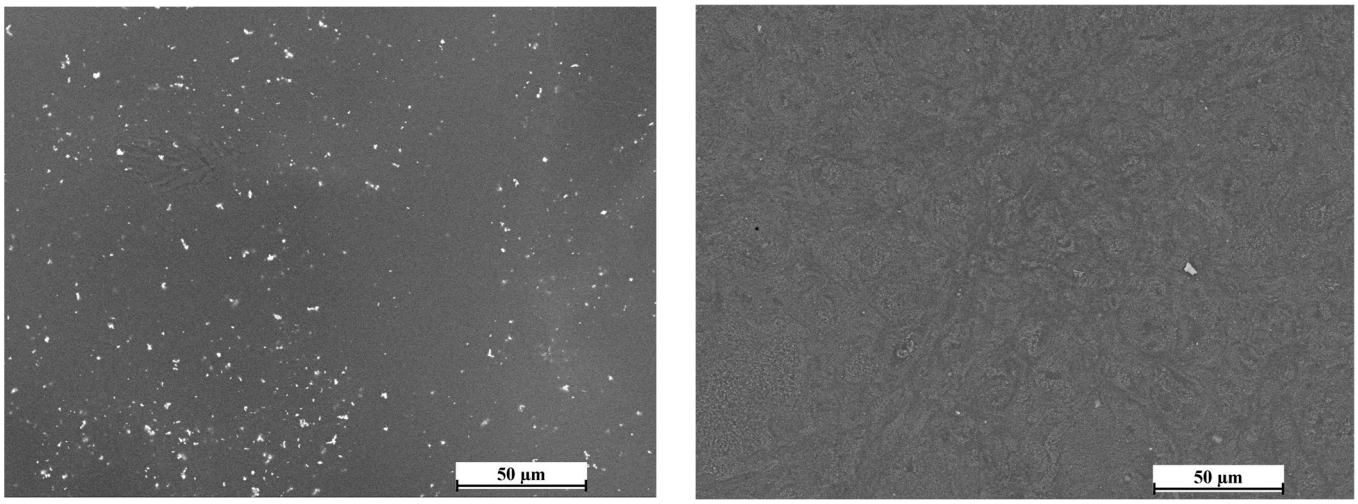
The resistance of the coatings to abrasion was studied through the PEI test [36], generally known for the evaluation of the abrasion resistance of tiles, and the Taber test, mostly used for paint coatings. According to the UNI EN ISO 10545-7(2000) standard [36], the PEI abrader instrument (Ceramic Instruments, Sassuolo, MO, Italy) was used. An abrasive medium composed of 3 g of F80 alumina powder, steel balls of different dimensions (70 g balls with a diameter of 5 mm, 52.5 g with a diameter of 3 mm, 43.75 g with a diameter of 2 mm, and 8.75 g balls with a diameter of 1 mm), and 20 mL of deionized water were applied to the sample surface, and a circular rotation at 300 rpm was imposed on the samples. In total, 5000 PEI cycles were performed, and the abrasion was evaluated by measuring the mass loss after 100, 250, 500, 1000, 2000, and 5000 cycles. The Taber abrasion test was carried out with a Taber Abraser 5131 (Taber Industries, Tonawanda, NY, USA), according to the ASTM 4060 standard [37]. The test involved the rotation of two abrading wheels (CS17) in the opposite direction compared to the sample rotation, for 5000 cycles, with a 250 g load. At defined steps, the mass loss was evaluated as an indication of the resistance to abrasion.

3. Results and Discussion

3.1. Coatings Characterization

From the SEM micrographs of the enamel sample surfaces revealed in Figure 1, pigments seem to be uniformly spread with a homogenous distribution. White particles are visible on the surface of the red enamel coating (Figure 1a), which corresponds to CdO, added to the frit formulation to confer the desired color. Both enamel surfaces appear quite flat, even if roughness measurements revealed higher Ra values (average roughness) for

the red enamel than for the white enamel (Table 3). However, the roughness of the enamel coatings is still lower than the outcomes measured on the corresponding painted samples, revealing a smoother morphology of the glassy layers. Surface roughness significantly impacts the aesthetic appearance of a coated surface. This is evident as both gloss and color perception alter in response to surface roughness. Beyond its aesthetic implications, surface roughness holds a pivotal role in the realm of building façades, particularly concerning cleaning convenience. When dealing with high surface roughness, the likelihood of the accumulation of pollutants and dirt increases, potentially rendering the surface more challenging to clean. Conversely, a smoother surface facilitates easier cleaning procedures.



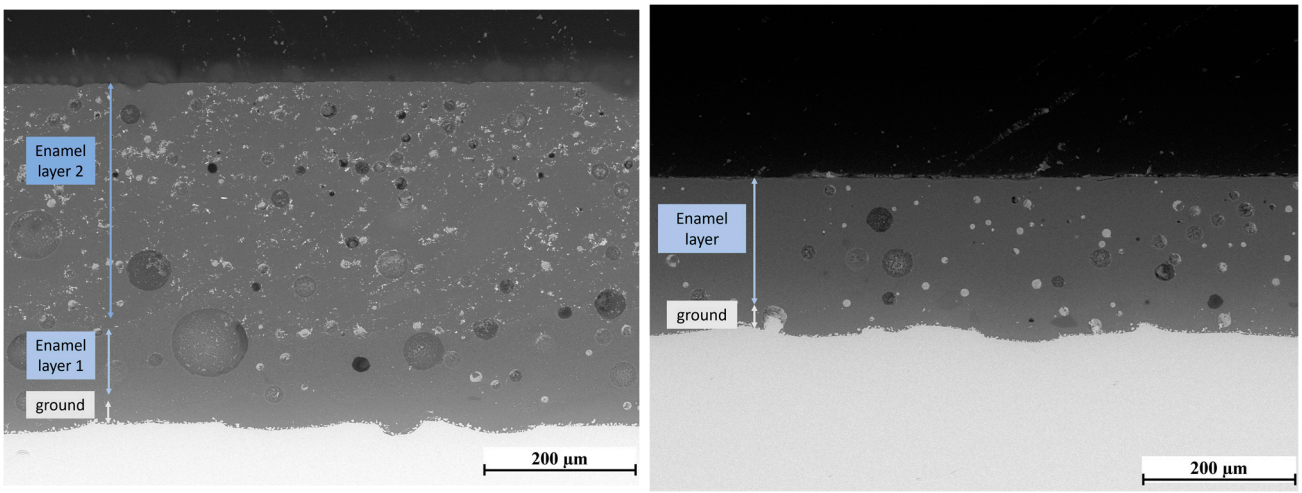
(**a**) (**b**)

Figure 1. Scanning electron micrographs of samples surface of the (**a**) red and (**b**) white enamel coatings.

Table 3. Thickness and roughness of the coatings.

Sample	Total Thickness [µm]	Roughness Ra [µm]
Red enamel	≈500	0.26 ± 0.03
Red paint	≈110	0.61 ± 0.05
White enamel	≈230	0.12 ± 0.02
White paint	≈110	0.42 ± 0.07

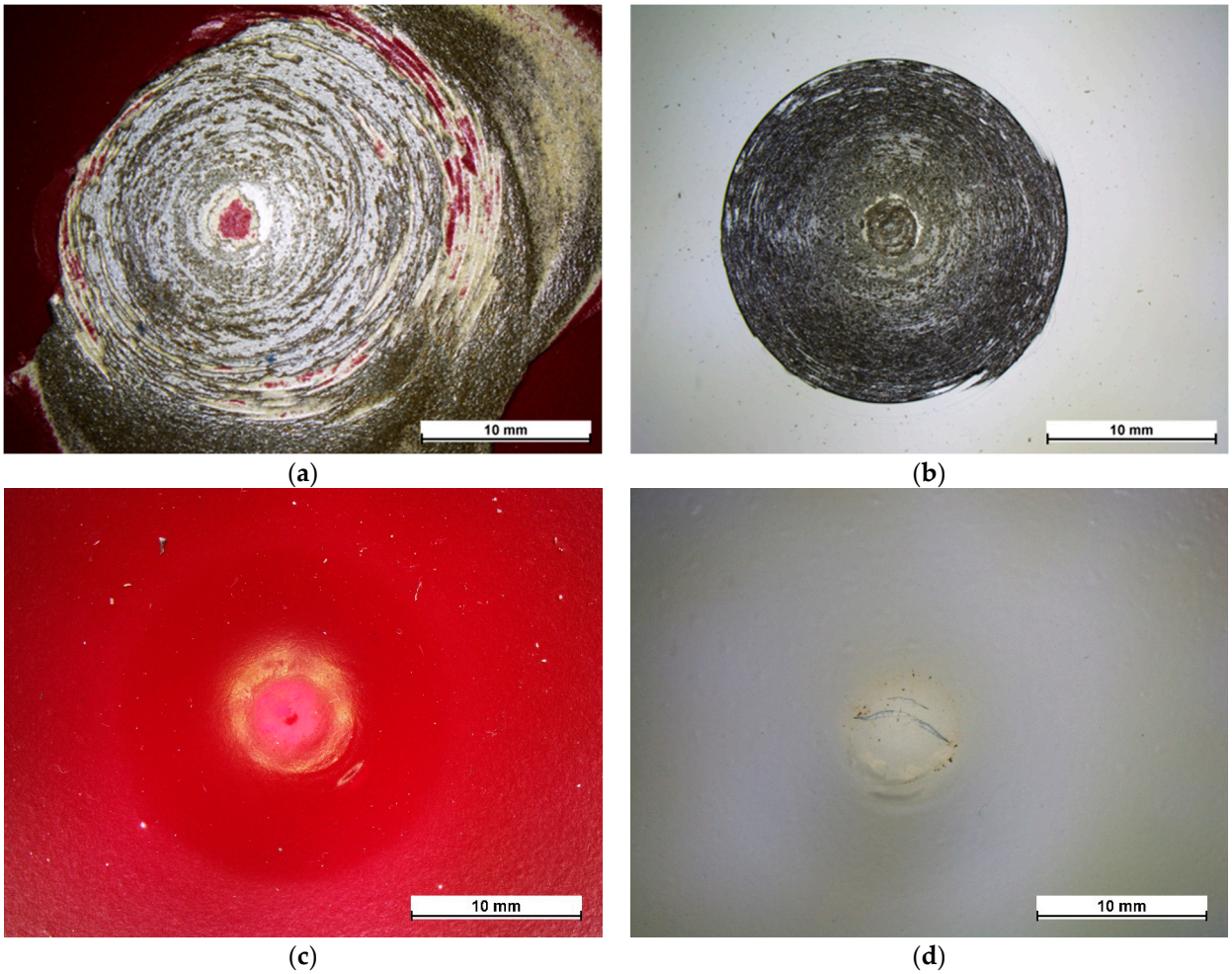
Figure 2 shows the scanning electron micrographs of the enamel cross-sections. The ground layer is equal for all the samples, with a measured thickness of about 35 µm. The intermediate layer cannot be distinguished from the enamel covering layer. Sample red (Figure 2a) exhibits a structure with two enamel-covering layers, consisting of a first white enamel layer measuring approximately 125 µm in thickness, followed by a second red layer with a thickness of around 320 µm. Thus, the red enamel displays an overall thickness of 500 µm. Instead, the white sample (Figure 2b) consists solely of a white enamel layer, which is about 200 µm thick. The total thickness of the white sample is thus approximately 230 µm. The presence of the additional layer in the sample red serves to enhance both the aesthetic properties and the durability of the coating.



(**a**) (**b**)

Figure 2. Scanning electron micrographs of cross-sections of the (**a**) red and (**b**) white enamel coatings.

The impact test was carried out to investigate the adhesion of the coating to the substrate. While the paint coatings display excellent adherence with the metal substrate, with the appearance of very small cracks on the coating layer (Figure 3c,d), the impacted zone in the enamel-coated samples is characterized by the loss of the coating after deformation. Paint shows a different behavior compared to enamel. In fact, paint is deformable, and thus, in the case of good adhesion, it follows the deformation of the substrate caused by the impact. The ASTM B916-01 [27] standard classifies the adherence of porcelain enamels depending on the amount of coating that remains after the deformation and the presence of substrate oxides. Accordingly, the white enamel shows very good adherence with a still visible oxide layer, which may be classified as grade 4 (Figure 3b). The adhesion between the red coating and the metal substrate seems to be weaker, with a broader impacted zone (Figure 3a). Since dendrites are clearly present at the steel–enamel interface, as shown in Figure 2 [21], and comparable in the red and white enamels, the different quality of adhesion is not explained by differences at the dendrite level. The worse performance of the red enamel in the impact test may nevertheless suggest that it is not properly fired due to the higher thickness of the coating. In fact, as outlined in Materials and Methods, the red and white enamels were produced according to the same protocol, but with the addition of an additional white layer below the red enamel. This correlates with a higher thickness of the coating and a higher amount of material to be fired during the firing step. Therefore, it is possible that the firing time is not sufficient for the red enamel to obtain a total performing layer, while it is for the white enamel. One may speculate that not enough oxygen comes to the substrate to favor complete oxidation.



(**a**) (**b**) (**c**) (**d**)

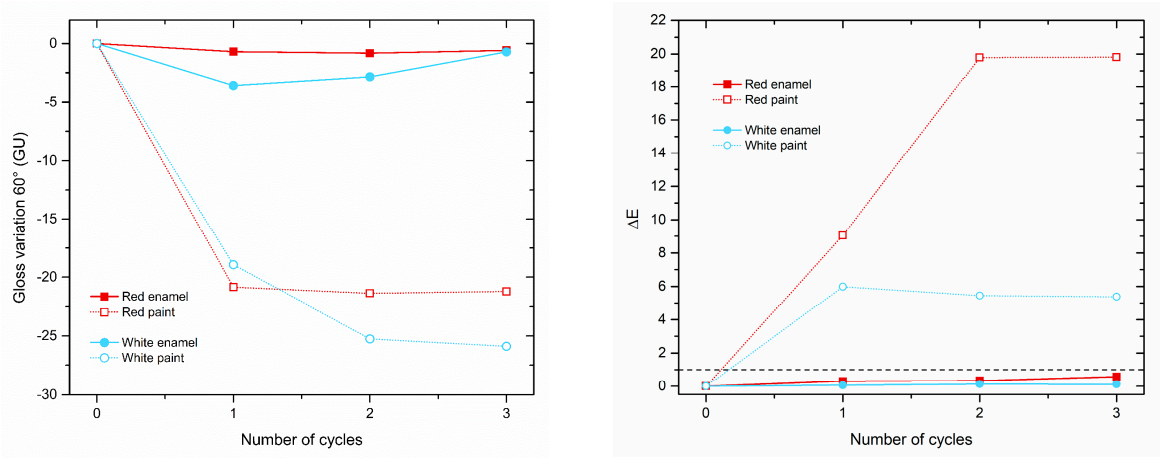
Figure 3. Optical micrographs of (**a**) red enamel, (**b**) white enamel, (**c**) red paint, and (**d**) white paint after the impact test.

3.2. Accelerated Weathering Tests

In the architectural sector, materials are frequently in contact with alkaline concrete matter and concrete products. Enamel coatings suffer in the presence of a basic pH [38], even if adjustments in the type and/or amount of mill additives were shown to improve the resistance of this type of material toward an alkaline pH [39,40]. The EN 12206-1 standard [28] was thus followed to test the resistance of the enamel coatings to basic concrete by evaluating variations in the color and gloss of the samples after contact with concrete matter. The contact with concrete did not alter the gloss of the enamel coatings, whereas it had a considerable impact on the gloss of the painted reference samples (Figure 4a). Both paints experienced a dramatic loss reduction already after the first application of concrete, with a decrease of about 20 gloss units. Then, gloss values stabilized for the red paint, while the white paint had a further reduction in gloss during the following two concrete applications. Similar results were obtained in terms of color variation (Figure 4b). The color stability of a coated surface is an essential aesthetic parameter in addition to gloss. According to the CIELab color space [30], color is identified by three parameters: (1) L* is the lightness and ranges from 0 (black) to 100 (white); (2) a* indicates the red-green scale (negative Δa* values mean a shift toward green, while positive a* variations mean a shift toward red); (3) b* indicates the yellow-blue scale (for positive Δb* values, a shift toward

yellow is observed, while negative b* variations are observed for shifts toward blue). The total color variation (ΔE*) is calculated as:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}. \quad (1)$$



(**a**) (**b**)

Figure 4. Variation of (**a**) gloss and (**b**) color during test of resistance to concrete products.

The enamel coatings demonstrated exceptional color stability, exhibiting ΔE values below 1 point. On the other side, the tested organic coatings showed a significant color variation, with the red paint showing more pronounced changes compared to the white paint. At the end of the test, the former had indeed a ΔE close to 20 points, while the latter had lower ΔE values.

The different results for paints and enamels can be attributed to the varying degrees of permeability exhibited by the two coating typologies. Enamels do indeed tend to have a lower permeability than paints, which restricts the diffusion of alkaline substances and thus minimizes chemical interactions, which may eventually lead to color changes. On the other side, paints have higher permeability. Accordingly, in addition to the significant color variation, by the end of the test, the surface of the painted panels was covered with blisters.

The salt spray test was carried out to investigate the adhesion and resistance of the coatings in corrosive and aggressive environments [31]. The enamel coatings showed excellent resistance. Indeed, after 1440 h of exposure, the enameled surfaces were in good condition without the presence of defects (Figure 5a). On the other side, after one week of salt spray exposure, blisters started to appear around the scratch of the painted samples, with a subsequent spread over the surface. Painted panels were exposed to salt spray just for 668 h, and the coating was severely damaged after that time. In fact, the surface appeared to be characterized by swelling and completely covered by blisters (Figure 5b).

Moreover, the adhesion between the coating and the steel substrate was investigated according to the UNI EN ISO 4628-8 standard [32]. Delamination was computed as:

$$d = (d_1 - w)/2, \quad (2)$$

where d_1 is the mean width of delamination, and w is the width of the original scribe. The enamel coatings showed good adhesion with the substrate, as no delamination was observed. Differently, complete delamination was obtained for the painted samples, pointing out a complete absence of adhesion between the coating and the substrate.

Enamels offer effective protection against the contact of Cl^- ions and aggressive solutions with the substrate due to their non-permeable characteristics and the strong adhesion with the substrate generated through chemical reactions during the firing process. Conversely, the higher permeability of paints, as well as the lower adhesion strength, allow the Cl^- ions to penetrate more easily and reach the substrate. The good adhesion of enamels

during the salt spray test seems to be in contrast with the impact test results, during which a weak adhesion was reported for the red enamel. Nonetheless, this is explained by the fact that the loss of adhesion during the impact test involves mechanical aspects, while the loss of adhesion during the salt spray exposure is linked to chemical degradation.

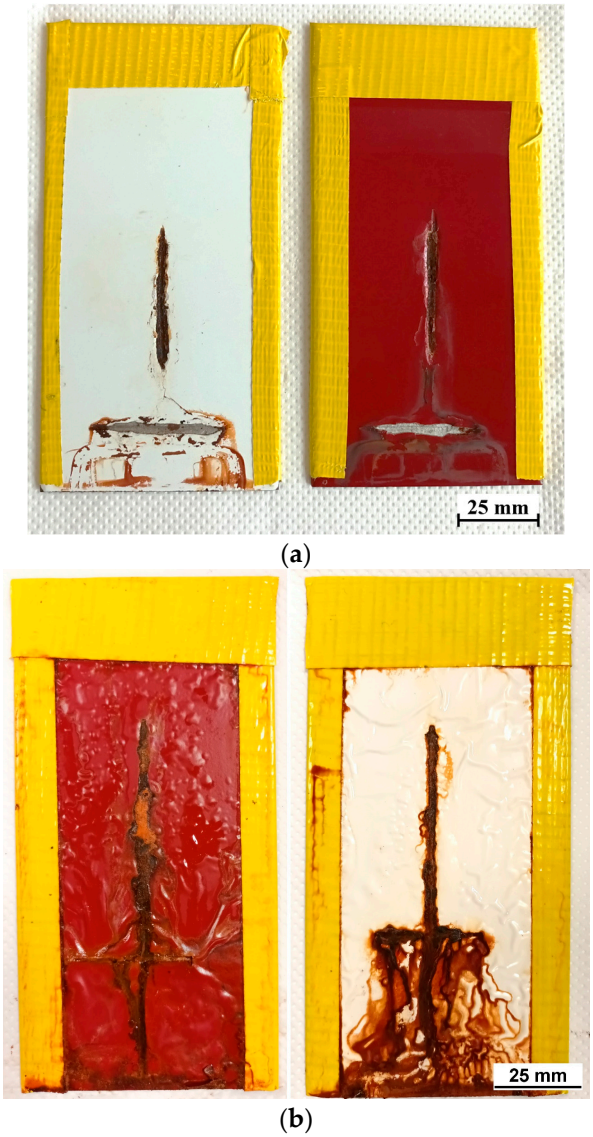
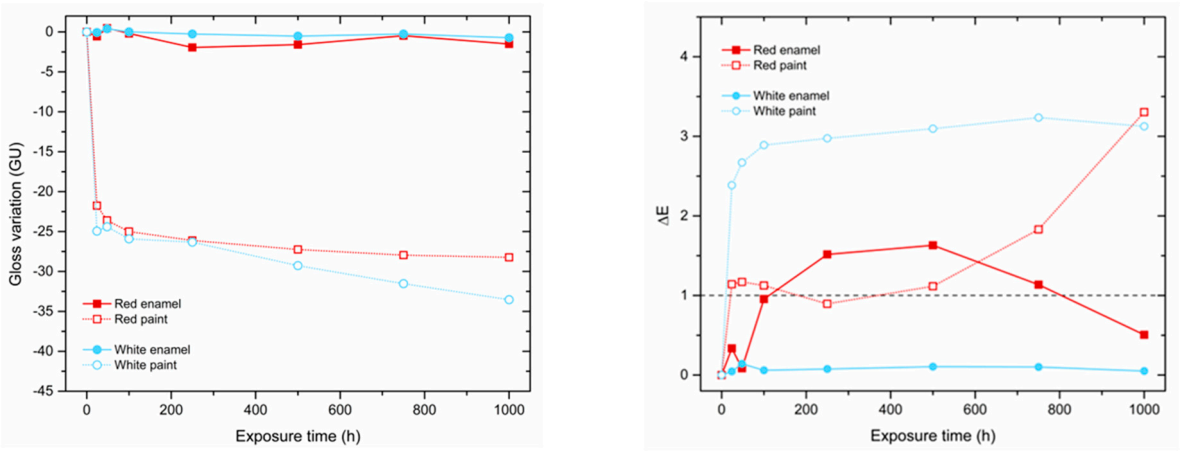


Figure 5. Enameled (**a**) and painted (**b**) samples after the salt spray test.

Continuous exposure to solar radiation may alter the aesthetic properties of a surface. To investigate the resistance of enamel coatings to solar radiation, panels were exposed for 1000 h to UV-B radiation, and changes in surface properties were evaluated through color and gloss change measurements.

Both the white and the red enamel coatings showed stable gloss values upon exposure to UV radiation. Differently, the paints experienced a significant reduction in gloss (Figure 6a). Furthermore, the paints displayed significant color changes following exposure in the UV chamber, with color change ΔE values exceeding 3 points (Figure 6b). The color change in the white paint primarily manifested as a shift towards more positive b* values, while the red paint exhibited a reduction of b* and a* parameters. If the white porcelain enamel shows extremely high color stability, the red one is more susceptible to UV-B exposure, with ΔE close to 1. This color variation in the red coating was primarily attributed to a decrease in the a* color parameter, indicative of a shift towards the green spectrum.

In fact, Se-based pigments tend to undergo photochemical reactions when exposed to UV radiation, which can result in color variation.

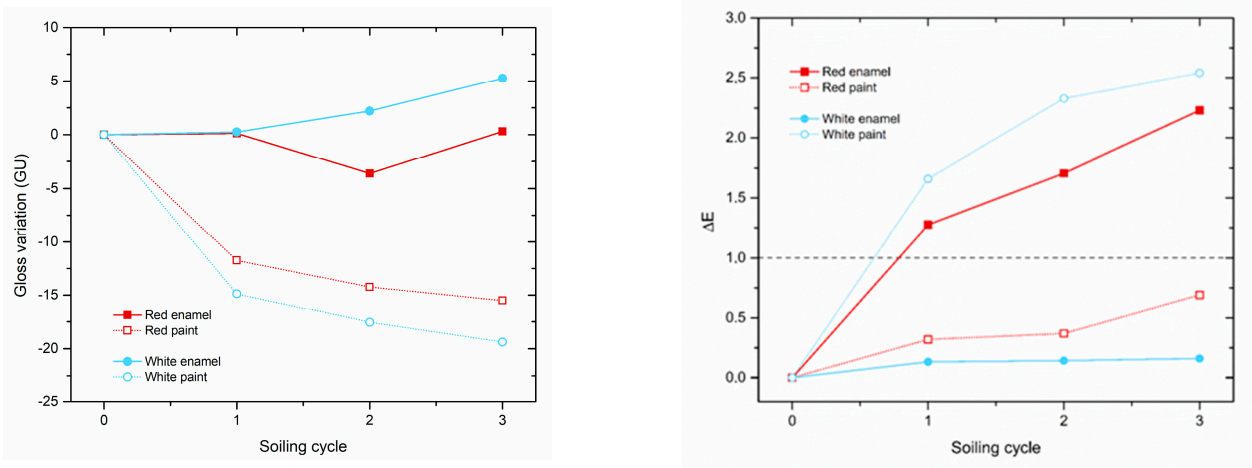


(**a**) (**b**)

Figure 6. Variation of (**a**) gloss and (**b**) color during the exposure to UV-B radiation.

Air pollution poses a major threat to the preservation of architectural structures. Different studies agree on the fact that air contaminants and pollutants significantly contribute to the degradation of buildings [41–44]. Thus, an ideal coating for panels of buildings should resist dust and pollutants present in the service environments. To assess the effects of weathering and soiling on enamel coatings, the procedures outlined in the ASTM D7897 standard [34] were followed. This involved the fouling of samples with a solution that mimics the presence of salts, particulate organic matter (POM), powders, and soot present in the service environment. After each cycle of weathering—soiling—weathering, color, and gloss measurements were performed to evaluate changes in the aesthetic of the surface.

A significant gloss variation was observed for paints but not for enamel coatings (Figure 7a). Moreover, in this case, the white enamel demonstrated higher color stability than the red enamel (Figure 7b). The latter indeed shows ΔE values higher than 1 already after one soiling cycle, with a shift of a* and b* toward more positive values and a decrease in the L* parameter. Due to their instability and reactivity, red pigments may have reacted with chemicals present in the soiling solution, exacerbating their degradation under the influence of UV radiation.



(**a**) (**b**)

Figure 7. Variation in (**a**) gloss and (**b**) color during the soiling and weathering test.

3.3. Damage Induced by Human Activities

In addition to the deterioration due to service exposure, building exteriors are often damaged by human activities. The application of graffiti on building façades is a common practice with very severe consequences. Indeed, in addition to the costly procedures for cleaning, building exterior surfaces may also be irreversibly damaged [45]. The use of a material able to resist both graffiti and aggressive solvents used for graffiti and surface cleaning would thus be an advantage for the building designers.

Figure 8 presents the results of the graffiti resistance test, specifically focusing on the variation in gloss and color parameters. The enamel coatings showed excellent resistance against graffiti and the aggressive solvents used for cleaning (MEK and xylene), maintaining unchanged gloss and color parameters. On the other side, the paint coatings suffered during this accelerated test. Indeed, after two cycles of graffiti application and removal, the paint detached from the substrate due to the interaction of polymeric matter with the organic solvents. The removal of the graffiti spray from painted surfaces proved to be challenging, either with MEK or with xylene solvents. Instead, already after just a few passes of the solvent-soaked cotton on the enamel surface, the graffiti spray easily detached, facilitated by solvent uptake, without causing damage to the appearance of the samples.

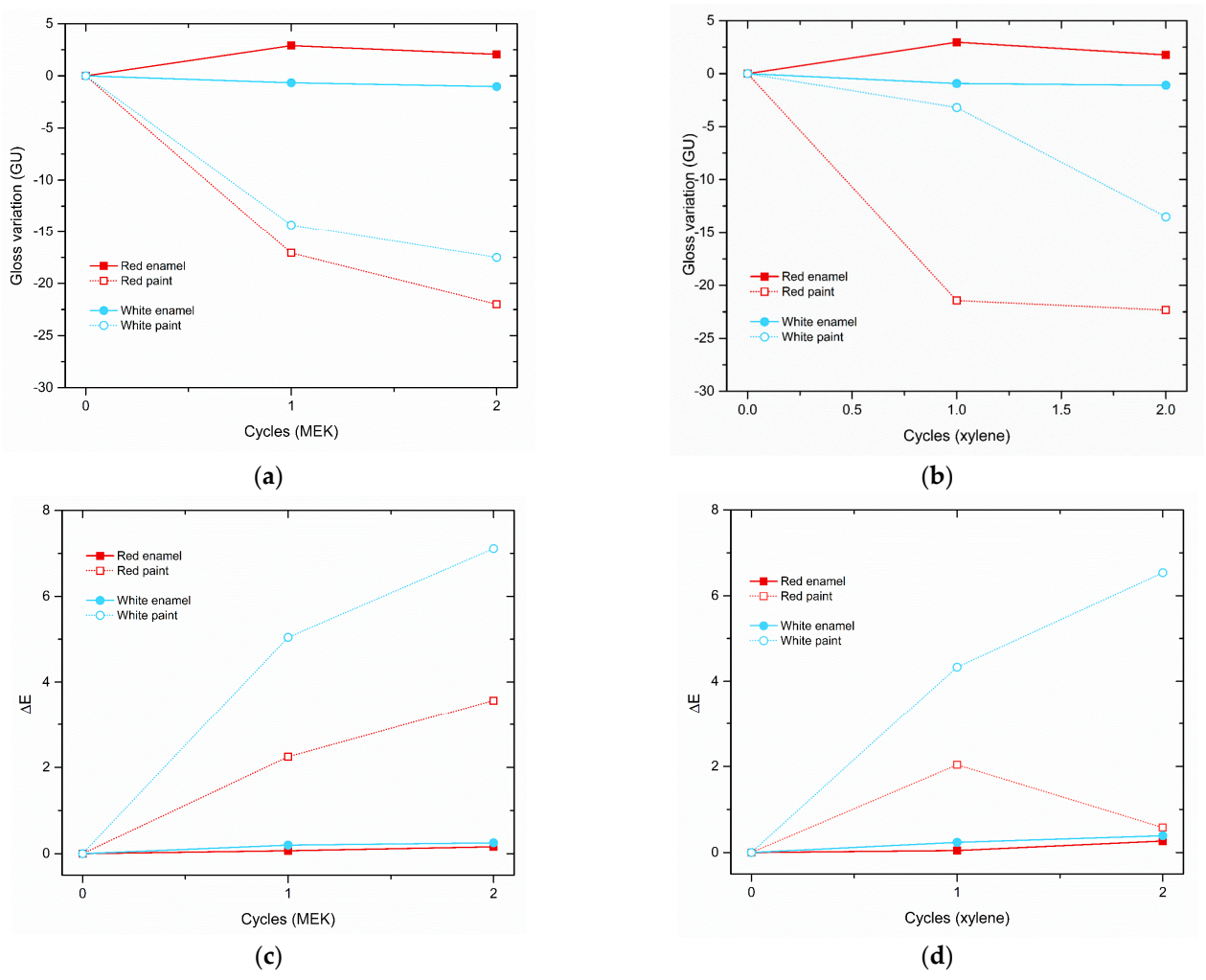


Figure 8. Variation in (**a**,**b**) gloss and (**c**,**d**) color during the graffiti resistance test using MEK and xylene solvents.

The use of xylene appeared to be more aggressive on the red paint than the use of MEK, as in the former case a steep gloss reduction was observed already after the first use

of the solvent (Figure 8a,b). Conversely, the white paint seems to be more sensitive to the MEK solvent.

These results highlight the superior performance of enamels in cases of contact with graffiti and aggressive organic solvents, which makes them a more favorable option for designers of building cladding.

Abrasion is one of the most frequent mechanical damages that enamel coatings must withstand. In an outdoor environment, abrasion is frequently induced by the action of wind; small particles of dust and sand carried by the wind may indeed damage surfaces due to long-term rubbing. Additionally, cleaning procedures also contribute to surface abrasion damage. Different studies have proved that the composition of the frit influences the abrasion resistance of enamels [46,47]. In this work, the abrasion resistance of the porcelain enamel coatings under study was evaluated through two abrasion tests, i.e., the Taber and the PEI tests, as they are employed for the study of the abrasion resistance of paints and enamels, respectively. The Taber and the PEI abrasion tests imply different abrasive processes, and they provide different information on the resistance of the coating. The two-body abrasion Taber test is generally used to investigate how abrasion mechanisms influence the aesthetic properties of organic coatings [48,49]. Abrasive particles present in the abrasive grinders induce sub-superficial damage with the formation of cracks on the coating surface. In the Taber test, debris accumulates in the areas of the enamel coatings that are comparatively weaker, specifically where sub-surface pores exist. This debris has the tendency to infiltrate the porosity to some extent while also contributing to surface abrasion through sliding wear by positioning itself between the grinding wheels and the substrate. The damage induced by the alumina together with the steel balls during the PEI test is instead more uniform, also thanks to the presence of water acting as a lubricant [46]. In the latter case, the damage is more uniform, with no formation of cracks.

By comparing the mass loss during the Taber abrasion test (Figure 9) and the PEI abrasion test (Figure 10), it is evident that paints suffer more during the Taber test, while enamels suffer more during the PEI test. Enamels were not affected at all by the Taber test, with no mass loss. The paint coatings showed instead a higher mass loss, about 260 mg after 5000 Taber cycles, which is quite similar for the two paint colors. Paints are more sensitive to Taber abrasion because of their softer nature, which allows the abrasive wheels to abrade and remove material from the surface more easily.

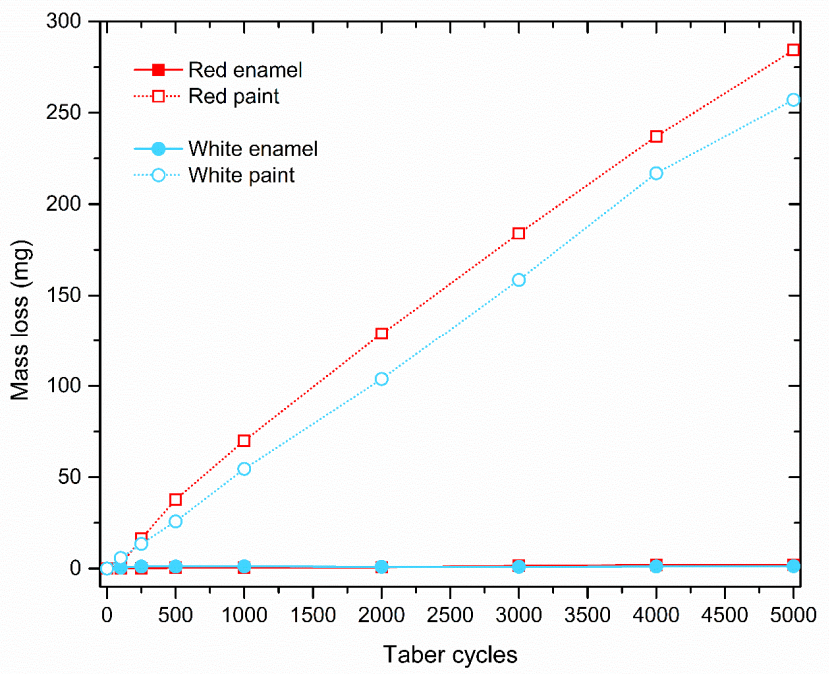


Figure 9. Mass loss during the Taber abrasion test.

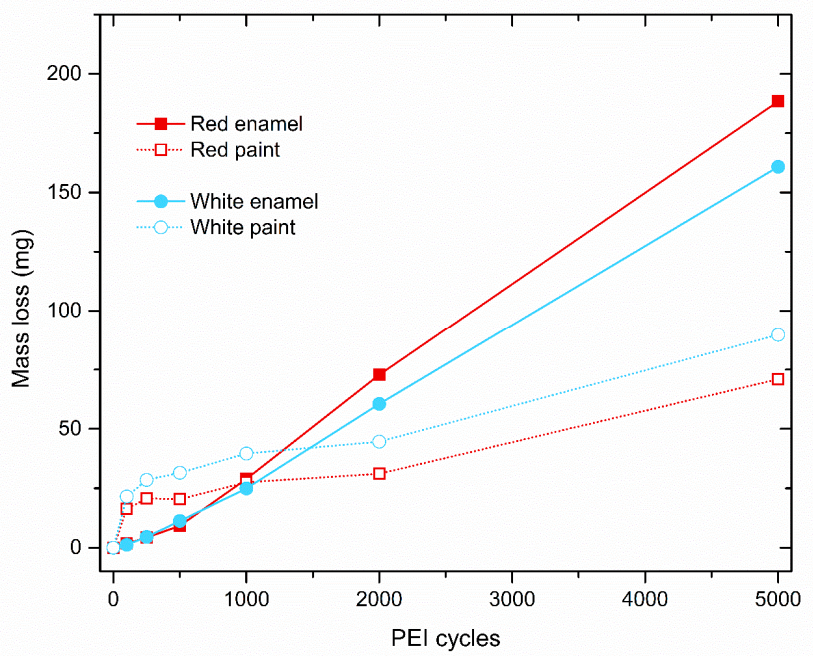


Figure 10. Mass loss during the PEI abrasion test.

Conversely, during the PEI abrasion test, enamel coatings were subjected to a higher mass decrease compared to paint coatings. After 5000 PEI cycles, the red enamel lost 188.4 mg, while the white enamel lost 160.8 mg. This difference might be due to the varying hardness of the coating. Overall, enamels are more sensitive to the PEI test compared to paints due to their brittleness, which makes them more susceptible to fracture in the presence of PEI abrasive forces. The enamel's hardness also renders them more susceptible to surface damage and wear.

4. Conclusions

In this work, different laboratory accelerated tests were conducted to test the potential of enameled steel in the architectural sector compared to that of paints, simulating a series of aggressive conditions to which building panels may be exposed during their service life. Two colors were tested, i.e., red and white, to investigate whether the difference in the composition of the frit might affect the durability of the coatings. The obtained enamel panels have a different thickness, much higher for the red coating than for the white coating. In terms of adhesion to the metal substrate, the white coating performed much better than the red coating. These findings may be explained by the higher values of thickness for the red enamel, which might lead to an inadequate firing.

Overall, enamel coatings displayed higher durability than paints throughout the accelerated tests. Specifically, the enamel coatings displayed:

- Excellent corrosion protection to the steel substrate, tied to a microstructure where porosity is closed and there are no through defects. Furthermore, the high thickness prevents the electrolyte contact with the substrate.
- High chemical resistance to aggressive alkaline pH and to aggressive solvents.
- Good color stability. While the white enamel showed excellent color stability during all the conducted accelerated tests, the red enamel displayed a slight color variation after exposure to UV-B radiation and after the soiling and weathering accelerated tests. Nonetheless, the color variation for red enamel is still significantly smaller than the variation for painted samples.

Ultimately, this work shows the potentiality of enamels as coatings for outdoor use. Indeed, they successfully resisted the aggressive situations tested, aimed at simulating the spectrum of exterior conditions to which coated panels for outdoor use might be exposed.

In addition to their high durability, enamels are advantageous in terms of aesthetics; in fact, high gloss values were reported for this type of coating, showing how exterior appearance is combined with good resistance. Eventually, despite the higher initial costs, all these aspects would reduce the requirement for maintenance procedures, making enamel panels environmentally sustainable as well.

Further studies are needed to foster the spread of enamel coating in the architectural sector. The main issue to address would probably be a reduction in the costs of production to make enamel economically competitive compared to the current favorite options and to encourage its industrial use. Then, future outlooks should be aimed at rendering the coating phase "greener". In addition to the architectural sector, an expansion of the enamel market can also be foreseen in the field of transportation (consider, for example, tunnels and galleries), where exposure to aggressive external environments demands high coating durability.

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