

Innovative coatings for corrosion protection of historical aluminium alloys in aerospace heritage

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HIGHLIGHTS

- New strategies for preventing corrosion of historic Al-alloys wrecks.
- Outdoor exposure simulated through accelerated ageing.
- Assessment of cutin-based polyurethane and 3-mercaptopropyl trimethoxysilane coatings.
- Evaluation of colour, physical and chemical changes after ageing.
- Best metal release suppression and highest polarization resistance for PropS-SH.

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ABSTRACT

The conservation of historical aluminium aircraft exposed to outdoor conditions requires protective systems combining corrosion mitigation, aesthetic compatibility and chemical stability. Within the PROCRAFT project two advanced coatings, namely, a bio-based cutin-derived polyurethane and a 3-mercaptopropyl trimethoxysilane (PropS-SH)-based system, were comparatively evaluated against the benchmark Paraloid B72 (PB72) on historic corroded and painted Duralumin substrates dating from World War II and the immediate post-war period. Coupons were subjected to an accelerated ageing protocol including simulated acid rain runoff, followed by thermo-hygrometric and UV cycling. Protective performance was assessed through a multi-analytical approach integrating electrochemical tests, colour analysis, SEM-EDS, ATR-FTIR, μ -Raman, and metal release quantification by MP-AES. On corroded substrates, both innovative coatings exhibited higher polarization resistance than PB72 and values two orders of magnitude greater than those of uncoated surfaces after ageing. PropS-SH provided inhibition efficiencies $\geq 95\%$ in terms of Al release, while the cutin-based coating achieved inhibition efficiencies $> 85\%$, outperforming PB72 under the same conditions. On painted substrates (already intrinsically protective) PropS-SH produced up to a one-order-of-magnitude increase in polarization resistance compared to the original paint system, whereas PB72 provided only marginal improvements. Spectroscopic analysis after ageing revealed progressive siloxane network densification in PropS-SH and, in the cutin-based coating, continued crosslinking accompanied by UV-mitigating behaviour attributable to residual natural antioxidants. Overall, both coatings provided effective corrosion protection on painted and corroded substrates, with PropS-SH exhibiting superior performance in suppressing metal release and enhancing polarization resistance, while maintaining good aesthetic stability throughout the artificial ageing process.

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1. Introduction

All-metal aircraft from World War II are a valuable part of industrial heritage, recognized for both their historical and technological significance, representing a tremendous advance in aeronautics. One of the key innovations was the implementation of Duralumin alloys, equivalent to the 2xxx Al-alloy family (Al–Cu and Al–Cu–Mg alloys), for hull and frame construction. While Duralumin provided superior mechanical performance, it exhibited inferior corrosion resistance [1,2], prompting the development of protective Al cladding, priming and specialized paint technologies.

Initially, protective paint layers included cellulose nitrate (CN) binders, later replaced or mixed with more stable polymers, such as alkyd resins. These were frequently coupled with plasticisers from the phthalate family, and emulsifiers like Zn stearate [3]. Inorganic fillers (e.g., CaCO_3 , BaSO_4 , etc.) and pigments (e.g., TiO_2 , ZnO , Fe_2O_3 , etc.) imparted colours specific to each army's paint schemes, and some provided corrosion inhibition capabilities (e.g., chromate-based compounds) [3–5].

Aircraft from this period, including their alloys, coatings and paints, often showed a high degree of technological complexity and innovation, along with continuous compositional differences, as standardization in aircraft production was still being established and raw material shortages were frequent [1,4]. Therefore, such different technical solutions, poorly documented and studied, are relevant for engineering, science and military history.

In addition, World War II aircraft serve as powerful symbols of political history, emotional resonance, and collective memory. These artefacts are deeply connected to the individuals who flew, fought, and often perished in them, as well as those who constructed and maintained it, anchoring their social significance in both local and global history.

As dramatic evidence of a critical period, reminders of a terrible event which led to Europe's modern identity, the conservation of WWII aircraft heritage, including their original metal components and paint layers [3,4,6], is urgent, even if it faces major challenges. Many aircraft were damaged or shot down, their wrecks dispersed across war zones, and thus, subjected to decades of outdoor exposure. Even when they survived the war, most of them were either dismantled for parts reuse or suffered post-war abandonment and neglect. As a result, only a relatively small number of WWII aircraft remain (even from previously abundant models), often in a fragmentary condition [6].

The condition and size of many WWII aircraft complicate their transportation, as well as the construction of confined, controlled environments for their protection. Especially when collected in big numbers, aircraft are either kept outdoors or housed in large hangars without environmental control, exposing them to harsh temperature and humidity fluctuations and solar radiation. These factors accelerate paint degradation and corrosion of metal components.

In such a scenario, conventional conservation approaches can be classified in two categories. The most frequent involves renovation, where degraded metal parts are replaced, and the entire aircraft is repainted at the end of the intervention with commercial products [1,7], such as Lesonal® and Dinitrol® [8,9]. This approach prioritizes the aircraft functional integrity. It aims to maintain the aircraft's airworthiness, protecting both original and new metallic parts, while presenting it under the most complete or like-new appearance as possible [1,7].

Although effective in preventing further corrosion and enhancing structural robustness, this approach results in the irreversible loss or obscuring of original components and paint layers, evidence of the period's technology. As WWII aircraft become rarer and more valuable, and technical documentary sources on the topic are scarce, the renovation and repainting approach has been increasingly questioned.

Therefore, less-invasive methods have been sought that better respect the historical integrity of heritage aircraft. Such conservation approaches aim at prolonging the life of the artefact without

significantly altering its materials or appearance and is particularly relevant for aircraft found in a wrecked or highly deteriorated state.

In the field of aerospace heritage, conservation practices aim to stabilize surviving components and mitigate further degradation, typically through the application of protective coatings. These treatments must strictly adhere to established cultural heritage criteria, ensuring reversibility, optical transparency, and long-term substrate protection. This kind of conventional conservation treatments employs microcrystalline waxes and acrylic resins, most notably Paraloid B72 (PB72—a methyl acrylate/ethyl methacrylate copolymer). While PB72 has demonstrated acceptable corrosion inhibition in multi-layered systems on patinated historical bronze artefacts within controlled museum environments [10], its protective efficacy has proven short-lived under more demanding conditions [11].

Although PB72 initially exhibits satisfactory barrier properties, its performance declines significantly upon exposure to aggressive media due to inherent moisture sensitivity. This degradation is characterized by a progressive loss of interfacial adhesion and the onset of localized corrosion, which may propagate beneath an apparently intact film, leading to severe substrate compromise. Consequently, the practical application of PB72 is largely restricted to rigorously controlled environments. This highlights a critical research priority: the development of transparent, ultra-thin protective coatings specifically engineered for outdoor and semi-confined conditions [1,7].

To circumvent the limitations of the traditional coatings, silane- and cutin-based formulations present highly promising alternatives. Silanes are well-established both as coupling agents to enhance adhesion between organic and inorganic phases and as fundamental components of hybrid protective systems [12,13]. Specifically, 3-mercaptopropyl-trimethoxysilane (PropS-SH) has been effectively employed in cultural heritage conservation as a protective barrier for historical and gilded bronzes [14–16]. Its efficacy stems from a dual bonding mechanism: the formation of robust covalent bonds with metals via the thiol moiety [17], and simultaneous interaction with surface oxides through hydrolyzable trimethoxysilyl groups [18–20]. Crucially, PropS-SH is not an environmentally harmful compound [21] that has already shown capability for the protection of modern Al 2024 alloys in industrial applications [18].

Alongside the use of safe synthetic compounds, the valorisation of biomass offers a sustainable, circular-economy pathway for advancing coating technology. The European Union generates over 700 million tonnes of agricultural waste annually, representing a vast feedstock for high-value applications. The development of protective coatings derived from agro-industrial residues and by-products—such as those from the tomato processing industry—constitutes a compelling strategy that must be further investigated and leveraged within the framework of a circular and sustainable economy.

Within this context, cutin—a naturally occurring hydrophobic polyester found in plant cuticles (accounting for 40% to 80% of dry weight)—provides an interesting alternative. Composed primarily of hydroxylated and epoxy-hydroxylated C16 and C18 fatty acids [22], its crosslinked structure confers low water solubility, high chemical stability, and pronounced hydrophobicity. Cutin is obtained via alkaline hydrolysis [23,24] from tomato peel waste, an abundant global by-product (10^5 – 10^6 tons/year) [25]. Previous research has validated cutin-based treatments on cellulose, glass, and metallic substrates, showcasing excellent adhesion and protective capabilities [24,26–29]. Conducted within the framework of the European PROCRAFT project (Protection and conservation of heritage aircraft, 2020–2023 [6,30]), the present study focuses on the development and validation of two innovative, non-hazardous coatings for WWII aircraft aluminium alloys and original paint layers exposed to outdoor environments. The two coatings selected for testing are based on PropS-SH and cutin oligomers respectively. The explicit hypothesis of this study is that bio-based cutin and hybrid PropS-SH formulations will outperform the traditional PB72 benchmark in simulated outdoor conditions by providing superior

interfacial adhesion and enhanced moisture barrier properties. Unlike PB72, PropS-SH exhibits excellent adhesion to the metal substrate, ensuring stable interfacial bonding, while the cutin-based coating is expected to exhibit improved durability in humid environments as a result of its intrinsic chemical architecture. The crosslinked polyester structure of cutin confers low water solubility and enhanced chemical stability, while its pronounced hydrophobic character is anticipated to provide an effective barrier against water and water vapour transport. These features are expected to limit moisture uptake and slow down degradation phenomena at the coating–substrate interface.

To evaluate the protective efficiency of these formulations against the PB72 benchmark, Duralumin samples sourced from historical aircraft (both painted and unpainted) were subjected to an artificial ageing protocol. This procedure simulated rigorous outdoor exposure, including the erosive action of heavy rain (runoff), UV radiation, and thermo-hygrometric cycles. The performance of the conservation treatments was then assessed through comprehensive surface characterization—comprising chemical, topographical, and colorimetric analyses—alongside electrochemical measurements and metal release quantification.

2. Materials and methods

2.1. Substrates

To evaluate the performance of the protective coatings, parts from two aircraft wrecks were selected as substrates, which were representative of WWII alloys and surface conditions.

Substrate selection was based on preliminary results from the PRO-CRAFT project, which studied a corpus of aircraft models from different nationalities [1,4]. After restoration by Arc'Antique in Nantes (France), the selected wrecks were sampled and analysed.

The metal substrates, both Al-based alloys from the Duralumin family (ca. 4 Cu, 0.6 Mg, 0.2 Si, wt.%), included: (i) a marine-corroded wrought propeller blade, and (ii) a rolled fuselage plate retaining original paint layers. Each will be referred to as the corroded (i) and painted (ii) substrates. The main features of these substrates are summarised in Table 1. The composition of the alloys was determined by EDS analysis of cross sections polished by conventional metallographic techniques. EDS acquisition was carried out on different areas of the metal core. Corrosion products and paint layers were analysed by SEM-EDS, FTIR and Raman spectroscopies, as detailed in the next sections.

2.2. Coating and sample preparation

The present study evaluated the effectiveness of two innovative protective treatments—specifically, a bio-based cutin formulation and a PropS-SH silane coating. Their performance was systematically

Table 1
Summary of the main features of aluminium alloy substrates.

	Substrate	Aircraft model	Original environment	Al-alloy constitution	Surface appearance
i.	Corroded substrate (a propeller blade)	Unknown (presumably from the United States)	Marine (Excavated underwater at Brest bay, France)	Wrought (forged and milled) Duralumin, composition similar to alloy 2017A	Dark grey with calcareous deposit remnants, localized spots of darker corrosion
ii.	Painted substrate (from a fuselage plate)	Morane-Saulnier 733, 1951 (France)	Rural outdoors (Blagnac, France)	Al-cladded, wrought Duralumin	Beige/chamois paint layer

compared against PB72, which served as the standard benchmark reference. Table 2 summarizes the main characteristics of the tested coatings and the types of accelerated ageing tests applied, as further detailed in the following Section 2.3.

The cutin-based coating was prepared according to the methods reported in Ref. [28]. Cutin oligomers were extracted from tomato peels [31] by alkaline hydrolysis and were supplied by Tomapaint Srl (Italy). After purification in demineralized water to remove residual inorganic salts, a pre-polymerization was carried out with 1,4-butanediol at 100 °C under vacuum, in order to increase polymer chain [31]. After esterification with butanediol, polymerization was performed in methyl ethyl ketone (MEK) with stoichiometric amounts of isophorone diisocyanate (IPDI) as crosslinker and dibutyltin dilute (DBLT) as catalyst. The resulting mixture was sprayed onto the coupons' surface and cured at room temperature, yielding a cutin-based polyester/polyurethane coating [28]. Notably, the formulated systems remained homogeneous and sprayable for at least 1 h prior to application, without noticeable viscosity increase or phase separation.

The PropS-SH coating (Merck KGaA, Germany) was obtained from a precursor solution prepared by mixing ethanol (ACS Reagent grade, CARLO ERBA Reagents Srl, Italy), PropS-SH, and demineralized water in a 90/5/5 vol ratio. The solution was acidified to pH 4 by adding a few drops of a 0.1 M sulfuric acid solution. The precursor solution was left to hydrolyse for 24 h. Subsequently, it was applied to the samples by spraying, followed by touch-up with a brush. The silane precursor solution demonstrates remarkable stability. Under refrigerated storage (<5 °C), it maintains its structural integrity and remains perfectly suitable for coating deposition even after 10 days, without any significant alteration of its original properties. The protected samples were then cured for 24 h at 40 °C, to allow the silane to crosslink through the polycondensation of OH groups into a siloxane network.

PB72 (AN.T.A.RES Srl, Italy) was applied from a 10% w/v solution in ethyl acetate. It was spread following a ratio of 85 mL of coating solution/m² of coated area, and left to dry for 5 days before characterization and ageing.

Before coating, each sample was divided into halves, coupon a) and b). The coupon's edges were protected with a bicomponent epoxy resin, and their backsides covered with Kapton tape (DuPont®). Coatings were applied by spraying followed by brushing, to ensure homogenous layers, on coupons from each substrate (corroded and painted), which were investigated both in uncoated and coated conditions. The coupons' surface dimensions were 2.5 × 2 cm², and their average thicknesses 3.8 mm for corroded and 1.2 mm for painted substrates.

The average dry film thickness of the coatings (DFT) was determined

Table 2
Summary of the main features of tested coatings.

Substrate	Coating type	Coating thickness (DFT, μm)	Artificial ageing
Corroded	Uncoated	n.a.	Runoff + CC
		n.a.	Runoff + CC with UV
		18.5	Runoff + CC
	PropS-SH	18.0	Runoff + CC with UV
		7.0	Runoff + CC
		7.0	Runoff + CC with UV
Painted	Cutin-based	8.5	Runoff + CC
		8.6	Runoff + CC with UV
		n.a.	Runoff + CC
	Uncoated ^a	n.a.	Runoff + CC with UV
		n.a.	Runoff + CC
		13.7	Runoff + CC
	PB73	14.4	Runoff + CC with UV
		5.1	Runoff + CC
		5.5	Runoff + CC with UV
	Cutin-based	19.4	Runoff + CC
		18.0	Runoff + CC with UV

n.a. - Not applicable. CC stands for Climatic Chamber ageing (see section 2.3).

^a The average thickness of the historical paint on painted substrates was 32 μm .

using a gravimetric method. The mass of each substrate was recorded before coating application and after the final curing step using an analytical balance. The average thickness was calculated according to Eq. (1):

$$DFT = \Delta m / A \rho \quad (1)$$

where Δm was the mass of the applied coating, A is the coated surface area, and ρ is the density of the cured film. The DFT values, are reported in Tables 2 and in Fig. S1. Each condition was replicated three times.

2.3. Accelerated ageing protocol

After preparation, the coupons were artificially aged by a two-step protocol: first, under intermittent synthetic acid rain runoff, for a total time of wetness of 20 days (Fig. 1A); and second, by 14 continuous days of cyclic ageing in a climatic chamber (28 cycles in total, Fig. 1B). The artificial ageing protocol was adopted to combine and accelerate specific environmental stressors under controlled conditions. It is used as a comparative tool to identify mechanisms and degradation trends, and to rank coating performance.

The initial ageing phase entailed the dripping of synthetic acid rain (AR) at a rate of 60 mL/h on the substrates, which were inclined at an angle of 45°. The AR runoff followed a weekly cycle comprising 3 days of dripping, a one-day break, two further days of dripping, and a final one-day break. The aforementioned cycle was repeated until a total of 20 days of time of wetness (ToW) was reached.

The AR solution (Table 3) had a pH of 4.25. It was prepared according to a previous formulation that replicates the composition of

urban acid rain [32] and Cl^- concentrations found in atmospheric deposition near the sea [33], to also reflect marine-influenced environmental conditions.

Over the course of dripping days, the AR solution was collected and subjected to microwave plasma atomic emission spectroscopy (MP-AES, with an Agilent 4210 MP-AES spectrometer). This allowed to quantify the release of Al (a marker for corroded substrates) and Zn (a marker for painted substrates). The limits of detection (LoD) and quantification (LoQ) were, respectively, 1.5 mg L^{-1} and 5 mg L^{-1} for Al, and 6 mg L^{-1} and 9 mg L^{-1} for Zn. Metal release per surface unit was calculated by averaging the results of three coupons and calculating the related standard deviation. The inhibiting efficiency of each coating was then calculated in terms of cumulative metal release (η_M) according to Eq. (2) [32,34]:

$$\eta_M = \frac{M_{\text{sol,NC}} - M_{\text{sol,C}}}{M_{\text{sol,NC}}} \times 100 \quad (2)$$

where M_{sol} : amount of metal M released in the ageing solution (Al or Zn in $\mu\text{g cm}^{-2}$); NC: uncoated coupon; C: coated coupon. η_M is 100% if no metal is released, 0% if release matches the non-coated one.

In the second step of the ageing protocol, coupons were placed in a climatic chamber (ClimaCell 111, MMM Group) to simulate outdoor exposure via cyclic variations of temperature (T), relative humidity (RH) and UV radiation. The 12-h cycle combined daily and seasonal variations in a four-segment sequence (Fig. 1B): 1) A temperature-increase ramp representing sunrise; 2) a plateau representing a warm summer day; 3) a temperature-decrease ramp representing sundown, and 4) a plateau representing a cold winter night. UV radiation was applied

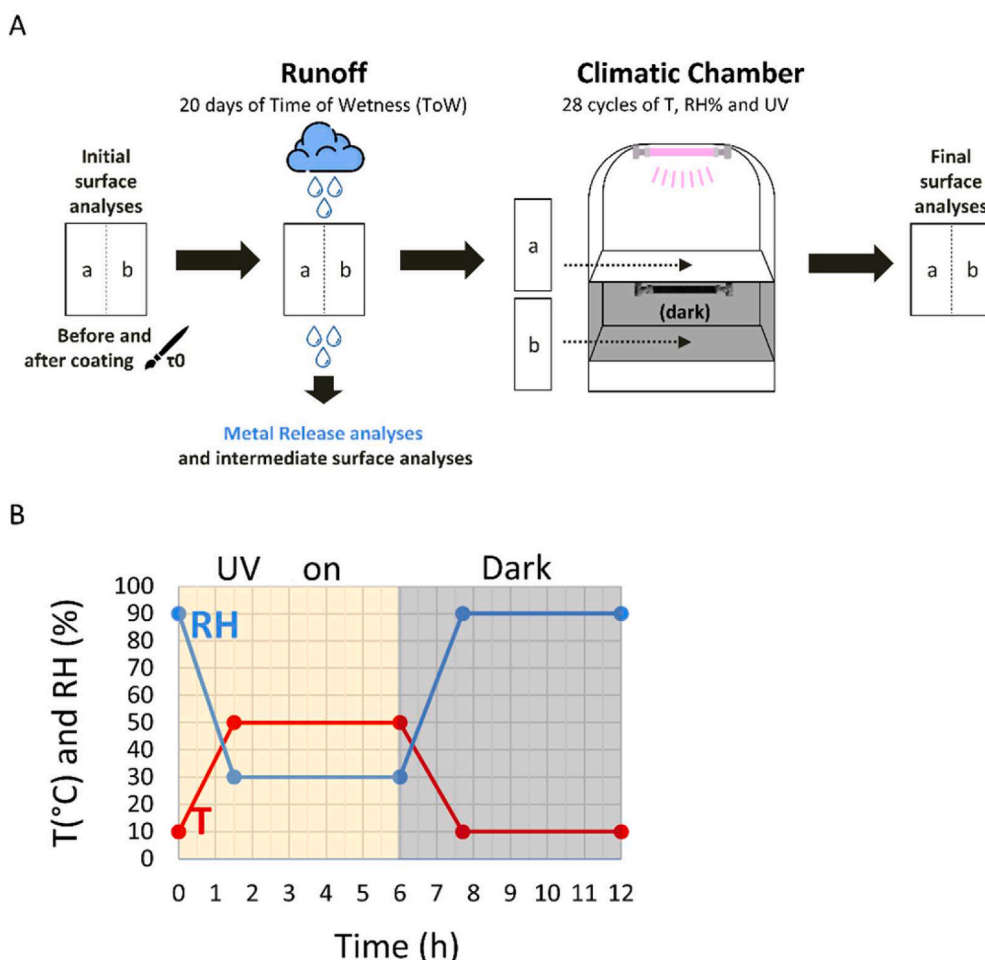


Fig. 1. Workflow and artificial ageing scheme (A); 12-h climatic chamber ageing cycle (B).

Table 3

Composition of the synthetic acid rain (AR) for runoff tests.

Ion	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	CH ₃ COO ⁻	HCOO ⁻	NH ₄ ⁺	Ca ²⁺	Na ⁺	H ⁺
mg/L	1.90	6.52	4.62	0.23	0.05	1.05	0.30	3.98	0.057

trough UVA lamps (emission range: 300–400 nm; 4 mW cm⁻²) during the morning ramp and day plateau, and switched off during the sun-down ramp and night plateau [35]. The cycle was validated in term of T and RH fluctuations by inserting external sensors into the chamber prior to the test, and UV irradiation stability was verified using a radiometer before and after the ageing protocol. One half of the samples was exposed to UV irradiation (labelled as “a” coupons), while the remaining samples (labelled as “b” coupons) were maintained in dark conditions throughout the cycle (Fig. 1A). The coupons were subjected to a total of 28 consecutive ageing cycles.

2.4. Surface and stratigraphic characterization

The coatings were assessed by comparing surface properties before and after coating as well as after ageing. Surface characterization was performed at 0, 10 and 20 days of ToW under runoff, and after climatic chamber exposure in dark conditions or under UV (Fig. 1).

The multi-technique approach included surface morphology observations, documented through a high-resolution reflex camera (Nikon D70s) and through 3-D Digital Optical Microscopy (Hirox HK7700).

Scanning electron microscopy (SEM, ZEISS EP EVO 50), coupled with energy dispersive spectroscopy (EDS, Oxford Inca 350), was employed to characterize the morphology and composition of the corrosion products, original paint, and protective layers. The equipment was operated under an accelerating voltage of 20 kV, and EDS analyses were performed both on large areas (1.0 × 0.5 mm²) and single spots.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, PerkinElmer Spectrum 3) and Raman micro-spectroscopy (Horiba XPlora Plus, 785 nm diode laser; Renishaw InVia, 785 nm laser and 514 nm Ar + laser) were used to characterize the chemical compounds at the coupons' surfaces.

ATR-FTIR spectra were acquired with a diamond ATR crystal over the 4000 to 400 cm⁻¹ range at 2 cm⁻¹ spectral resolution, integrating 32 scans per measurement, ensuring good crystal contact and spectra comparability by matching pressure percentages. Normalization and intensity change measurements were performed with Omnic® software. Intensity was considered as the corrected height of the band after drawing a linear baseline between two fixed low points.

μ-Raman analyses were optimised to avoid sample degradation and to obtain a satisfying S/N ratio (range 100–5180 cm⁻¹, acq. time 1 s, three accumulations, laser power output 1–10%). A linear baseline subtraction was conducted with Omnic® software.

Colour measurements were performed in the CIELAB colour space, operating the spectrophotometer (Datacolor D400) in d/8° geometry with a D65 illuminant, 10° observer configuration, a 6.6 mm aperture and specular component included (SCI). Two measurements were acquired and averaged per coupon to determine its colour; one measure was taken from its upper and the other from its lower half. A jig was used to take measurements at the same points each time. Colour difference (ΔE*) was calculated according to Eq. (3):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (3)$$

where L*, a* and b* represent the lightness, the red/green and the yellow/blue axis, respectively.

Colour change due to coating applications and ageing was determined by averaging ΔE* of at least 4 points from different coupons and calculating the standard deviation.

Finally, to detect changes in the stratigraphy, cross-sections of corroded and painted substrate (uncoated, with PropS-SH and cutin-

based coatings) were characterised via optical microscopy and SEM-EDS. The cross-sections were prepared both from coupons before ageing and after the final step of ageing (climatic chamber exposure with UV). Cross-sections were cold-mounted in epoxy resin and dry-polished with emery paper down to 4000 before imaging. This was performed under reflected visible light with an inverted optical microscope (E3 Reichert-Jung), and by SEM-EDS with the same operating conditions as superficial observations.

2.5. Electrochemical tests: Electrochemical Impedance Spectroscopy (EIS) and polarization curves

The protective efficiency of the coatings was evaluated by Electrochemical Impedance Spectroscopy (EIS), carried out on corroded and originally painted substrates, both in protected and unprotected conditions, before and after ageing.

The EIS measurements were carried out using a three electrode “contact” electrochemical cell. This cell comprised an AISI 316 stainless steel net, as a counter electrode, positioned on the surface of the coupon covered with several layers of filter paper soaked with AR solution. A saturated calomel reference electrode (SCE) was inserted into an opening of the counter electrode net and positioned near the surface of the coupon in contact with the AR-impregnated paper.

A Princeton Applied Research - PARSTAT 2263 potentiostat/galvanostat/FRA was utilized under the following experimental conditions to acquire the EIS measurements: polarization at the open circuit potential (E_{oc}) with a ±4 mV rms alternating potential signal for uncoated substrates and a ±20 mV rms alternating potential signal for coated substrates, respectively; a scan frequency range of 100 kHz to 1 mHz was employed, and 10 data points per decade were collected. The EIS spectra were recorded after the E_{oc} value had stabilized or when the changes in E_{oc} were less than 2 mV/10 min. This stable condition was typically achieved after approximately 30 min of E_{oc} monitoring.

From each EIS spectrum, the value of the R_p was evaluated by estimating the limit of the real part of the impedance at frequency tending to 0, using parameters obtained by fitting of the experimental data. Polarization resistance (R_p) values were calculated as the difference between R_p' and the solution resistance (R_s) value, according to equation (4):

$$R_p = R_{p'} - R_s \quad (4)$$

Each test was performed in triplicate. The R_p values were calculated by averaging the results of the measurements and are reported with their corresponding standard deviations.

3. Results

This section presents the results of surface morphology observations, localised chemical analysis, colour change, metal release and EIS measurements. The findings are presented in separate sections for corroded substrates and then for painted substrates, discussing in both cases all the investigated surface conditions (uncoated, coated with PB72, PropS-SH or cutin-based protectives) at each ageing step.

At the beginning of the sections dedicated to each type of substrate, the evolution of surface morphologies during ageing (either with or without protective coatings) is compared. Within subsections dedicated to specific coatings on each substrate, additional aspects (such as stratigraphy and phase composition of surface layers) are discussed and compared. At the end of the section dedicated to each substrate

(corroded or painted), the performance of coatings is compared and discussed in terms of colour changes, metal release during ageing and electrochemical behaviour.

3.1. Corroded substrates

The elemental composition of the corroded substrate alloy (bare metal core) is reported in Table 4.

Before ageing, the corroded surface observed by reflex macrophotographs (Fig. 2A, first row), optical microscopy (Fig. S2) and SEM-EDS (Fig. 3A, first row) exhibited a heterogeneous topography, mostly covered by a grey corrosion layer, likely $\text{Al}(\text{OH})_3$ due to its high Al and O content (identified via SEM-EDS). Corrosion-free regions displayed shallow scratches, while other regions retained porous calcareous deposits of marine origin and darker corrosion products. Raman spectroscopy (Fig. S3) identified the calcareous concretions as calcium carbonates (likely aragonite, dolomite and ankerite), while darker corrosion regions likely contained hematite.

During the runoff step, calcareous material dissolved from the uncoated corroded surface, increasing the exposed bare alloy surface area (Fig. S2; Fig. 2C and Fig. 3C, first row). EDS surface analyses during and after the runoff step (Fig. S4) confirmed this dissolution, demonstrated by the simultaneous decrease in the amount (wt%) of Ca and increase in Cu and Al.

Afterwards, climatic chamber ageing led to the formation of a thin, whitish corrosion layer with a matte appearance, as macroscopically documented in high-resolution optical macrographs (Fig. 2D and E, first row).

3.1.1. Corroded substrates coated with PB72

Visually, no changes were apparent upon PB72 application, due to its high transparency (Fig. 2B, second row). SEM observations (Fig. 3D, second row) allowed instead to verify the increase of surface smoothness, suggesting that the coating evenly covers the surface of the sample.

After runoff, macroscopic documentation (Fig. 2C, second row) revealed no significant visual changes in PB72-coated coupons. The final climatic chamber ageing step also did not cause significant morphological modifications on the macro scale, regardless of UV exposure conditions (Fig. 2D and E, second row). Furthermore, 3D-digital microscopy did not detect significant changes (Fig. S5). SEM-EDS, however, revealed microscopic surface damage of the PB72 layer in each ageing step, including coating discontinuities and reduction of its smoothness (Fig. 3C, D and E).

Macro ATR-FTIR measurements (Fig. 4) indicated no evident changes in PB72 response during ageing, as the diagnostic bands exhibited intensity variations of less than 3%. This implied relative chemical stability of the methyl acrylate/ethyl methacrylate copolymer under such conditions. Previous studies [36] suggest that photooxidation primarily occurs in the outermost shallow layer of PB72, while macro ATR-FTIR, which penetrates up to a few microns [37], may not reveal chemical degradation reported for thinner PB72 films or detected by nanoATR-FTIR analyses after irradiation including UVC-UVA (emission range: 200–700 nm, 39 mW cm^{-2}) [38].

3.1.2. Corroded substrates coated with PropS-SH

Clearly evident by SEM observations (Fig. 3B, third row), the deposition of the silane-based coating induced only minimal macroscopic changes on the substrates, such as a very faint darkening of the surface (Fig. 2B, third row).

Table 4

Elemental composition (EDS, wt%) of the bare alloy core of the corroded substrate.

Element	Al	Cu	Mg	Mn	Fe	Si	Others
wt%	93.7	4.1	0.6	0.6	0.4	0.2	Balance

Runoff led to the formation of macro and microcracks in the PropS-SH coating applied on corroded substrates, clearly visible in reflex photographs (Fig. 2C, third row) and SEM-EDS images (Fig. 3C, third row). SEM-EDS also documented a thinning of the coating after dripping. Together with the microcracks, thinning intensified after climatic chamber ageing (Fig. 3D and E, third row). Despite the cracks, cross-section observations (Fig. 5A) confirmed the coating still covered most of the surface after ageing.

SEM-EDS analysis of cross-sections (Fig. 5B) showed that PropS-SH prevented the dissolution of underlying calcareous concretions during AR exposure.

ATR-FTIR spectroscopy (Fig. 4) detected minor chemical changes in PropS-SH after dripping and UV exposure, including a new small, broad band around 1645 cm^{-1} associated with molecular coordinated water adsorbed to the Si–O–Si structure [39,40]. UV exposure induced another broad signal at 3385 cm^{-1} , attributable to OH stretching, possibly upon Si–C bond photolysis and formation of silanol groups [15,20], with an intensity increase of 4.2 times compared to an unaged PropS-SH film.

Additionally, the $\nu_{\text{Si-OH}}$ band at 874 cm^{-1} shifted to 904 cm^{-1} after UV exposure. This band could be influenced by the presence of calcareous material, but that is unlikely due to the absence of signals at 1400 and 700–713 cm^{-1} in the uncoated substrate before ageing.

Therefore, the change suggests a decrease in Si–OH hydrogen-bonding, possibly due to increased network reticulation, which reduced Si–O bond length and increased hydrophobicity [20,40,41]. This is consistent with similar findings on UV-aged PropS-SH coatings on bronze substrates [15].

3.1.3. Corroded substrates protected with the cutin-based coating

Upon application, the cutin-based coating caused noticeable darkening and reddening of the surface, as documented by reflex photography (Fig. 2B, fourth row). However, the red hue significantly attenuated after UV exposure (Fig. 2D, fourth row). This change was confirmed by colour analysis, and its cause was further explored via Raman spectroscopy (section 3.1.4). Moreover, the cutin-based coating did not fully cover calcareous concretions, which protruded from the protective layer (Fig. 3B, fourth row).

ATR-FTIR spectroscopy (Fig. 4) identified other chemical changes: the $\nu\text{-N=C=O}$ band at 2264 cm^{-1} , attributed to remaining IPDI crosslinker, decreased over time (88% intensity reduction after runoff, and $\geq 98\%$ reduction after climatic chamber ageing), whereas the amide I absorbance at 1651 cm^{-1} increased between 13% and 27% in intensity. These changes (emphasised in Fig. S6) suggest ongoing crosslinking during the ageing tests, with IPDI reacting with prepolymer OH groups, forming an amide-containing polyurethane [42]. The process continued over time, independent of UV exposure.

After runoff, SEM-EDS observations showed that the calcareous protrusions emerging from the cutin-based coating slightly decreased in height during dripping (Fig. 3C, fourth row).

In fact, cross-section observations by SEM-EDS (Fig. 6) showed that the heterogeneous calcareous deposit was partly dissolved also in the presence of the cutin-based coating, because this thin protective layer was not able to fully cover the rough surface. However, the cutin-based coating contributed to limit dissolution of the calcareous deposit by comparison to the uncoated substrate.

3.1.4. Surface colour: comparison between coatings on corroded substrates

The ΔE^* values for colour change after coating and ageing when compared to unaged, uncoated coupons (Fig. 7 and Table S1) showed that PB72 and PropS-SH fell within the colour change threshold considered acceptable for outdoor preservation conditions ($\Delta E^* = 5$) [43,44]. Uncoated coupons exhibited instead greater change at the end of ageing, i.e., after climatic chamber exposure. However, when the coated coupons after ageing were compared with the corresponding unaged ones, PropS-SH showed more yellowing under UV exposure ($\Delta b^* = 4.8 \pm 1.3$) than without irradiation ($\Delta b^* = 2.9 \pm 0.8$, unchanged

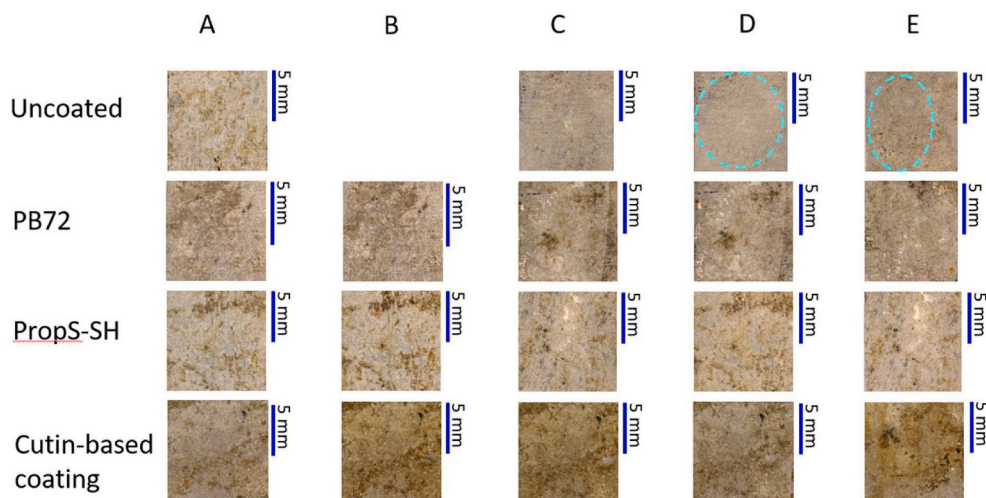


Fig. 2. Reflex photographs of corroded substrates before coating (A), after coating and before ageing (B), after runoff tests with 20 days of ToW (C), and after climatic chamber ageing with UV (D) or in dark conditions (E). Blue ovals highlight areas where the thin, whitish corrosion layer formed after ageing in the climatic chamber. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

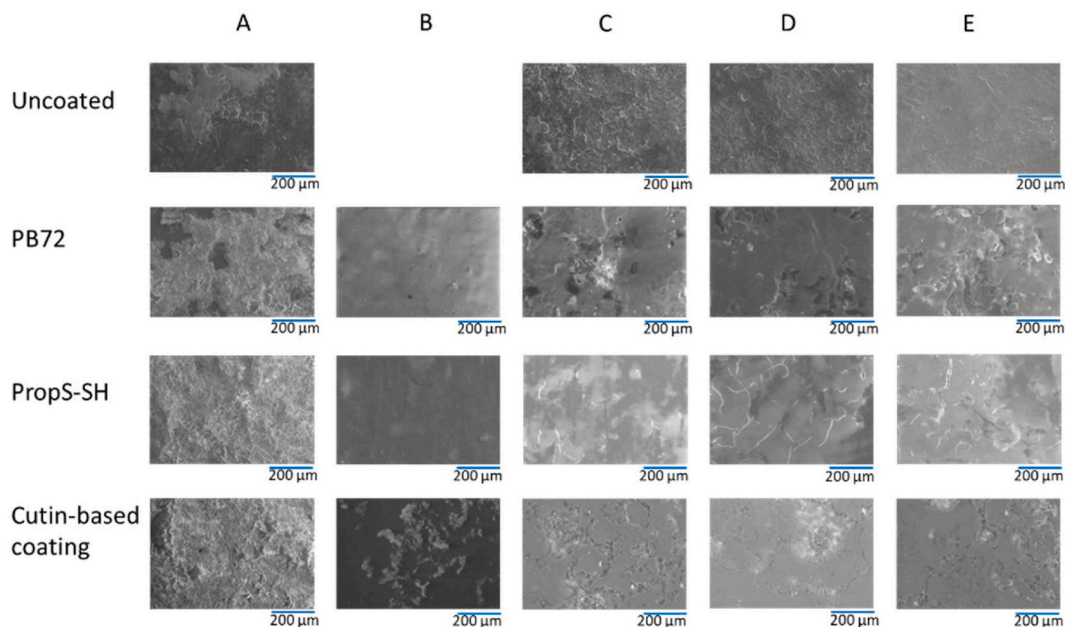


Fig. 3. SEM images of corroded substrates before coating (A), before ageing (B), after runoff tests with 20 days of ToW (C), and after climatic chamber ageing with UV (D) or in dark conditions (E). Secondary electron (SE) images are reported except for cutin-based coating, where backscattered electron (BS) images are shown.

after the runoff step), suggesting photo-degradation of the polymer. Dark spot formation in PropS-SH coatings exposed to UV has been reported for bronze substrates [15], likely due to thermal and photooxidation processes in thiol-containing polymers [45].

The cutin-based coating, conversely, exceeded acceptable colour change thresholds, but reverted to an acceptable ΔE^* , particularly upon UV exposure. This colour shift after UV irradiation would be advantageous for sunlit outdoor settings. Photolysis of lycopene residues in the coating likely contributed to such colour change [46]. This is suggested by the decrease in intensity of the characteristic Raman bands of this compound [47] with each ageing step, until their disappearance after UV irradiation (Fig. 4). Lycopene presence may also play a photo-protective role by scavenging free radicals [48], which contribute to polyurethane photo-degradation under UV [49].

3.1.5. Metal release from uncoated and coated corroded substrates

The release of Al in the runoff solution was quantified by MP-AES and used as a corrosion marker for corroded substrates. For uncoated corroded substrates a linear increase over exposure time (Fig. 8; periodic values in Fig. S7) was found. Conversely, all coated substrates showed reduced Al release during runoff. It has to be pointed out that for the coupons coated with PB72 and the cutin-based coating, the Al concentrations in the runoff solutions were always close to or below the LoQ or even below the LoD values, whereas for the coupons coated with PropS-SH, the Al concentrations were always lower than the LoD. The trends shown in Fig. 8B must therefore be considered from a qualitative point of view. However, based on these results and making a very conservative assumption (i.e. assuming that Al concentrations were always equal to LoQ for PB72 and cutin-based coatings, or to LoD for PropS-SH), it can be stated that η_M is always $>85\%$ and even $\geq 95\%$ for PropS-SH.

The slightly better efficiency in terms of Al release that PropS-SH

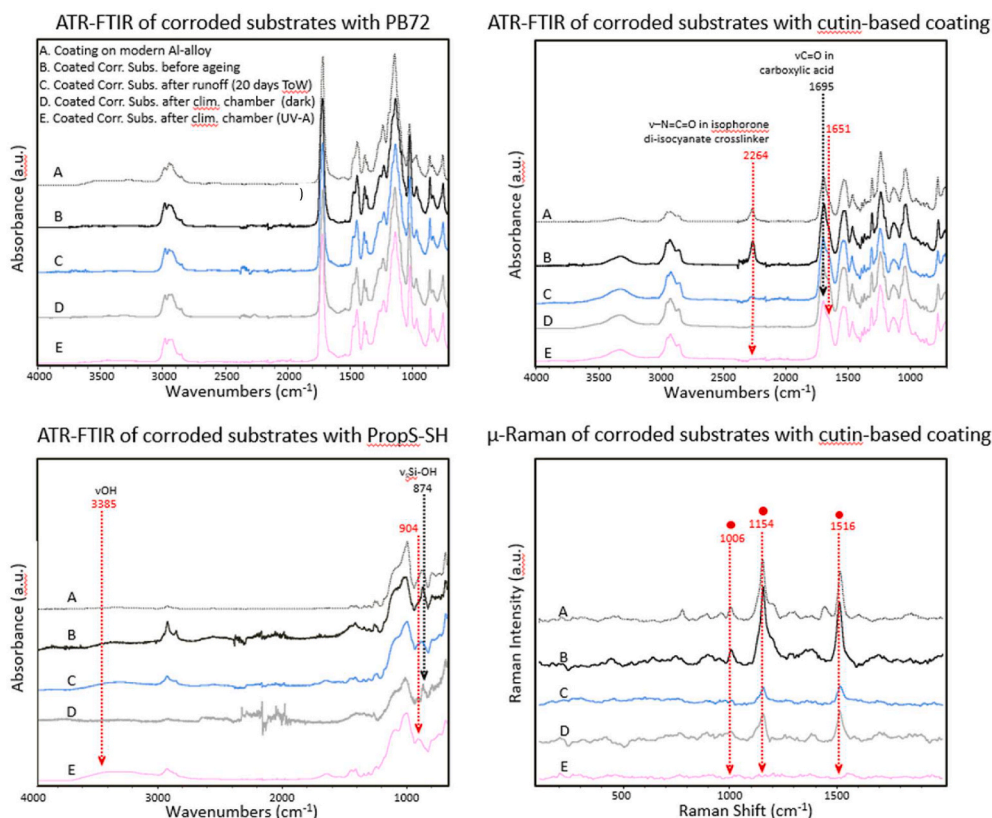


Fig. 4. ATR-FTIR and μ -Raman spectra of coated corroded substrates. Each group shows a reference spectrum for each coating formulation, followed by spectra of the coated corroded substrates before and after each ageing step. ATR-FTIR spectra were normalised considering the strongest infrared band. Raman spectra were baseline corrected. Changes in lycopene bands in cutin-based coatings are marked with red dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

appears to confer is probably due to the formation of strong Al–O–Si covalent bonds that develop at the metal/coating interface as suggested by X-ray photoelectron spectroscopy (XPS) on coated industrial Al alloys [43].

3.1.6. Electrochemical tests on corroded substrates

To assess the protective capabilities of the selected treatments, the sample surfaces were non-destructively characterized before and after each ageing stage. This characterization was performed in situ using Electrochemical Impedance Spectroscopy (EIS) with a three-electrode contact cell.

Fig. 9 reports the EIS results obtained for both the uncoated and coated corroded substrate.

Under non-aged conditions, all applied treatments effectively protected the corroded substrate. However, the cutin- and silane-based coatings exhibited significantly higher protective efficacy compared to the PB72 reference. Specifically, after treatment, R_p values of 5.5×10^6 , 2.6×10^7 and $3.4 \times 10^7 \Omega\text{cm}^2$ were measured, yielding protective efficiencies of 87%, 97% and 98% for the PB72, cutin- and silane-based coatings, respectively.

The plain corroded substrate (uncoated) exhibited a significant decrease in R_p values to approximately $1.1 \times 10^5 \Omega\text{cm}^2$ after being exposed to runoff. This value remained essentially unchanged after further climate chamber exposure to UV radiation and increased only slightly after exposure without UV radiation. The limited R_p variations measured during accelerated ageing (within the measurement variability) suggest that the initial runoff phase damaged the naturally occurring film of corrosion products on its surface. As a result, the system remained in a more active state throughout the subsequent accelerated ageing phases, failing to regain its initial, more protective condition.

The application of protective treatments significantly reduced the substrate's corrosion rate, showing average R_p values approximately two orders of magnitude higher than those observed for the untreated samples. For PB72, R_p values of 1.22×10^7 , 1.1×10^7 , and $1.32 \times 10^7 \Omega\text{cm}^2$ were measured after exposure to runoff, temperature and humidity cycles with UV and in dark conditions, respectively.

The PropS-SH treatment exhibited the highest R_p values, and trends indicated that its protective performance was not significantly impaired by accelerated ageing, in fact values of 3.8×10^7 , 2.4×10^7 and $4.2 \times 10^7 \Omega\text{cm}^2$ were measured after runoff, exposure to climatic chamber with and without UV respectively. Although superficial micro-cracking is observed on the PropS-SH coating (Fig. 3), it does not compromise the overall protective efficacy. Cross-sectional analyses (Fig. 5B) demonstrate that the silane-based treatment penetrates deeply into the defects of the underlying corrosion products layer, effectively sealing the inherent porosities and consolidating the porous matrix. Throughout the ageing process, the EIS spectra revealed an increase in the coating capacitance, which is indicative of electrolyte uptake. However, the low-frequency impedance modulus remained consistently high throughout the test. These findings suggest a dynamic protective mechanism: while the aggressive solution may initially permeate through the superficial micro-cracks or coating porosities, the subsequent precipitation of corrosion products within these defects leads to a pore-blocking effect. This phenomenon actively seals the penetration pathways, thereby providing a durable barrier against aggressive media.

The cutin-based protective coating showed R_p values slightly higher than those of the PB72 but lower than those of the silane-based coating (1.6×10^7 , 1.7×10^7 and $1.4 \times 10^7 \Omega\text{cm}^2$, respectively).

The EIS data confirmed the trends of the data obtained from metal release analyses and by the characterization of the coatings performed after the various ageing stages; it can be concluded that, overall, the

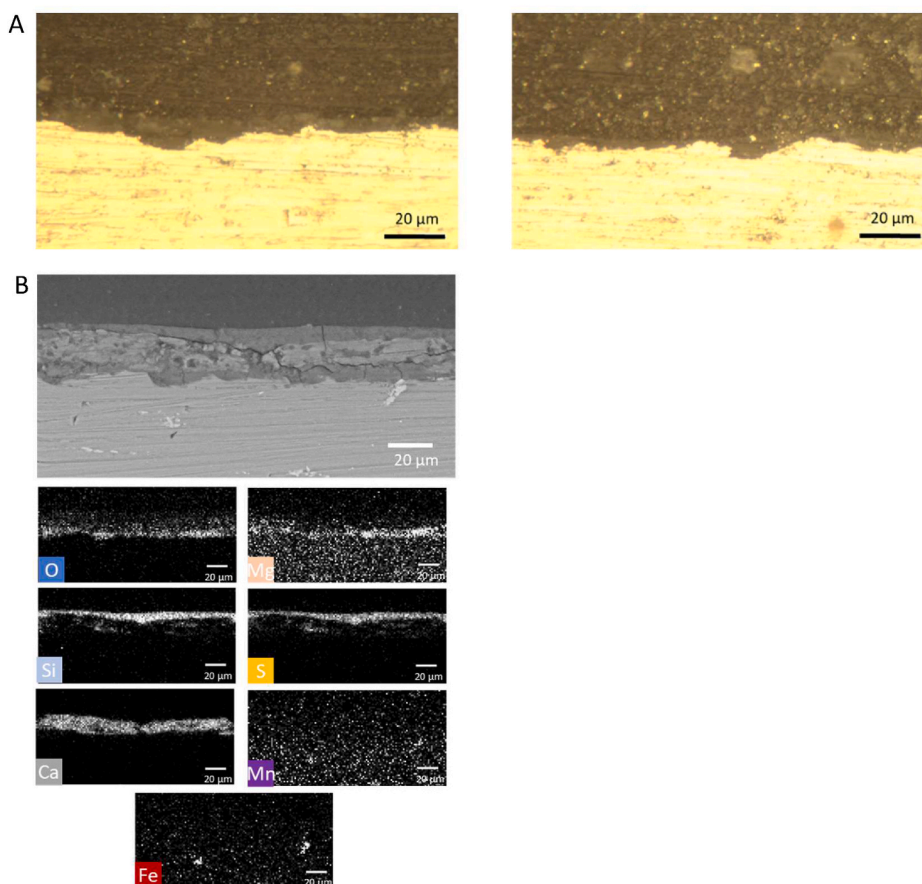


Fig. 5. Cross-sections of a corroded substrate coated with PropS-SH. A: Optical micrographs before ageing (left), and after climatic chamber ageing with UV (right). B: Cross-section SEM image (SE) and EDS elemental mapping after climatic chamber ageing with UV.

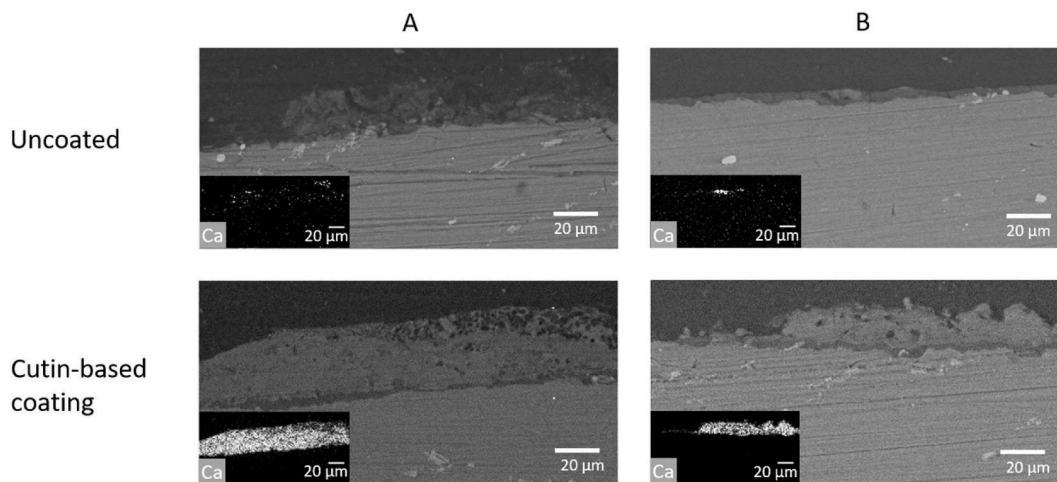


Fig. 6. SEM (secondary electron, SE) images and EDS elemental mapping of corroded substrates' cross-sections before ageing (A), and after climatic chamber ageing with UV (B).

protective coatings exhibit a comparable behaviour and provide high protection to the substrate. In fact, protective efficiencies ranging from 94% to 98% were measured for all coatings after the different ageing phases.

3.2. Painted substrates

Cross-section observations of painted substrates with SEM-EDS, as

well as FTIR, XRD and PyGCMS previously performed [4], revealed that the paint stratigraphy included a thin primer (layer 0), seemingly including zinc chromate and phosphate content, followed by an original cellulose nitrate and alkyd resin paint layer (layer 1). This layer included diethyl phthalate (DEP) and 2-ethylhexyl phthalate (DEHP) plasticisers, as well as rutile (TiO_2), zincite (ZnO), barite (BaSO_4) pigment particles. Zn and Ca stearates have been detected (as subsequently reported in the discussion of ATR-FTIR results, Fig. 13), likely inserted as emulsifiers or

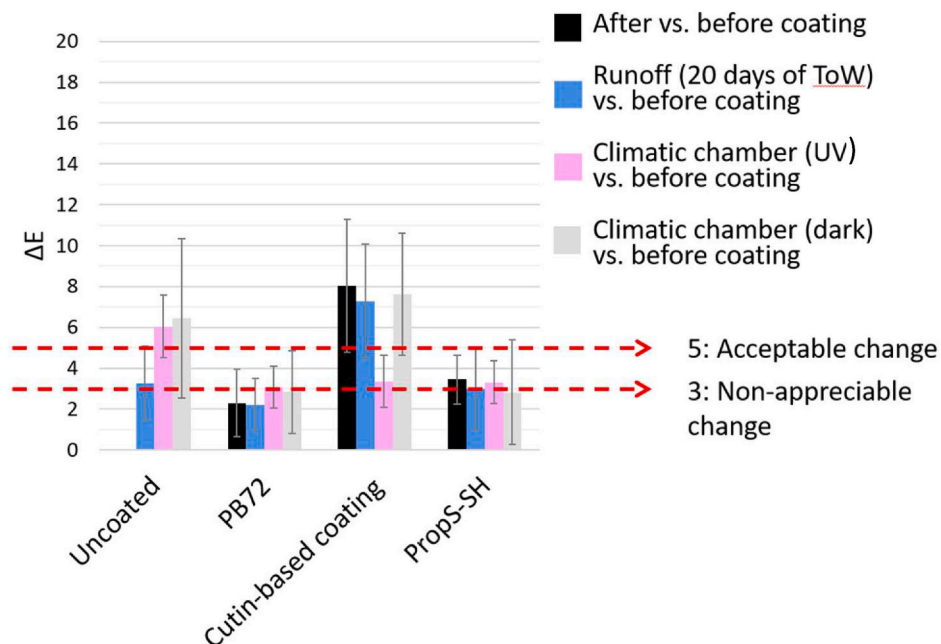


Fig. 7. Surface colour change (ΔE^*) of corroded substrates, after coating and ageing, compared to an unaged, uncoated reference. Dashed lines indicate conventional ΔE^* thresholds for cultural heritage exposed in outdoor conditions. ΔE^* values are the average of ΔE^* measured on 4 points (2 per coupon) and error bars correspond to the related standard deviations. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

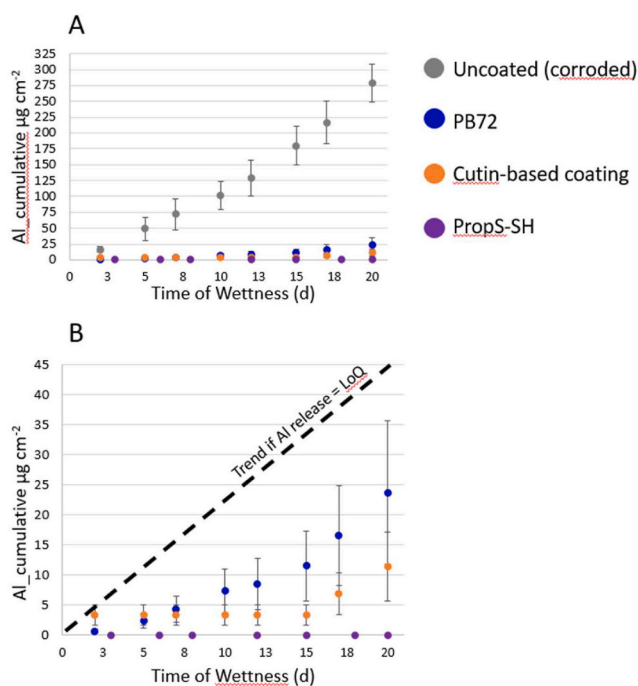


Fig. 8. Cumulative Al release from corroded substrates over ToW (mg cm^{-2}). The full graph (A) includes release from coated coupons, shown in a magnified detail (B). Reported values are the average of three coupons, error bars correspond to the related standard deviations. Black dashed lines simulate the cumulative trend that would occur if all sampled solutions had Al concentrations equal to the limit of quantification (LoQ).

auxiliary curing agents respectively [50], or resulted from interactions between pigments and the alkyd binder [51].

The composition of the alloy under the Al cladding is reported in Table 5.

During the various ageing steps, the comparison of the surface

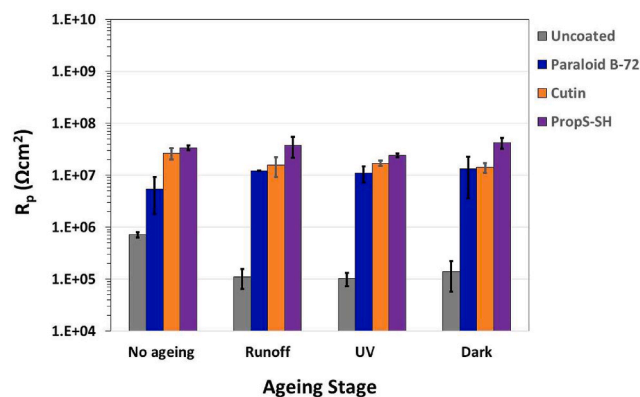


Fig. 9. Polarization resistance (R_p) values and standard deviations measured on uncoated and coated corroded substrates after each accelerated ageing step.

Table 5

Elemental chemical composition (EDS, wt%) of the alloy under the Al-cladding in the painted substrate.

Element	Al	Cu	Mg	Mn	Fe	Si	Others
Wt. %	93.6	3.9	0.7	0.8	0.4	0.6	Balance

morphology revealed no significant macroscopic or microscopic changes in the uncoated painted surface, as shown by reflex macrophotographs (Fig. 10, first row), digital microscopy (Fig. S8) and SEM-EDS observations (Fig. 11, first row).

EDS analyses during ageing (Fig. S9) and elemental mapping of cross-sections (Fig. 12) revealed that after two weekly runoff cycles (10 days of ToW), the concentration of Zn on the surface decreased notably. Instead, Ti concentration remained relatively stable. These two elements are related to inorganic pigments in the paint [4], and Zn probably also to Zn soaps used as alkyd emulsifiers. The results indicate that more soluble Zn compounds are leached, particularly during the initial stages of runoff, resulting in a depletion of Zn on the surface after 20 days of

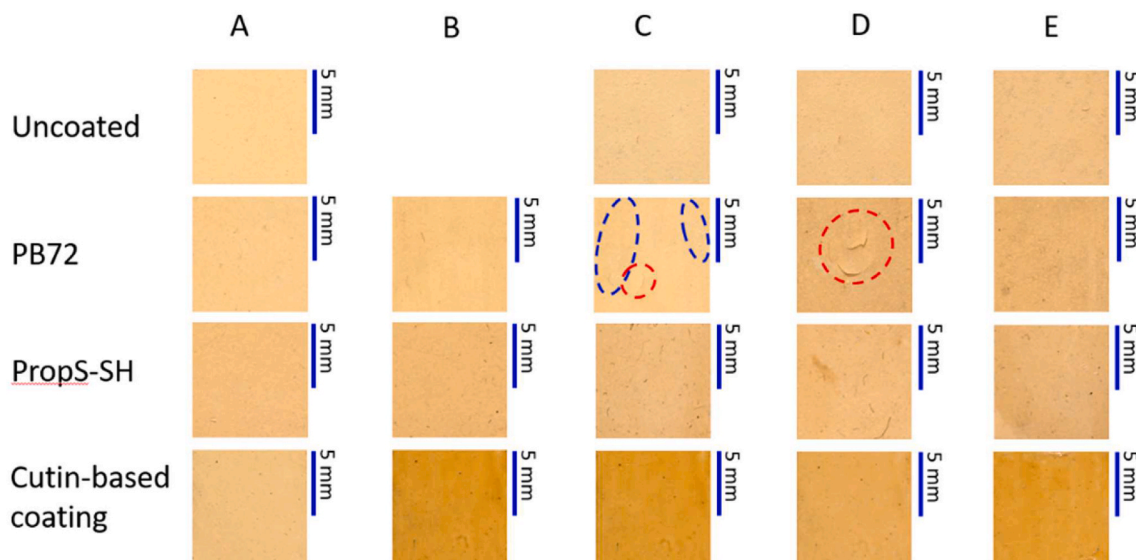


Fig. 10. Reflex photographs of painted substrates before coating (A), before ageing (B), after runoff tests with 20 days of ToW (C), and after climatic chamber ageing with UV (D) or in dark conditions (E). Red ovals highlight cracks, and blue ones indicate emergence of bubbles. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

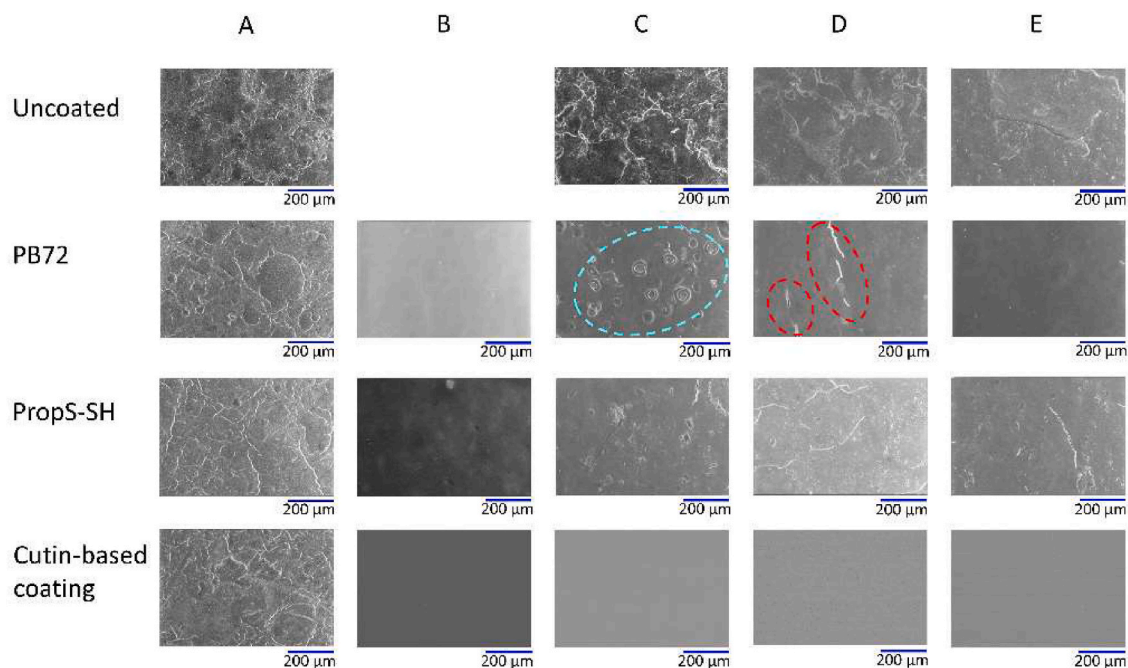


Fig. 11. SEM images of painted substrates before coating (A), before ageing (B), after runoff tests with 20 days of ToW (C), and after climatic chamber ageing with UV (D) or in dark conditions (E). Secondary electron (SE) images are reported except for the cutin-based coating, where backscattered electron (BS) images are shown. Red ovals highlight cracks, and blue ones indicate emergence of bubbles. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

ToW. The Ti-related species were less affected due to their very low solubility. The concentrations of both elements exhibited a slight increase with time within the climatic chamber, which may be attributed to the degradation of the organic matrix.

Accordingly, ATR-FTIR analyses (Fig. 13) after runoff showed a decrease of 65% and 33% in the νCOO^- band intensities at 1538 and 1582 cm^{-1} , respectively, suggesting leaching of soap species, likely Zn or Ca soaps [51]. Zn and Ca stearates may have been present either as emulsifiers or auxiliary curing agents respectively [50], or they may have resulted from interactions between pigments and the alkyd binder

[51].

By calculating the intensity ratios of diagnostic bands νNO (829 cm^{-1})/ νCOC (1060 cm^{-1}), and νNO_2 (829 cm^{-1})/ νCOC (1060 cm^{-1}) [52], the response of the nitro groups of the cellulose nitrate appeared to increase between 21% and 16% after runoff. This suggests mechanical surface abrasion of the paint layer, leading to the exposure of inner, less altered binder. Interestingly, the νNO band (previously identified as particularly sensitive to changes in the degree of substitution of the polymer when analysed by ATR-FTIR [52]) exhibited, after exposure in the climatic chamber, intensity ratios that decreased to values closer to

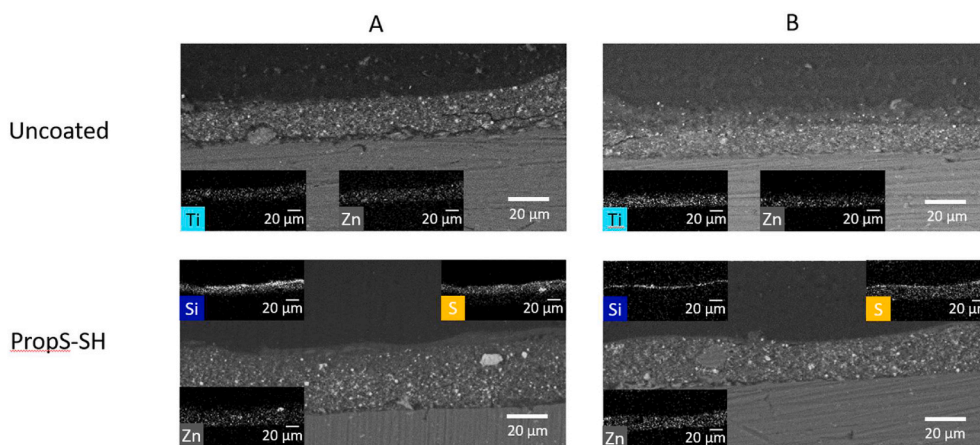


Fig. 12. SEM (SE) images and EDS elemental mapping of cross-sections of painted substrates before ageing (A), and after climatic chamber ageing with UV (B).

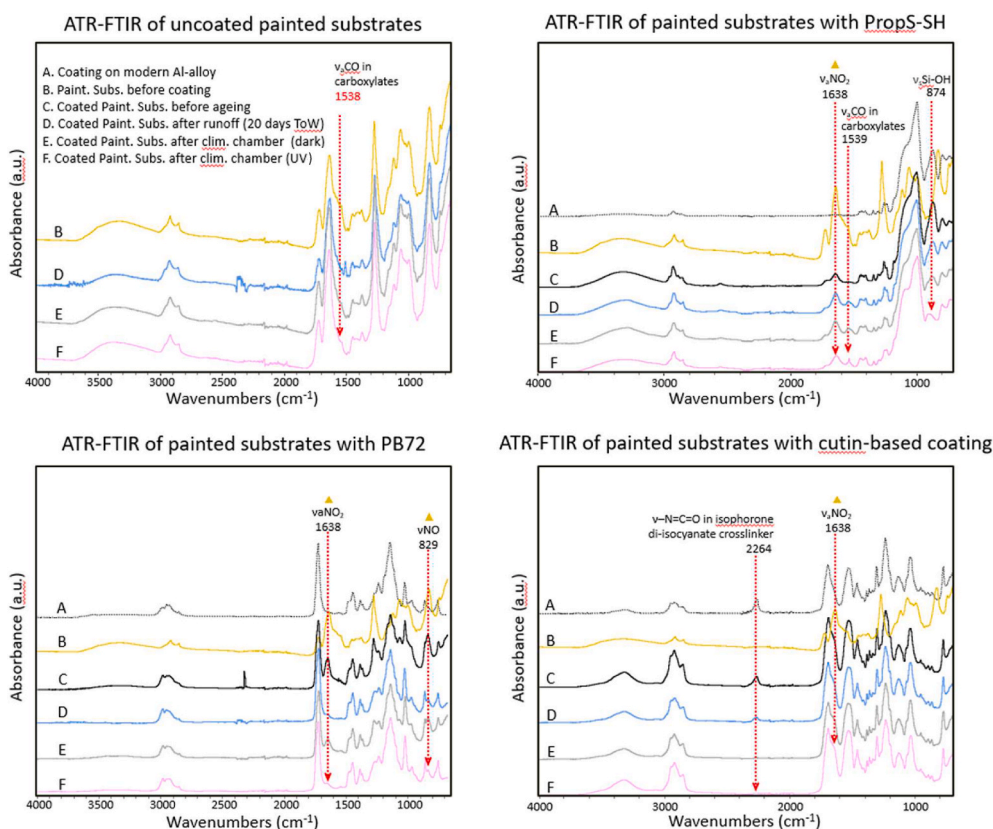


Fig. 13. ATR-FTIR spectra of uncoated and coated painted coupons. Each group shows a reference spectrum for each coating formulation, followed by spectra of painted substrates before coating, before ageing, and after ageing. The spectra were normalised considering the strongest infrared band. Changes in CN bands are marked with a yellow triangle. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

those of the unaged samples: specifically, from 21% higher after runoff to 5% (Dark) and 3% (UV) higher than the unaged sample. Such variations in the intensity ratio may be related to a denitration process triggered by thermal and UV weathering.

3.2.1. Painted substrates coated with PB72

The application of PB72 did not significantly affect the aspect of painted surfaces on the macroscopic scale (Fig. 10B, second row); the hardly perceivable changes in saturation proved to have almost no impact on the substrate's colour (Section 3.2.4).

After ageing, distinct morphological changes appeared macroscopically (Fig. 10) and were further examined with SEM-EDS (Fig. 11).

Bubbling and cracking emerged after runoff (highlighted by blue and red ovals in Fig. 10C and 11C, second rows), with cracking increasing after climatic chamber ageing (Fig. 10D and 11D, second rows). PB72 lacks OH, SH or other functional groups for metal ion complexation. This might lead to poor adsorption onto the coupons' surface [53], reduced adhesion and bubbling detachments during runoff. The causes of the cracking formation remain unclear. However, their increase after climatic chamber mainly in UV presence could suggest that radiation significantly influence the process.

ATR-FTIR spectroscopy (Fig. 13) showed that bands from CN (ν_{NO₂} at 1638 cm⁻¹ and ν_{NO} at 829 cm⁻¹ [52]) were visible immediately after PB72 application. This may indicate partial paint dissolution by ethyl

acetate, or PB72 coating discontinuities. CN bands decreased in intensity after dripping (82% and 63% reduction, respectively), suggesting CN degradation or dissolution. After climatic chamber ageing and UV exposure, these bands remained unchanged, with slight intensity increases in dark conditions. The PB72 copolymer itself showed no significant chemical variation during ageing and colour change was minimal, as supported by colour measurements (Section 3.2.4).

3.2.2. Painted substrates coated with PropS-SH

PropS-SH caused minor colour changes after coating, as confirmed by colour measurements (section 3.2.4). Only after UV exposure, localised discolorations appeared (Fig. 10D, third row), while SEM-EDS surface morphology observations indicated microcracking after climatic chamber ageing in both lighting conditions (Fig. 11D and E, third row).

ATR-FTIR measurements during ageing (Fig. 13) showed a progressive weakening of the ν Si-OH band at 874 cm^{-1} (respectively, 50%, 70% and 89% intensity decreases after runoff, climatic chamber exposure in the dark and under UV irradiation) with a minor shift towards higher wavenumbers, likely due to gradual reticulation. Concurrently, both the ν NO₂ band at 1638 cm^{-1} from the original paint binder and the ν CO carboxylate signal at 1538 cm^{-1} became more intense (approximately 0.2-0.6-fold and 3.5-4.5-fold increases, respectively), suggesting coating thinning during ageing.

Cross-section observations by optical microscopy (Fig. 14) and SEM-EDS (Fig. 12, second row) allowed to determine that, after application, PropS-SH formed a thin layer over the historical paint, permeating its top layer. After ageing, the coating appeared thinner but denser, concentrating in the permeated paint. This suggests a crosslinking-induced volume reduction, coherent with ATR-FTIR results. Such density increase, reported to occur in PropS-SH over time [54], could enhance its long-term corrosion resistance [55].

3.2.3. Painted substrates coated with the cutin-based protection

Reflex photography (Fig. 10B, fourth row) as well as SEM observations (Fig. 11B, fourth row) showed that the application of the cutin-based layer modified the colour and morphology of the historical painted substrate. It smoothed out and homogenised its surface, while visibly darkening and reddening it. Such colour change was more evident than on the corroded substrates, darker and more inhomogeneous.

However, the surface with the cutin-based protective did not display significant morphological modifications after any of the ageing steps, both on the macro- and the micro-scale (Figs. 10 and 11, images from C to E, fourth row). After UV exposure, the typical reddish hue of the coating was attenuated, as observed also on corroded substrates (see Section 3.1.4).

ATR-FTIR (Fig. 13) showed initial presence of the ν -N=C=O band of IPDI at 2264 cm^{-1} , which progressively decreased in intensity over time (59% and $\leq 95\%$ reduction after runoff and climatic chamber ageing, respectively). The spectral range associated with amide I vibrations (see detail in Fig. S10) evidenced minor changes, with an initial 14% decrease in intensity after runoff, followed by a slight increase after UV exposure, reaching values comparable to those of the unaged

conditions. This behaviour could indicate continued crosslinking leading to the formation of an amide-containing polyurethane, particularly under UV [42]. For the painted substrates, this spectral region could also be influenced by contributions from the ν NO₂ band of the CN binder at 1638 cm^{-1} , which would increase as the coating thinned.

3.2.4. Surface colour: comparison between coatings on painted substrates

ΔE^* values for painted substrates (Fig. 15 and Table S1) echoed trends observed for corroded ones. Both PB72 and PropS-SH produced colour changes below the threshold for regular human vision detection ($\Delta E^* \leq 3$, [56,57]). The cutin-based protection caused greater colour shifts upon coating than it did for the corroded substrates, due to the clearer and more homogenous colour of the paint. It produced notable changes in all the colour space axes, especially in b^* (average $\Delta b^* = 13 \pm 2$), owing to its orange hue. UV exposure greatly reduced the colour difference, suggesting longer-term exposure may return it to an acceptable colour change range through lycopene photolysis [46].

3.2.5. Metal release from painted substrates

Zn release, attributed to solubilisation of original paint constituents (see section 3.2), was monitored during runoff to assess paint degradation. Al concentration in the ageing solution was always undetectable, suggesting that the presence of corrosion-resistant paint and cladding layers prevented Al release. In the case of uncoated substrates, the release of Zn was observed to decrease with increasing exposure time (Fig. 16). After 10 days of ToW, a stabilisation of the Zn release was noted, as also evidenced by periodic measurements (Fig. S11). This was a consequence of the depletion of soluble Zn compounds on the surface.

The coatings were able to limit or prevent Zn release, especially the cutin-based and PropS-SH protectives. In fact, Zn concentrations were only slightly above the LoQ in a few solution samples related to PB72, whereas they were always below the LoQ for the cutin-based and PropS-SH coatings. Therefore, the trends shown in Fig. 16B are reported for qualitative purposes only. Nevertheless, making the conservative assumption that Zn concentrations were always equal to the LoQ for PB72 and to the LoQ for cutin-based and PropS-SH coatings, it is possible to estimate that η_M is $>60\%$ for PB72 and $\geq 70\%$ for cutin-based and PropS-SH coatings.

3.2.6. Electrochemical tests on painted substrates

Fig. 17 shows the results of the EIS measurements carried out before and after the accelerated ageing tests on the painted substrate, both in its original condition and after the application of the additional protective treatments.

In the unaged conditions, i.e. before the accelerated ageing test, the EIS measurements performed on the protected substrates showed a clear increase in R_p values, from $2.66 \times 10^7\ \Omega\text{cm}^2$ measured on the originally painted substrate, to 4.03×10^7 , 1.36×10^8 , $6.61 \times 10^8\ \Omega\text{cm}^2$ recorded on substrates coated by PB72, cutin-based, and PropS-SH coatings, respectively. These data demonstrated that the additional surface treatments increased the initial protective efficiency by 34%, 80%, and 96%, respectively.

Concerning the originally painted substrate, the R_p values exhibited

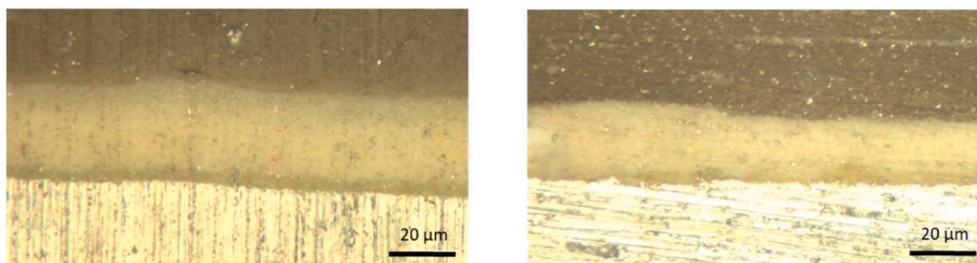


Fig. 14. Cross-section optical micrographs of a painted substrate with PropS-SH before ageing (left), and after climatic chamber ageing with UV (right).

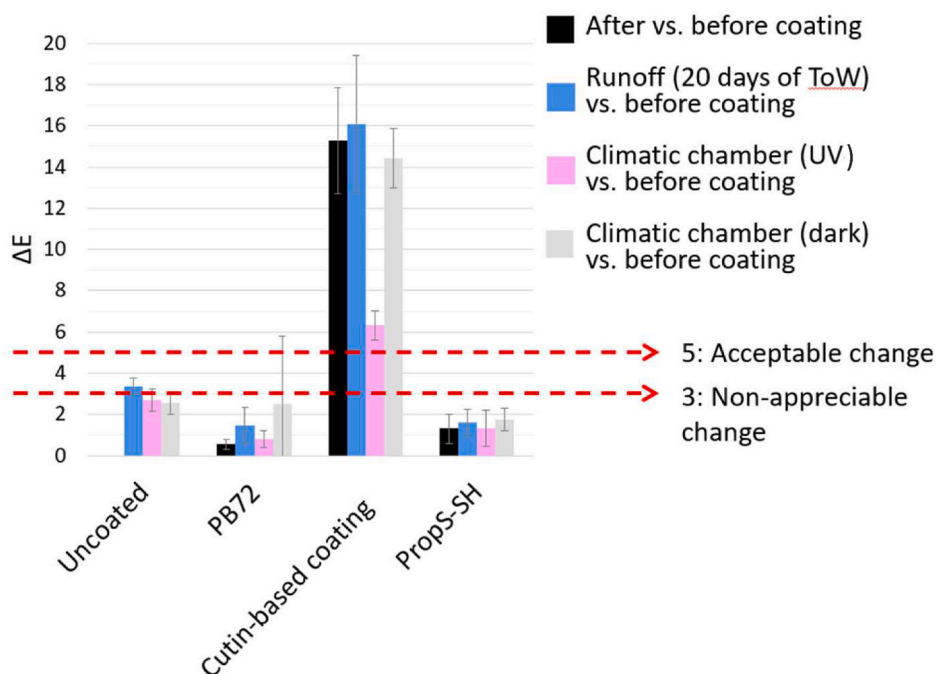


Fig. 15. Surface colour change (ΔE^*) of the painted substrates, after coating and ageing, compared to an unaged, uncoated reference. Dashed lines indicate conventional ΔE^* thresholds for cultural heritage exposed in outdoor conditions. ΔE^* values are the average of ΔE^* measured on minimum 6 points (2 per coupon) and error bars correspond to the related standard deviations. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

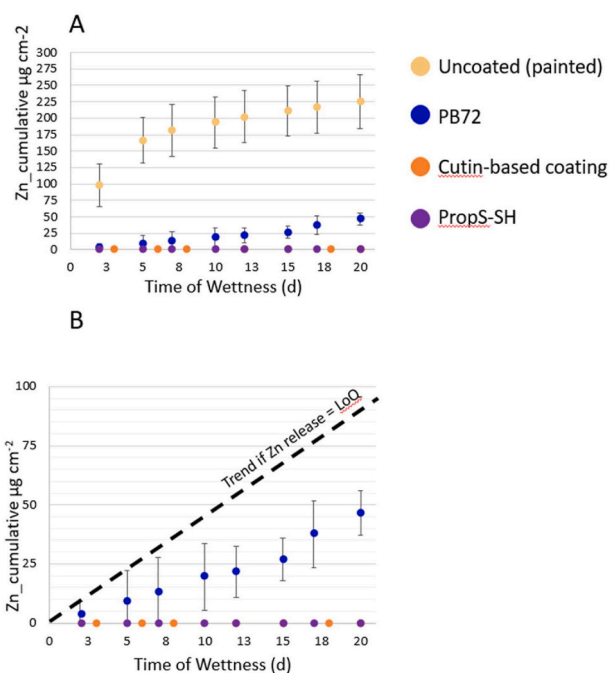


Fig. 16. Cumulative Zn release from painted substrates over ToW (mg cm^{-2}). The full graph (A) includes release from coated coupons, shown in a magnified detail (B). Reported values are the average of three coupons, error bars correspond to the related standard deviations. Black dashed lines simulate the cumulative trend that would occur if all sampled solutions had Zn concentrations equal to the limit of quantification (LoQ).

a dynamic evolution across the different aging stages, though maintaining a generally high level of protection.

After exposure to simulated runoff, the polarization resistance slightly increased to $6.3 \times 10^7 \Omega \text{cm}^2$.

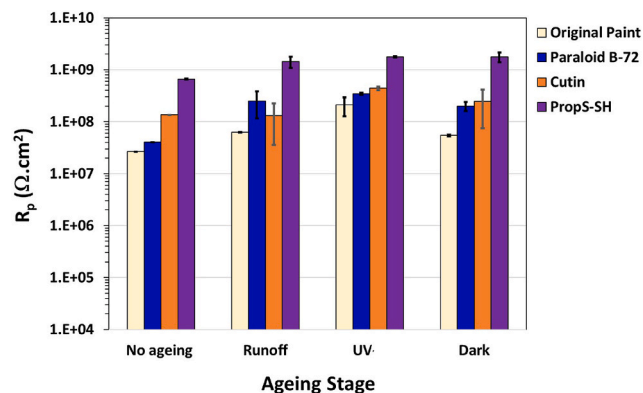


Fig. 17. Polarization resistance (R_p) values and standard deviations measured on uncoated and coated painted substrates after each accelerated ageing step.

The subsequent exposure to the climatic chamber in the presence of UV irradiation led to a further, notable increase up to $2.1 \times 10^8 \Omega \text{cm}^2$; conversely, after the final climatic chamber phase without UV, the R_p value decreased to $5.4 \times 10^7 \Omega \text{cm}^2$. This enhancement could be ascribed to a thermal drying effect induced by UV cycles, which promote evaporation of the previously absorbed moisture and temporarily increases the resistance of the polymeric binder, accompanied however by photochemical degradation of the polymer matrix as confirmed by ATR-FTIR analysis. Conversely, after the final climatic chamber phase without UV exposure and in the presence of high humidity only, the R_p value decreased as a result of renewed water uptake and matrix plasticisation; this was accompanied by thermal degradation of the binder.

When evaluating the over-coated systems the application of additional PB72 and cutin-based protective coatings produced a limited increase in R_p values, especially after ageing in climatic chamber with UV. This suggests that such treatments, in these specific ageing conditions, do not provide a substantial improvement to the protection offered by

the original paint.

On the contrary, the specimens treated with PropS-SH demonstrated a remarkable and statistically consistent increase in polarization resistance, in some cases one order of magnitude higher than the original substrate. Indeed, R_p values of $1.4 \times 10^9 \Omega \text{cm}^2$, $1.7 \times 10^9 \Omega \text{cm}^2$ and $1.78 \times 10^9 \Omega \text{cm}^2$ were recorded after exposure to runoff, and climatic chamber exposure with and without UV, respectively. This highlights the effectiveness of the PropS-SH coating in enhancing corrosion protection, regardless of the type of environmental stress.

The overall data suggest that exposure to runoff represents the most aggressive ageing condition for most coatings, as the lowest polarization resistance values were generally found at the end of this phase. A notable exception is the PropS-SH treatment, which offers consistent protection regardless of the exposure conditions.

Interestingly, the cutin-based treatment showed good performance at the end of the climatic chamber phase with UV exposure. This result can be attributed to the presence of lycopene in the cutin extracted from tomato peels. Lycopene is a natural carotenoid known for its antioxidant properties and its ability to protect against free radicals generated by UV exposure, thus helping to reduce the photo-oxidative degradation of the coating. This observation is further supported by colour analyses, which revealed a lighter tone of the cutin treatment after UV irradiation, suggesting that lycopene absorbed the generated radicals, preventing alteration of the cutin-based coating.

Impedance measurements showed that the original paint continues to provide excellent protection. Despite the surface defects and small delaminations observed (both superficial and in cross-section), the average polarization resistance values remain high. This suggests that surface defects do not significantly compromise the overall protective capabilities of the historical paint because of its thickness and the presence of anticorrosive pigments such as ZnCrO_4 , which continue to perform their protective function.

However, a crucial aspect that emerged from this analysis is that the application of additional protective coatings on the painted substrate did not result in a proportional increase in the overall protective effectiveness. Despite the increase in the thickness of the protection system, the overall increase in polarization resistance is not comparable to the results obtained when the same protective treatments were applied directly on a corroded substrate.

These findings could be attributed to the presence of solvents in the spray-applied protective coatings, such as 2-butanone, ethyl acetate and ethyl alcohol for cutin, PB72 and PropS-SH based coatings, respectively. It is hypothesized that these solvents can interact with the binder of the original historical paint, altering its structure and causing localized swelling, partial dissolution, or alteration of its compact structure. Such interactions can render the original paint layer more permeable to aggressive agents, thereby inherently limiting the expected barrier benefits of the additional protective layers.

4. Discussion

All investigated coatings significantly improved the corrosion resistance of aluminium substrates, reducing metal release and increasing polarization resistance throughout accelerated ageing. Despite comparable macroscopic protection levels, the coatings differed in their interfacial interactions, ageing response and protective behaviour.

PB72 seems to primarily act as a physically stable barrier, showing minimal chemical alteration and negligible colour change ($\Delta E^* < 3$) under ageing. On corroded substrates, it effectively reduced corrosion rates (Fig. 9) despite the development of microscopic discontinuities. However, the absence of functional groups able to strongly interact with the substrate limited adhesion, particularly on painted substrates, where runoff induced bubbling and cracking, likely exacerbated by solvent–binder interactions (section 3.2.1).

PropS-SH exhibited the highest and most stable protective efficiency across all substrates and ageing conditions (Figs. 9 and 17). Its superior

performance is attributed to its ability to penetrate deeply into the corrosion products layer, thereby sealing and consolidating the porous matrix. Furthermore, the formation of Al–O–Si covalent bonds at the metal interface and the progressive cross-linking of the siloxane network (Section 3.1.2) increase the coating's density and hydrophobicity over time. Despite the occurrence of superficial micro-cracking (Section 3.1.2), the overall surface coverage and electrochemical protection were largely preserved (Section 3.1.6), owing to an active defect-plugging mechanism. On painted substrates, PropS-SH permeated the upper paint layers and densified during ageing (Section 3.2.2), further enhancing corrosion resistance (Fig. 17).

The cutin-based coating showed a more complex behaviour. Partial surface coverage on rough corroded substrates allowed limited dissolution of calcareous deposits during runoff (Section 3.1.3), although corrosion was still significantly mitigated (Fig. 9). Ongoing crosslinking during ageing improved cohesion, while the presence of lycopene provided antioxidant and photo-protective effects, contributing to good performance under UV exposure and attenuation of the initial reddish colour (Sections 3.1.4 and 3.2.4).

Substrate condition strongly influenced coating effectiveness. On corroded substrates, all coatings produced a substantial improvement relative to the unprotected condition, as they directly addressed active corrosion sites. On painted substrates, however, the original paint system already provided high intrinsic protection, limiting the relative benefit of additional coatings. In particular, for PB72 and the cutin-based coating, solvent–paint interactions may have partially offset the expected improvements by increasing permeability or inducing surface defects. Conversely, PropS-SH provided a significant enhancement of corrosion resistance, even beyond that provided by the original paint, due to its ability to chemically integrate with the paint surface and densify over time.

These results highlight that interfacial chemistry and ageing-induced structural evolution are more critical than initial film continuity alone in determining durable protective performance.

5. Conclusions

This study presents a quantitative and comprehensive evaluation of two innovative coatings (a cutin- and a silane-based) for the protection of historic aircraft aluminium alloys under simulated outdoor exposure. Their performance was compared to that of Paraloid B72 (PB72), the acrylic resin commonly used in metal conservation. The following conclusions can be drawn.

- The protective performance of the coatings is primarily governed by interfacial chemistry and ageing-driven structural evolution rather than nominal coating thickness and initial film continuity alone. Substrate condition plays a decisive role, particularly when additional layers are applied over original painted surfaces.
- The silane-based coating (PropS-SH) did not alter the colour of the original substrates either upon application or after ageing. It exhibited the highest and most stable protective efficiency on both corroded and painted substrates, outperforming PB72 under all tested conditions. On corroded alloys, it increased polarization resistance (R_p) by up to two orders of magnitude compared to uncoated substrates, while achieving inhibition efficiencies $\geq 95\%$ in terms of Al release. On painted systems, it provided up to a one-order-of-magnitude increase in R_p compared to the original paint and markedly higher values than PB72. Its durability is attributed to strong interfacial bonding, penetration into porous corrosion layers, and progressive densification of the siloxane network. This high protective efficiency is driven by morphological and chemical changes—specifically, an enhanced barrier effect resulting from continuous crosslinking over time.
- The cutin-based coating also provided R_p increases of up to two orders of magnitude relative to uncoated alloys during ageing, with

generally higher stability than PB72, and inhibition efficiencies >85% in terms of Al release (conservative assumption). On painted substrates, its performance was comparable to or moderately superior to PB72. Continued crosslinking and the presence of natural antioxidant species contributed to limit photo-oxidative degradation during UV exposure, which attenuated the slightly reddish hue observed immediately after coating application.

Although long-term validation under real outdoor conditions remains necessary, the investigated coatings demonstrate clear advantages over the traditional acrylic benchmark for aerospace heritage conservation. PropS-SH emerges as the most effective candidate for the protection of large outdoor aluminium aircraft structures, while the cutin-based coating represents a viable bio-based alternative.

CRedit authorship contribution statement

Marco Valente Chavez Lozano: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Elena Bernardi:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Carla Martini:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Andrea Balbo:** Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Elena Buratti:** Resources. **Federica Zanotto:** Investigation. **Cristina Chiavari:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Cristina Chiavari, Andrea Balbo reports financial support was provided by Joint Programming Initiative on Cultural Heritage. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 1 includes free icons from Microsoft Office's stock, Alamy (<https://www.alamy.de>) and Freepik (<https://www.freepik.com>).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2026.132454>.

Data availability

Data will be made available on request.

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