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Exploring Sustainable Coating Solutions for Applications in Highly Corrosive Environments

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Abstract: To protect carbon steel from degradation via corrosion, it is usually coated using a multilayer system of paints composed of petroleum-based polymers. The chemical industry is currently moving towards more sustainable chemistry, in which one of the main objectives is to reduce fossil fuel use and the derived raw materials. However, the replacement of petroleum-based raw materials with those that are bio-based is not straightforward since the properties of these new materials are often inferior to the traditional ones. One of the most used resins in primer paints is Diglycidyl ether bisphenol A (DGEBA). This is an epoxy resin synthesized from bisphenol A (BPA), a toxic and carcinogenic petroleum-based compound. This study investigates the substitution of the primer coating in a three-layer coating system with two different types of primer coating formulations, one which is partially bio-based and another that is BPA-free. The corrosion protection effectiveness of these sustainable coatings is assessed not only at the laboratory scale but also in real offshore conditions. Moreover, the adhesion of the different coating systems is evaluated before and after each ageing test. The results reveal that these novel coatings exhibit comparable performance to conventional paints while providing a more sustainable corrosion protection alternative.

Keywords: corrosion protection; sustainable coatings; offshore corrosion

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1. Introduction

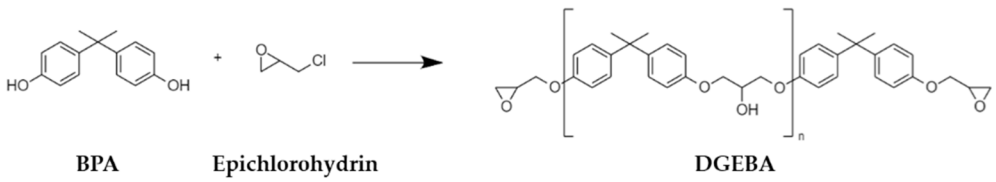
Carbon steel has found extensive use across a diverse range of applications owing to its favourable mechanical properties coupled with cost-efficiency. Its versatility spans from such uses as household kitchenware all the way to structural and industrial components in civil engineering. Carbon steel is often required to operate in highly demanding conditions [1,2], such as harsh offshore environments, where it encounters aggressive media. Such marine applications require very effective and robust corrosion protection, since the materials are subjected not only to a highly corrosive environment rich in chloride salt, but also to ultraviolet radiation, frequent wetting and drying cycles, violent wind, the presence of microorganisms, and abrasion caused by sand and ocean currents [3,4]. Hence, the standard ISO 12944 "Coatings and varnishes—Corrosion protection of steel structures by protective coating systems" classifies coastal and marine conditions as the most corrosive naturally occurring conditions [5–12].

Carbon steel used for offshore structural materials is usually covered with a system of multilayer coatings to protect it from corrosion. In general, this coating system consists

of three layers: a primer, an intermediate coating, and a top-coat. The primer, which is the first coat to be applied, confers the coating system with sufficient adhesion to both the metallic substrate and the subsequent coating layers and provides the main corrosion protection. The intermediate coat is used to add more barrier properties to the system as well as providing a smooth and paintable surface for the top layer. The top-coat is usually designed to impart colour stability, gloss, and resistance to weathering (UV light, erosion, etc.) [2–4,13]. In addition, factors such as substrate pretreatment, primer, and top-coat selection need to be carefully adjusted to prevent coating failures. Thus, a cost-effective reliable protective coating should not only impart corrosion resistance, but also durability and adhesion to the substrate.

Sustainability is also increasingly becoming a crucial factor to consider when developing new coating materials to avoid the use of industrial processes and to decrease petroleum dependency [14–19]. Multilayer coating systems are often organic in nature, and each coating is composed of four main elements: a carrier, pigments, additives, and a binder [13,20]. Among these elements the binder plays a crucial role in establishing the physical structure of the coating as it enables it to support and encapsulate pigments and additives. Beyond providing structural integrity, the binder is responsible for key coating properties such as adhesion to the metal, internal cohesion, high mechanical strength, and low permeability. Frequently, the performance of a coating is closely tied to the strengths and weaknesses of its binder family [20], of which the most used are alkyd, acrylic, ethyl silicate, epoxy, polyester, polysiloxane, and polyurethane [9,21]. However, not all binders are suitable for the development of high-performance barrier coatings. Polymers with numerous hydrophilic groups, such as alkyd, do not create barrier systems that outperform those containing hydrolysable bonds, such as polysiloxane, epoxy, or polyurethane. In addition, the presence of polar groups generally enhances adhesion to metal substrates because they form hydrogen bonds with the metal oxide surface. Therefore, epoxy and polyurethane are the most widely used polymers for the corrosion protection of steel for marine applications [13].

Epoxy resins is a term applied to both prepolymers and already cured resins. Prepolymers contain reactive epoxy groups, while in cured resin, these groups have already reacted [22]. Diglycidyl ether bisphenol A (DGEBA) is one of the most used thermoset epoxy resins in applications such as coatings, adhesives, and composites due to its excellent chemical and mechanical properties. There is currently a strong dependency on fossil fuels for the synthesis of DGEBA, and most of its molar mass comes from petro-based materials [23]. The main raw materials for DGEBA synthesis are epichlorohydrin and bisphenol A (BPA, Scheme 1). Traditionally, both chemicals come from petro-based raw materials. The production of epichlorohydrin starts from allyl chloride that is reacted with hypochlorous acid, followed by dehydrochlorination with lime [22]. BPA is obtained by reacting acetone and phenol with an acid catalyst such as sulphuric acid or dry hydrogen chloride acid gas. As both materials come from petro-based chemicals, efforts are being made to synthesize raw materials that are less dependent on fossil fuels [24]. In addition, BPA has detrimental impacts on human health as it has been found to be toxic for living organisms and to act as an endocrine disruptor [25]. Thus, significant efforts have been made to replace BPA with a more sustainable alternative [23,26].

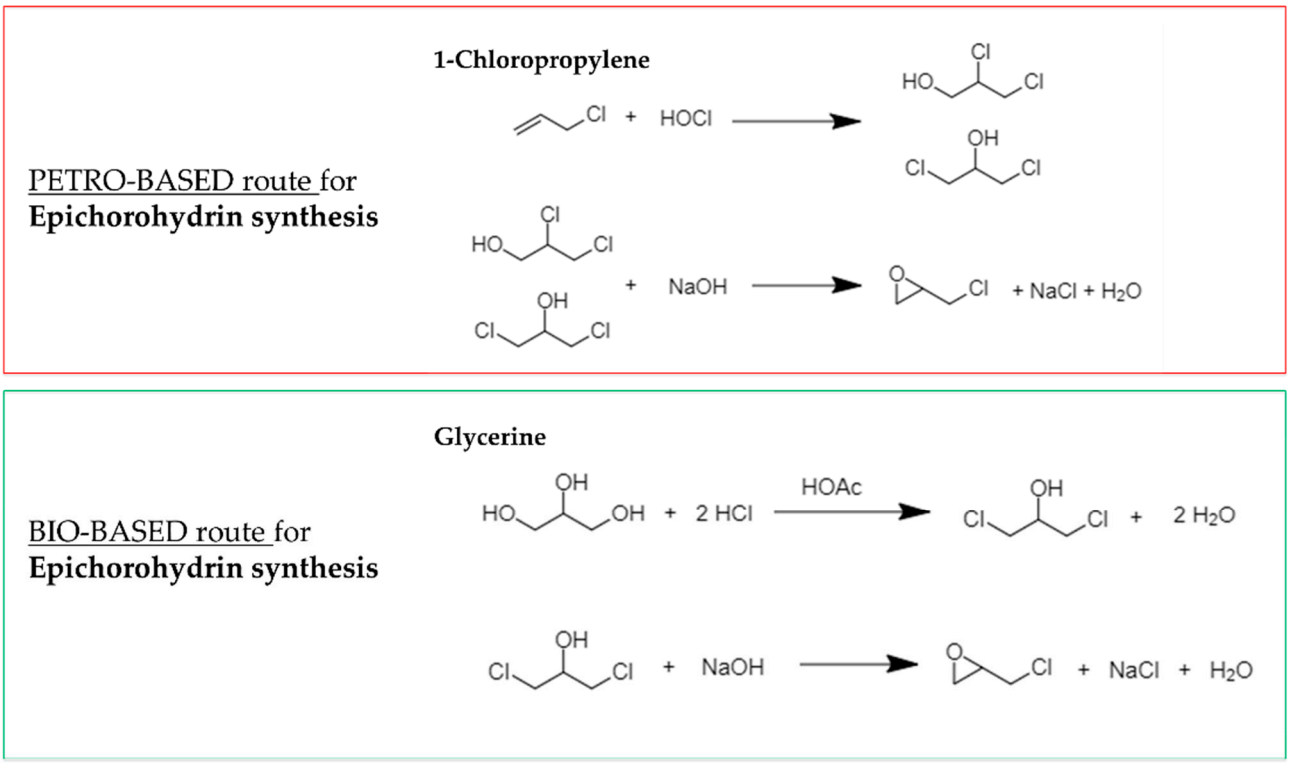


Scheme 1. Main reaction pathway to obtain DGEBA epoxy resin.

One route to obtaining more sustainable chemicals is to start from bio-based raw materials. These are materials that come from renewable biological sources, such as

plants, animals, microorganisms, crop waste, etc. However, their corrosion performance, mechanical strength, and durability do not match their petro-based counterparts [27]. Therefore, ensuring that the coating maintains sufficient strength and protection while being more sustainable is still a challenge that requires significant research effort [23].

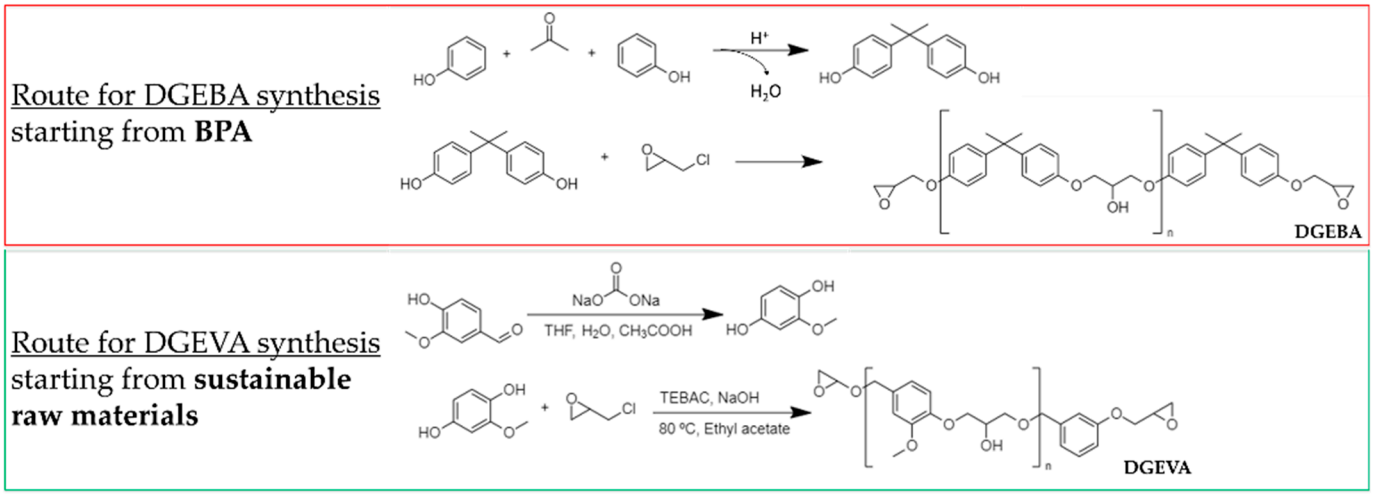
To obtain a more sustainable epoxy resin like DGEBA or similar, there are two main possibilities. On one hand, instead of starting from petroleum–propylene for the synthesis of epichlorohydrin, the renewable resource glycerine can be used [28]. A schematic diagram of the synthesis of epichlorohydrin from petro-based and from bio-based raw materials is shown in Scheme 2. Using the bio-based route for epichlorohydrin synthesis and maintaining the petro-based BPA, a partially bio-based resin is obtained in which the epichlorohydrin used is 100% bio-based in origin; however, the bio-based content of the resulting resin would only be around 30% [29]. This option is commercially available (Entropy Resins, Entropy ONE system) and has been used in this study (bio-based epoxy resin and hardener: ER-ONE and EH-ONF).



Scheme 2. Synthesis of epichlorohydrin derived from petro-based vs. bio-based raw materials.

On the other hand, BPA replacement is more complex. The aromatic ring of BPA confers good thermal and chemical resistance to epoxy resins; therefore, with the investigated alternatives, we aim to obtain a similar chemical structure. Biomass is a potential source of biopolyphenols structurally similar to materials already utilized for this purpose. In this context, eugenol, which is a major component (70%–90%) of clove oil, is a good example of a renewable phenol compound from which bio-based epoxy resins may be synthesized [23,30]. Rosin, a solid form of resin obtained from plants such as pines, has also been used for the synthesis of bio-based epoxy resins due to its aromatic structure, which is generally required to obtain high mechanical and thermal stabilities of the resulting resins [31]. In addition to these compounds, lignin has gained much attention since Lignocellulosic biomass stands out as the most abundant renewable feedstock and is notably more cost-effective than crude oil [32]. Lignin is a complex non-crystalline polymer present in the cell wall of vascular plants and is the second most abundant biomass on Earth after cellulose [33,34]. The main bio-based, readily available source of lignin is found in

wood fibres from paper industries [35] and can be extracted using a range of methods. The aromatic rings present in lignin make it an ideal candidate for the synthesis of bio-based polymers [36]. Chemically, lignin is composed of a random network of phenylpropane groups with three basic structural monomer units: coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [37]. From lignin, vanillin may be naturally obtained, and this compound may be used as a raw material for the synthesis of a bio-based epoxy resin. There are numerous works where vanillin epoxy resins have successfully been used as epoxy resins for a range of applications [17,18,23,38–40]. In this work, a vanillin epoxy compound (Diglycidyl ether of vanillyl alcohol, DGEVA) commercially available and obtained from specific polymers [41] is used to produce a polysiloxane hybrid organic–inorganic coating developed by the sol–gel method to replace the use of BPA [35–37]. Scheme 3 shows a schematic diagram of the synthesis methods for traditionally used DGEBA and bio-based DGEVA [23].



Scheme 3. Synthesis of DGEBA vs. DGEVA.

The use of polysiloxane hybrid organic–inorganic coatings developed by the sol–gel method is a promising chemical technique for the replacement of traditional epoxy primer due to its high bond strength with the metal and subsequent paint layer. These superior adhesion properties stem from the coating chemistry and its hybrid nature. The inorganic component forms a highly effective bond with the metal through Fe-O-Si bonding, while the organic part exhibits excellent affinity with the overlying coating. The ability to balance the properties of inorganic components (mechanical resistance, hardness) with those of organic components (flexibility and density) provides a versatile approach for tailoring materials to specific needs. Furthermore, the covalent bonding between the organic and inorganic moieties also contributes to the enhancement of the barrier properties of coating with very low thicknesses (ranging from nm to a few μm). Thus, the material needed for corrosion protection is significantly reduced, obtaining a more sustainable option that could not only improve the performance (corrosion protection and adhesion) but also reduce environmental concerns such as sea pollution caused by the release of microplastics. Indeed, a recent study reveals that particles from paint constitute more than half (58%) of all microplastics entering the world's oceans and waterways annually [15,16]. Therefore, hybrid coatings in which the organic part comes from renewable sources that can be used to replace thicker amounts of paints are an interesting sustainable option for marine corrosion protection. However, due to the need for an organic counterpart in these types of coatings, the search for alternatives to BPA-based compounds has become essential. This is becoming increasingly important, as a strong synergy between the silica, organic epoxy, and aromatic components in such thin coatings has been demonstrated [42–44].

Despite the evident benefits that sustainable coatings have for the environment, there are concerns related to the chemical composition and physical properties that require more research: the durability and corrosion performance of bio-based and hybrid coatings for corrosion protection has not been extensively studied. Furthermore, the mechanical properties of bio-based epoxy resins are one of their major drawbacks, and do not match those of their petro-based counterparts [23,24]. On the other hand, hybrid sol–gel coatings, due to their chemical nature, have consistently shown very good adhesion to metal substrates (due to their inorganic part being capable of forming a siloxane chemical bond (Fe-O-Si), and the interlayers of the coating system (due to the organic part)).

In this study, two novel coatings with different levels of bio-based components were developed for use as primers. For the partial replacement of petro-based components, a paint formulation was created where 30% of the resin content was bio-based (Primer Coating 1, PC1). This resin was acquired from Entropy Resins and is based on glycerine as a renewable resource, to replace epichlorohydrin, which is a petro-based compound. On the other hand, a hybrid organic–inorganic sol–gel coating was also formulated (Primer Coating 2, PC2) by replacing the BPA component with a vanillin epoxy resin, a sustainable organic precursor that may be synthesized from bio-based precursors (DGEVA). Table 1 shows a summary of the technology and sustainability of the primers used. The anticorrosion protection of both primers, incorporated in a three-layer coating system, was tested in the laboratory and through field exposure under offshore conditions. Both novel primers were compared with a commercial one (Primer Reference Coating, PRC) in terms of performance and sustainability. The novelty of this work resides in the development of two novel primer formulations designed to improve the sustainability of the corrosion protection system. The first primer contains 30% bio-based resin in order to substitute the petro-based BPA, the second primer is a BPA-free hybrid sol–gel coating. Furthermore, we complement the laboratory NSS test with 10-month field exposure in a highly corrosive environment.

Table 1. Summary table of primers under study.

Primer	Technology	Resin	Sustainability
PRC	Paint~70 µm	DGEBA	Petro-based
PC1	Paint~70 µm	BIO-DGEBA	30% bio-based
PC2	Hybrid sol–gel~5 µm	DGEVA	Thinner and BPA-free

The selected primer for the PRC and the upper layers of all systems for the three-layer coating study are commercial coatings that are currently used in the protection of steel structures in aggressive environments. They are the following:

- Primer: BPA-based Zn-rich solvent-based epoxy (Primer Reference Coating, PRC)
- Middle coat: solvent-based epoxy (Middle Coating, MC)
- Top-coat: solvent-based polyurethane (Top Coating, TC)

The approximate thickness employed for each layer is depicted in Figure 1.

In this work, when tests are performed on the complete systems, the reference commercial primer (PRC) is substituted for two other primers (PC1 and PC2). This study is focused on the performance of the primer because this is the coating responsible for adhesion between the metal and the rest of the coating layers. In addition, the primer is the most important coating layer in terms of corrosion protection since it is in direct contact with the metal [44]. The coating layers MC and TC are kept the same in all the studied configurations.

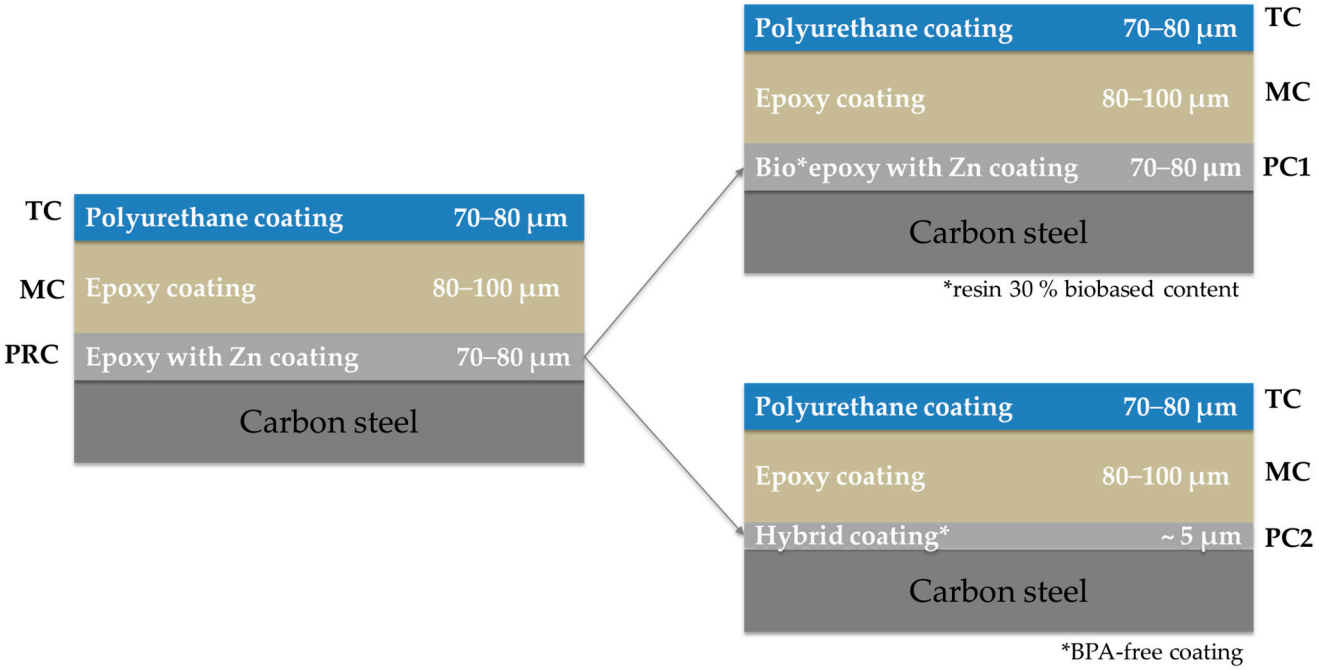


Figure 1. Selected commercial 3-layer coating system and alternatives studied.

2. Materials and Methods

2.1. Materials

Solvents such as 1-butanol (99%), n-propanol (>99%), and xylene (mixture of isomers) EssentQ, as well as reagent acetyl acetone (acac), zinc metal powder, and Zinc oxide (ExpertQ®, ACS, Reag. Ph Eur) were purchased from Scharlab, S.L. (Sentmenat, Spain) and were used for analysis without further purification. Sulphuric acid (H_2SO_4, 95–97%) was also obtained from Scharlab, S.L. (Sentmenat, Spain) and diluted to prepare a 0.1 M solution. Tetraethyl orthosilicate (TEOS), diethoxy(3-glycidyloxypropyl)methylsilane (GPTMS), Titanium(IV) isopropoxide (TISP), and reactive diluent dodecyl and tetradecyl glycidyl ethers of technical grade were obtained from Merck KGaA, Darmstadt (Germany). Vanillin bis epoxy (DGEVA Diglycidyl ether of vanillyl alcohol) was purchased from Specific Polymers, Castries (France), and the bio-based epoxy resin and hardener (ER-ONE and EH-ONF) were procured from Entropy Resins.

2.2. Coating Formulations

In Figure 1, the selected 3-layer commercial coating system typically used in the protection of steel structures is shown, along with the alternative systems studied. In this work, the primer reference coating (PRC), which was petroleum- and BPA-based, was substituted with two different types of primer as follows:

Primer Coating 1 (PC1): partially bio-based paint

PC1 is a solvent-based zinc-rich epoxy primer containing an epoxy resin with 30% bio-based content. It is a two-component (2-K) formulation, and its composition is given in Table 2.

For the preparation of this primer, first, the solvents were properly mixed with the ER-ONE resin using Dispermat® CV-PLUS at 400 rpm using a lightweight stainless steel dissolver disc with 5 mm hole in it. Zinc powder and zinc oxide were then slowly added and dispersed at 3000 rpm for 15 min. Once the paint dispersion was complete, the hardener (EH-ONF) was added in the mix ratio provided by the resin distributor.

Table 2. Formulation of PC1.

Component A	**wt. Max %**
Xylene	6
Butan-1-ol	3
Entropy ER-ONE resin	13
Dodecyl and tetradecyl glycidyl ethers	1
Zinc powder	74
Zin oxide	3
Component B	
Entropy EH-ONF hardener	

Mix ratio of 100:43 by weight given by the provider.

Primer Coating 2 (PC2): Hybrid organic–inorganic sol–gel coating

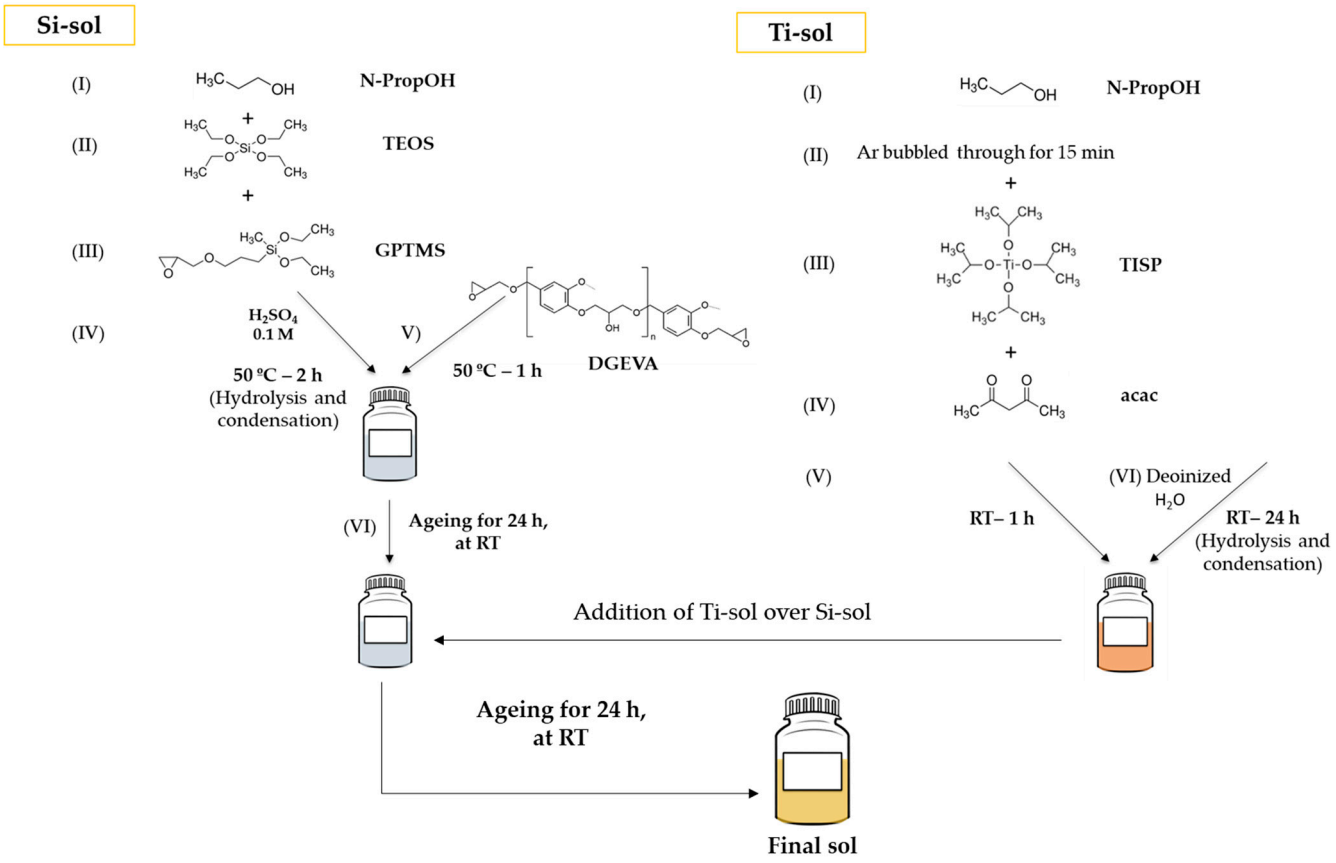
This coating was synthesized by the sol–gel method. Two suspensions (also called sols) were synthesized and mix to obtain the final sustainable sol. A silicon-based sol (Si sol) was prepared from tetraethyl orthosilicate (TEOS) and diethoxy(3-glycidyloxypropyl) methylsilane (GPTMS) with the subsequent incorporation of vanillin bis epoxy DGEVA. For the preparation of the Si-sol, 1-propanol, TEOS, and GPTMS were mixed in a Schott bottle (see Table 3 for all molar ratios). To this mixture, 0.1 M H_2SO_4 was added and stirred for 2 h at 50 °C in a glycerine bath. DGEVA was then added and the whole mixture was stirred for an extra hour at 50 °C. Once the 3 h reaction took place, the sol was aged for 24 h under stirring at room temperature.

Table 3. Molar ratios of components used for preparation of hybrid coating formulation.

Precursors' Final Sol	**Molar Ratios**
TEOS	1
GPTMS	3
n-PropOH	4
H_2SO_4 0.1 M	8
DGEVA	1
TISP	0.4
acac	0.4
n-PropOH	6.5
Deionized H_2O	0.8

A second titanium sol (Ti sol) was synthesized from Titanium (IV) isopropoxide (TISP) and acetyl acetone (acac). In this case, 1-propanol was weighed, and argon was bubbled through for 15 min to remove the oxygen in the solvent. Then, TISP was added and acac was gradually poured to facilitate the chelation of titanium. The mixture was stirred for 1 h at room temperature, and deionized water was then slowly added. The resulting mixture was left to age for 24 h at room temperature under continuous stirring.

The final solution was prepared from the combination of the Si-sol and Ti-sol mixtures and allowed to age for another 24 h at room temperature under stirring conditions. The steps for the preparation flow are shown in Scheme 4. The molar ratio of the formulation with respect to TEOS is shown in Table 3.



Scheme 4. Flow diagram of sol synthesis.

2.3. Preparation of Test Coupons and Characterization of Coatings

Carbon steel of grade S355 was provided by "SIDENOR Aceros Especiales" and, in addition to Fe, contained the following elements and amounts: 0.13% C, 1.27% Mn, 0.32% Si, 0.012% P, and 0.007% S. The surface of the carbon steel was sand blasted with two different Al_2O_3 grades depending on the nature of the coating applied as a primer. For the primers PRC and PC1, Al_2O_3 with a size of 425–600 µm (F36) was used, whereas in the case of the PC2, Al_2O_3 with a size of 45–75 µm (F220) was used. In the case of PRC and PC1 the roughness was ~5.7 µm, whereas for PC2 (a coating with ~5 µm thickness), good adhesion behaviour was achieved with a substrate roughness of ~0.8 µm [43].

All coatings (PC1, PC2, and the reference PRC primers) were applied onto carbon steel coupons. For the laboratory study, samples with dimensions of 75 × 75 × 5 mm were used. For the field exposure, samples with dimensions of 150 × 75 × 5 mm in the case of the PRC and PC1 coatings, and with dimensions of 75 × 75 × 5 mm in the case of PC2, were used. In all cases, the uncoated backside and edges of the panels were isolated with paint to avoid corrosion of the steel substrate affecting the results.

The chemistry of PRC and PC1 differs from that of PC2. PRC and PC1 are zinc-rich epoxy coatings, while PC2 is a hybrid organic–inorganic coating based on SiO_X-TiO_X-epoxy. These types of coatings have very low viscosities when compared to organic coatings (~25,000 mPa·s for a paint such as PRC or PC1 [45,46] vs. ~8 mPa·s for PC2). The viscosity of coating formulations is related to the thickness of the coatings, where lower viscosity results in thinner coatings. In addition, due to the different chemical nature of the coatings, they were applied to the substrate in a different manner. PRC and PC1 primers were applied to the steel panels by a Quadrangular applicator Neurtek instruments with four groove depths or coat thicknesses from. For the primer coating, a groove depth of 150 µm wet thickness was applied. In the case of the intermediate coat (MC) and the top-coat (TC), the groove depth chosen was 200 µm. On the other hand, PC2 was applied by an

in-house-made dip-coater. The withdrawal speed was controlled and fixed at 350 mm/min to ensure a homogeneous thickness, and the coating deposition was carried out after 24 h of Si-Ti mixture ageing. This method was selected due to the low viscosity of PC2. The dip-coating method is a recognized technique for ensuring the formation of a homogenous hybrid coating. It involves immersing the substrate in the solution and then withdrawing it vertically at a constant speed. Crucial factors for controlling the coating thickness when using this method include the withdrawal speed, the viscosity and density of the solution, and the type of solvent, among others [42].

The curing of the coatings depended on the coating's nature: PRC and PC1 were allowed to dry for 24 h at RT. The same procedure was carried out for the MC and TC. However, in the case of the PC2, a thermal treatment of 180 °C for 1 h was needed to achieve the required crosslinking.

For both the laboratory ageing tests and field tests, a minimum of two coupons were prepared and tested, with the data of all samples presented in the Results Section.

Thickness measurement: the total dry film thickness (DFT measured) was measured by magnetic induction in accordance with ISO 19840 [47] using a FISCHER thickness gauge, model DUALSCOPE MP0R.

The thickness of the hybrid coating PC2 was measured by profilometry on soda lime glass. For this purpose, the coating was applied to a soda lime substrate under the same conditions as in the case of the steel panels. After the thermal treatment, the coating was scratched from the top to the bottom of the soda lime substrate. Using a Dektak 150 contact profilometer, five scans were measured across the 50 mm long scratch, and the coating thickness was calculated by measuring the step height.

Adhesion: A pull adhesion test was carried out on new and aged panels coated with the 3-layer complete coating systems, according to ISO 4624 [48]. Dollies of 20 mm diameter were attached to the coating panel using epoxy adhesive. The adhesion strength was measured with a DEFELSKO adhesion device, model POSITEST AT. One sample was measured for each system. In samples with large surface areas (150 mm × 75 mm), three different zones were tested in each panel; however, in samples with smaller dimensions (75 mm × 75 mm), only two zones could be tested on each panel. On the panels with a scribe line, one test was performed. The fracture mode was evaluated according to ISO 4624 to indicate interface adhesive failure (between layers) or cohesive failure (within a layer). Interface failures are indicated as A/B, B/C, C/D, D/Y, and Y/Z, where A is the metallic substrate, B, C, and D are the different layers of the coating systems, Y is the glue used to attach the dolly, and Z is the dolly (Figure 2). Cohesive failures within one layer are indicated by the corresponding layer letter indicator. This test was performed on the samples before ageing and after both the salt spray test and field exposure.

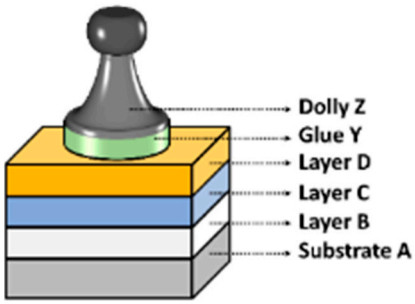


Figure 2. Schematic of the coated substrate layers and their designation in the analysis of the fracture mode.

2.4. Artificial Laboratory Ageing

Primers only: A neutral salt spray test (NSST, ISO 9227 [49]) was performed for the primers PRC, PC1, and PC2. Due to the different thicknesses of each coating, PRC and PC1

(~75 µm) were subjected to the salt spray test for 1000 h, while for PC2 (~5 µm), the test was performed until red corrosion appeared (72 h).

Complete 3-layer systems: The NSST (ISO 9227 [49]) of the 3-layer complete system lasted 1440 h independently of the primer used. The samples were evaluated considering the standard 12944 [43]. A 2 mm wide scribe line was produced as an artificial defect as described in ISO 12944-9 [12], annex A.1., for at least one of the three tested samples.

Corrosion penetration at scribe line (creep): This was evaluated following the recommendations in ISO 12944-6 [10]. The corrosion penetration (M) was calculated following the equation:

$$M = (C - W)/2 \quad (1)$$

where W is the original width of the scribe line (2 mm), and C is the maximum width of the corrosion across the scribe line in mm, estimated by averaging nine points (the midpoint of the scribe line and four other points, 5 mm apart, on each side of the midpoint) of the width of corrosion across the scribe line.

2.5. Field Exposure Condition

To complement the laboratory testing, the corrosion resistance of the primers in the complete coating system were also assessed by exposing them to a real offshore environment at TECNALIA's floating platform-laboratory HarshLab (HL) [50], located at the Bay of Biscay. The platform is moored in the Cantabrian sea, in the BiMEP area, 2.2 km from the coast. HarshLab is a unique offshore infrastructure designed for testing new materials and solutions against corrosion, ageing, and fouling in immersion, splash, and atmospheric zones (Figure 3). The environmental conditions of the test site are listed in Table 4. The test panels were exposed to the atmospheric zone at the HarshLab facility for a period of 10 months.

Table 4. Environmental conditions of the HarshLab testing facility.

Parameter	Value
Annual precipitation	1500 mm/year
Mean interannual temperature	Min 10 °C, Max 16 °C
Average interannual temperature	13 °C
Average insolation	1825 h/year
Average annual wetting time (RH * > 80%, T > 0 °C)	5960 h
Water temperature	Min 11 °C (January), Max 22 °C (August)
Significant wave height	Min 1.15 m, Max 9.62 m, Average 1.67 m
Average salinity	35 USP.
Average dissolved O_2	6 mL/L
Average transmittance	88%

* RH stands for relative humidity.

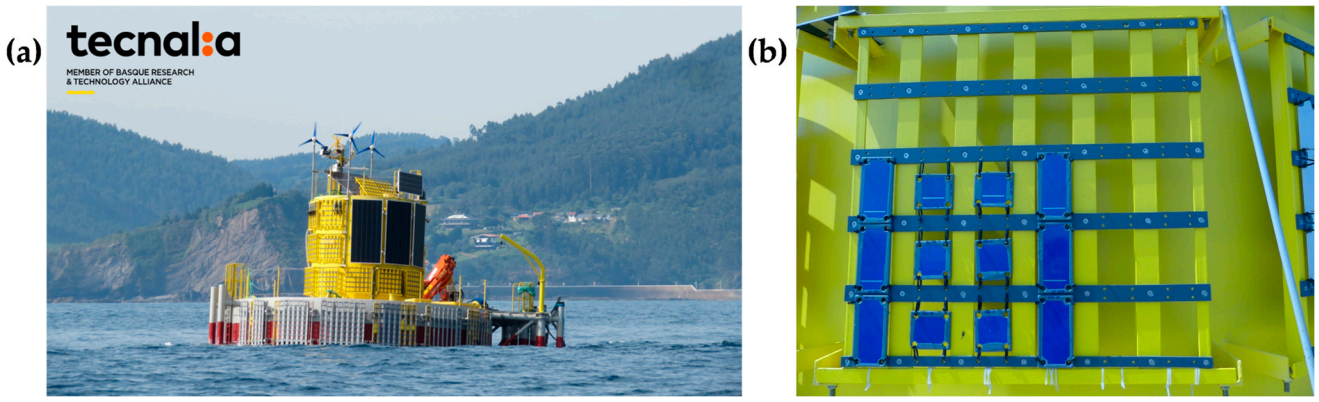


Figure 3. (**a**) HarshLab platform; (**b**) samples studied in this work mounted in the atmospheric zone of HarshLab.

After exposure at HL, the samples were visually evaluated to check for the possible appearance of blistering, rusting, cracking, and flaking on the coating surfaces [10].

3. Results and Discussion

3.1. Coating Layer Characterization

3.1.1. Primer Coating Thickness

The thicknesses of the three primers measured are shown in Table 5. As expected, the thicknesses of PRC and PC1 are very similar since PRC1 is based on an epoxy resin similar to PRC, with the only difference in that PRC1 is partially bio-based. The thickness of PC2, in contrast, is very low compared to PRC and PC1 due to the different nature of the coating. It is well known that for sol–gel coatings developed through the acid catalysis alkoxy route, the thickness of coatings is very low (ranging from nm to a few μm). The thickness of these types of coatings is dependent on factors such as the solvent used, the amount of organic precursor (organic precursors usually increase the coating thickness), the viscosity of the complete sol formulation, and the withdrawal speed when depositing the coatings using the dipping method, among others.

Table 5. Thickness (μm) of primer coatings PRC, PC1, and PC2.

Primer	Average Thickness ± Standard Deviation (μm)
PRC	73 ± 3
PC1	76 ± 3
PC2	4.9 ± 0.2

3.1.2. Corrosion Characterization of Primers

To assess the corrosion protection properties of the new primers, panels coated with the new formulations and the reference primer PRC were subjected to the NSST. Figure 4 shows the different visual appearance of PRC and PC1 before exposure (0 h) and after 168, 500, and 1000 h of exposure to the NSST. Both coatings initially exhibit a smooth surface, gradually developing a slight whitish hue over time due to the oxidation of zinc within the coating. While PC1 displays a uniform whitish colour across its entire surface, PRC shows concentrated whitish areas in specific regions. Notably, after 1000 h, the most pronounced whitish region on PRC reveals a red spot, indicating iron corrosion from the steel substrate. In contrast, PC1 develops a small white pit on its surface which does not become red after 1000 h. Thus, it can be concluded that the performance of PC1 is comparable to that of the reference primer PRC. All samples after 168 and 500 h show a 0% rusted area and an Ri 0 degree of rusting following the ISO 4628-3 standard [51]. After 1000 h, the left sample of PRC shows one pit of corrosion and a 0.05% rusted area, which corresponds to an Ri 1 degree of rusting. However, the other sample of PRC and the two samples of PC1 after 1000 h do not show corrosion products on their surface (0% rusted area and Ri 0 degree of rusting).

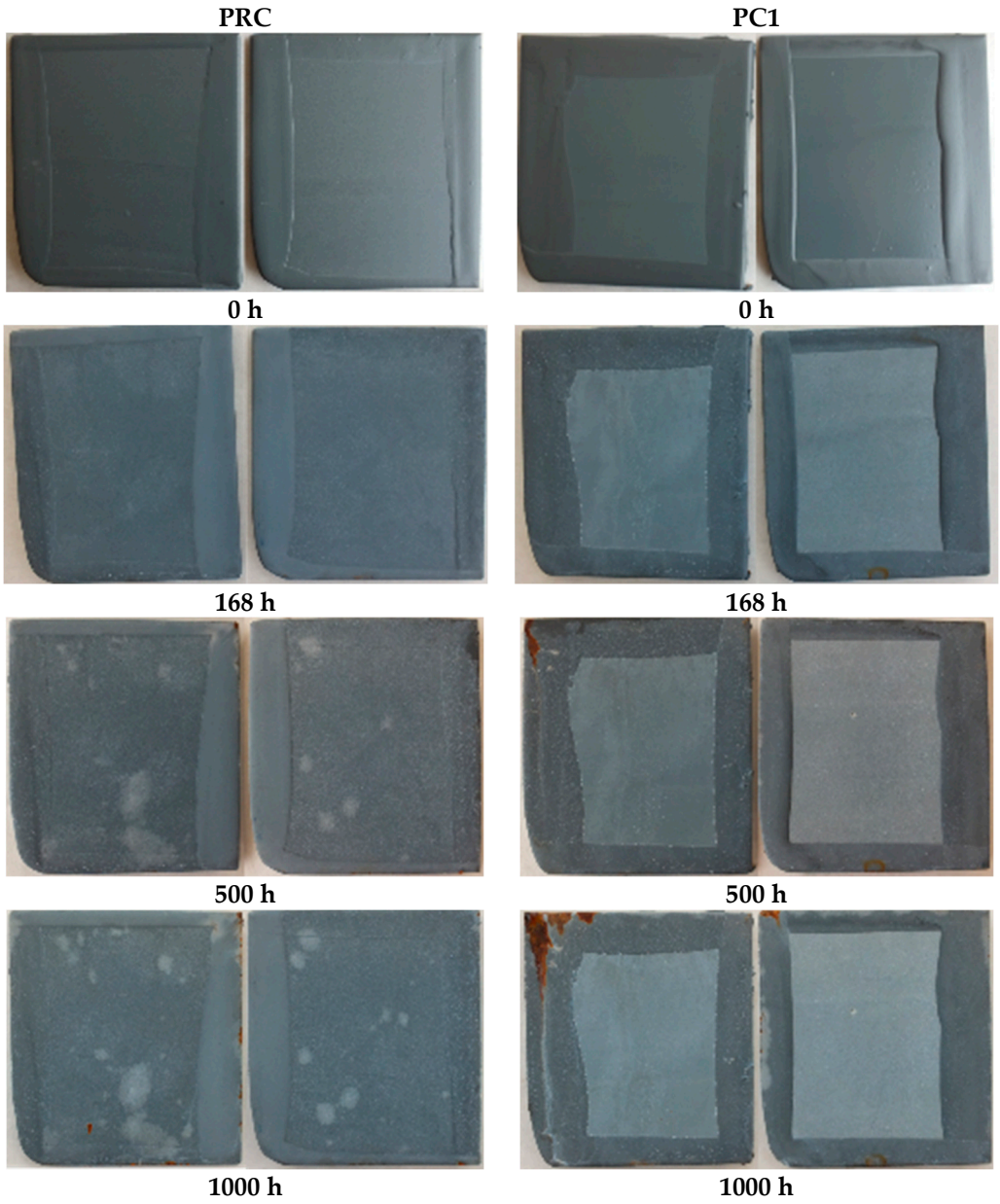


Figure 4. NSST results of reference primer PRC vs. PC1 after 1000 h of testing.

The hybrid organic–inorganic coating PC2 was also subjected to the NSST; however, as expected, it does not exhibit the same level of performance as PRC and PC1. After 72 h of exposure to the NSST, PC2 shows a high amount of corrosion product on the surface. The samples after 72 h show an Ri 5 degree of rusting with more than 50% of its area rusted. This is attributed to the fact that hybrid coatings are considerably thinner and primarily serve to enhance the adhesion of the metal to the subsequent coatings through siloxane chemical bonding (Fe-O-Si), thereby improving the overall corrosion resistance of the complete three-layer systems. When evaluating primers independently, it should be emphasized that a coating thickness of ~75 µm cannot be directly compared to coatings with a thickness of ~5 µm. The significant difference in coating thickness influences corrosion resistance, as higher thicknesses tend to retard corrosion more effectively when one single coating layer is used. The results of PC2 under 72 h NSST conditions are shown in Figure 5.

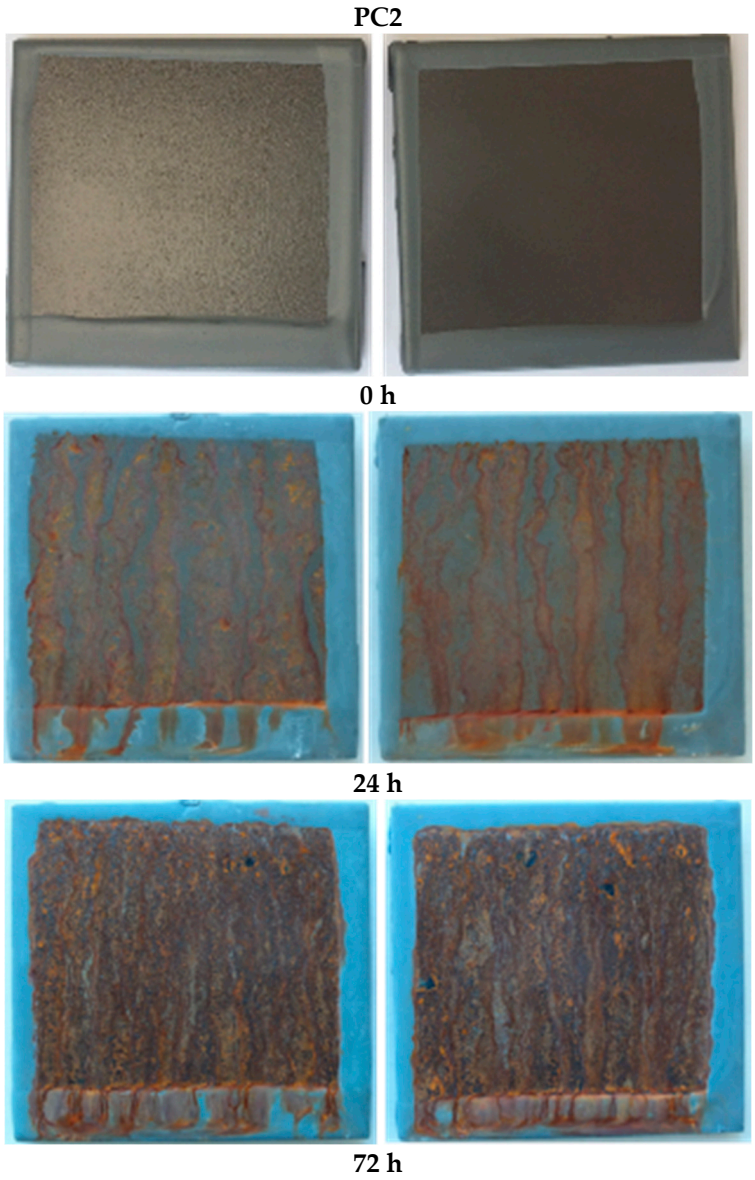


Figure 5. NSST results of PC2 after 72 h of testing.

3.2. Characterization of Complete Three-Layer Coating Systems before Ageing Tests

The thickness of the complete coating system with the different primers was measured and the mean values for each complete coating system are shown in Table 6. As expected, for the primer paints (PRC and PC1), the complete coating system had a similar thickness. However, in the case of the use of PC2 as a primer, the complete coating thickness was much lower. This difference is due to the difference in the primers' thickness (~5 vs. 75 µm).

Table 6. Mean thickness of complete coating systems depending on the primer used.

Coating System	Average Thickness ± Standard Deviation (µm)
PRC	235 ± 8
PC1	235 ± 15
PC2	193 ± 6

Next, an evaluation of the adhesion strength of the three systems before ageing was also performed following ISO 4624; the images of the fractured paint and the dollies are shown in Figure 6, and the average values are shown in Table 7. In the three cases, the

loads needed for fracture are very similar and high, all in the range of 16–19 MPa. In the systems with PRC and PC2, the nature of the fracture is mainly cohesive on the top-coat, while in the system with PC1, there is also a percentage of cohesive failure on the primer coating (layer B); however, the fracture load difference between the different coatings is almost negligible. The high adhesion strength values suggest that the adhesion between the layers in the three different coating systems under study is very good.

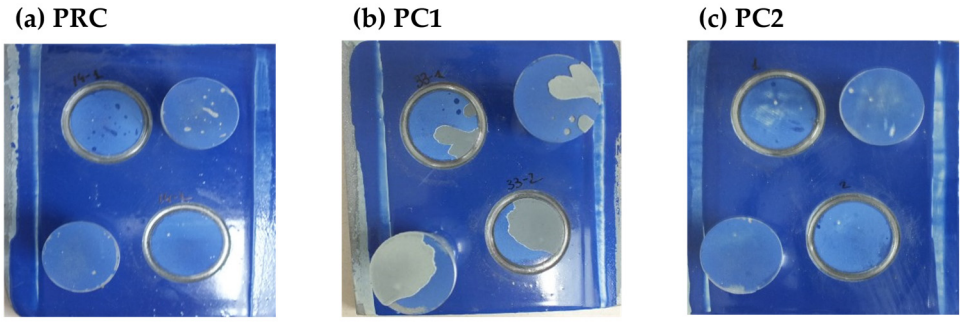


Figure 6. Pull-off adhesion before the ageing tests on the different complete coating systems with (**a**) PRC, (**b**) PC1, and (**c**) PC2. Numbers 1 and 2 below the images indicate number of dollies.

Table 7. Pull-off strength (average and standard deviation) of the complete coating systems which contain the different primers. Values represent an average of all measurements for a given system.

Coating System	New Panels (MPa)	After 1440 NSST (MPa)	After 10 Months of Field Exposure (MPa)
PRC	19 ± 0	10 ± 2	15 ± 2
PC1	18 ± 1	7 ± 1	14 ± 2
PC2	16 ± 1	13 ± 4	15 ± 2

3.3. Complete Coating System Anticorrosion Performance

3.3.1. Laboratory Testing Results

The complete systems were aged for 1440 h in a salt spray cabinet. Images of the samples before and after being subjected to the 1440 h ageing NSST are shown in Figures 7 and 8, respectively. After the test, none of the samples showed any blisters, rust, cracks, or flakes on their surface over the entire time of exposure; the only sign of corrosion is observed around the scribe line. Therefore, following standard ISO 4628-3 all the samples show an Ri 0 degree of rusting with a 0% rusted area. Figure 9 shows the extent of the corrosion penetration beneath the coating after removing the coat around the scribe line. The corrosion penetration (M) was calculated using Equation (1). The results (Figure 9) are very similar in the three cases under study and amount to 1.1 mm in the case of PC1 and 0.9 mm in the case of PC2; the reference coating for PCR shows M = 1.2 mm. These results are encouraging since they indicate that substituting a petro-based resin present in PRC with a partially bio-based one in PC1 does not adversely affect the corrosion protection of the system. On the other hand, the replacement of the petro-based commercial primer PRC with the much thinner bio-based hybrid coating, PC2, shows comparable corrosion performance. This can be seen in Figure 9, where it is observed that the corrosion penetration at the scribe line diminishes from 1.2 and 1.1 mm (PRC and PC1, respectively) to 0.9 mm in PC2.

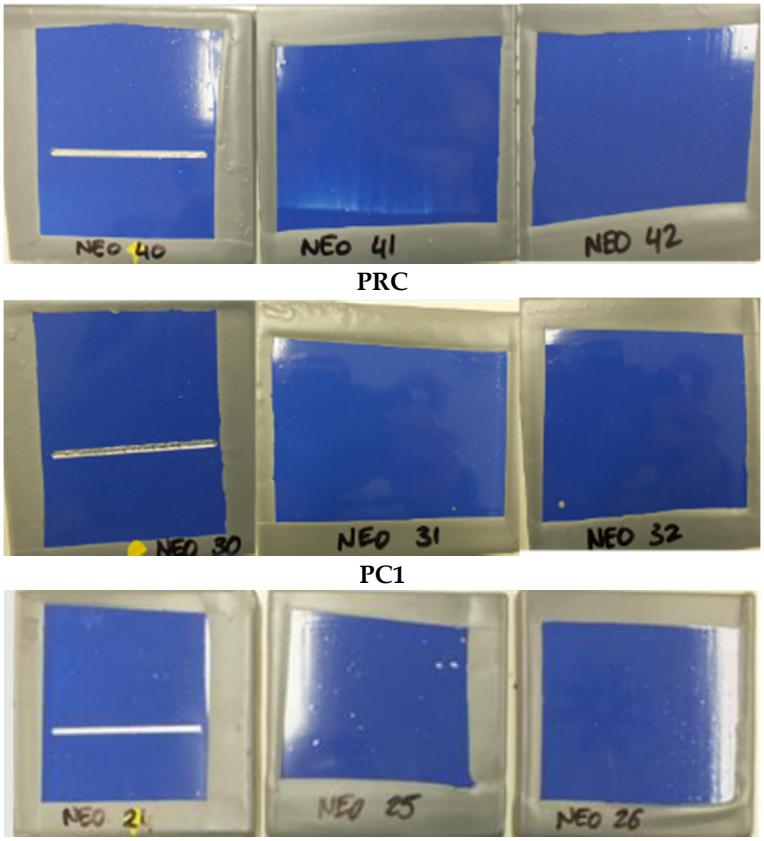


Figure 7. Coating systems PRC, PC1, and PC2 before being subjected to the NSST.

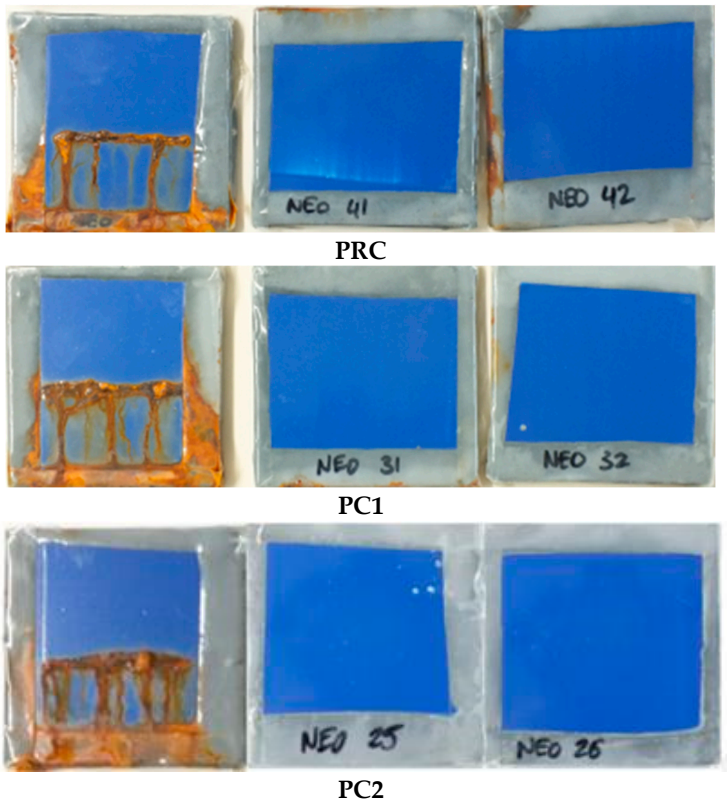


Figure 8. Coating systems PRC, PC1, and PC2 after 1440 h NSST.

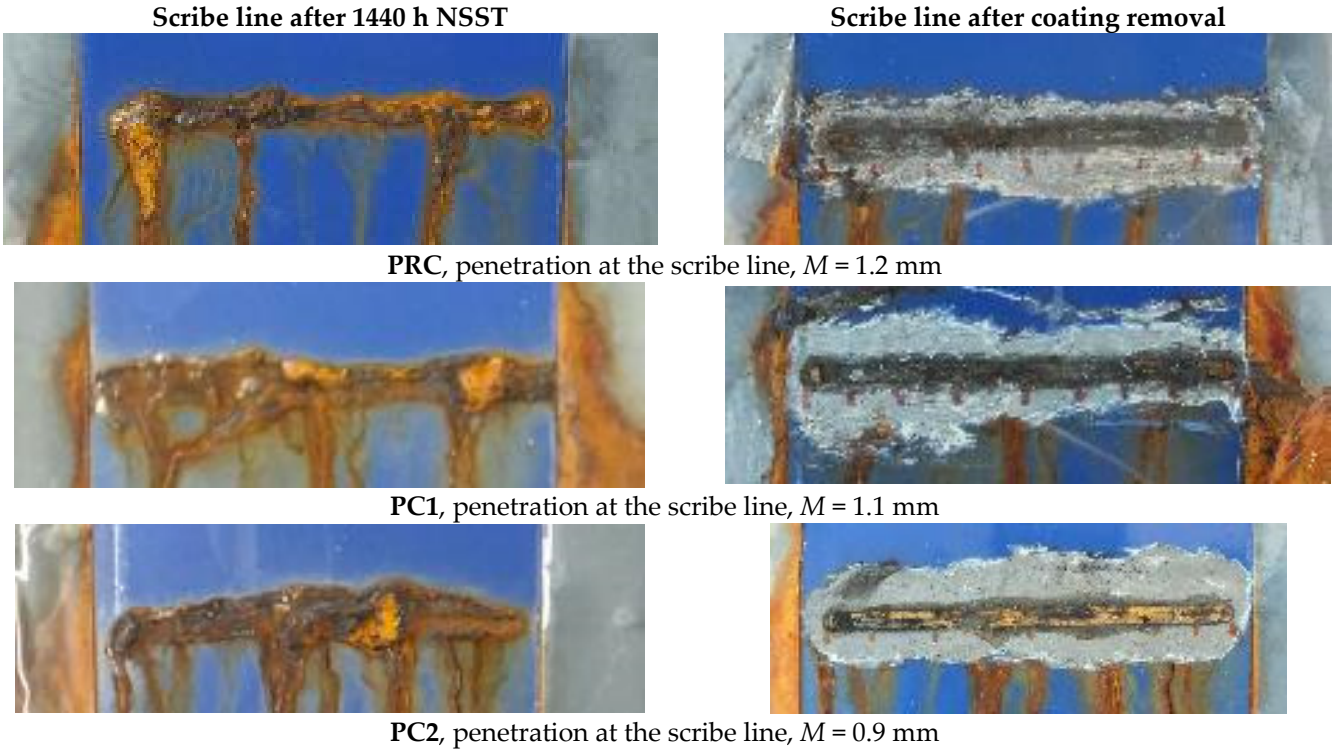


Figure 9. Images of coating scribe lines before and after removal of surrounding paint.

After the NSST, the pull-off adhesion strength of all the samples was tested; the results are shown in Table 7 and Figure 10. The coating system containing the reference PRC shows adhesive failure between the steel and the primer, which is the most undesirable type of fracture. However, the pull-off value is higher than 5 MPa, which means that the coating has acceptable adhesion properties. The system with PC1 also shows 100% adhesive failure, but the failure appears between the primer and the intermediate coat. This phenomenon is referred to as intercoat adhesion failure, which occurs when there is insufficient compatibility between the intermediate coating and the primer, preventing them from effectively bonding to each other [52]. The drop in adhesion strength after the NSST in both PRC and PC1 is significant (9 and 11 MPa, respectively) in contrast in the case of the coating system containing PC2; the failure is mostly 100% cohesive in the top-coat, and the drop in the pull-off strength after the NSST is only 3 MPa. This indicates that PC2 could serve as a reliable coating and has the potential to outperform the commercial primer PCR by enhancing the adhesion with the metal and between the layers of the system.

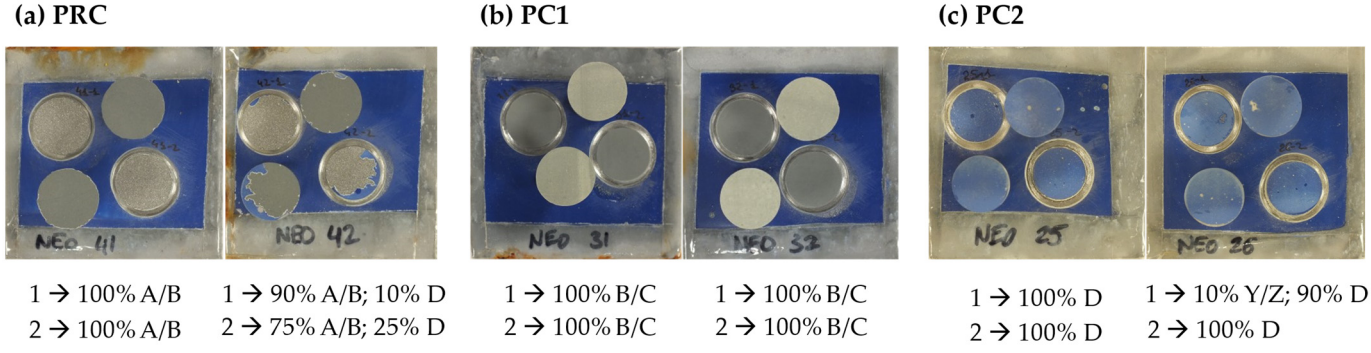
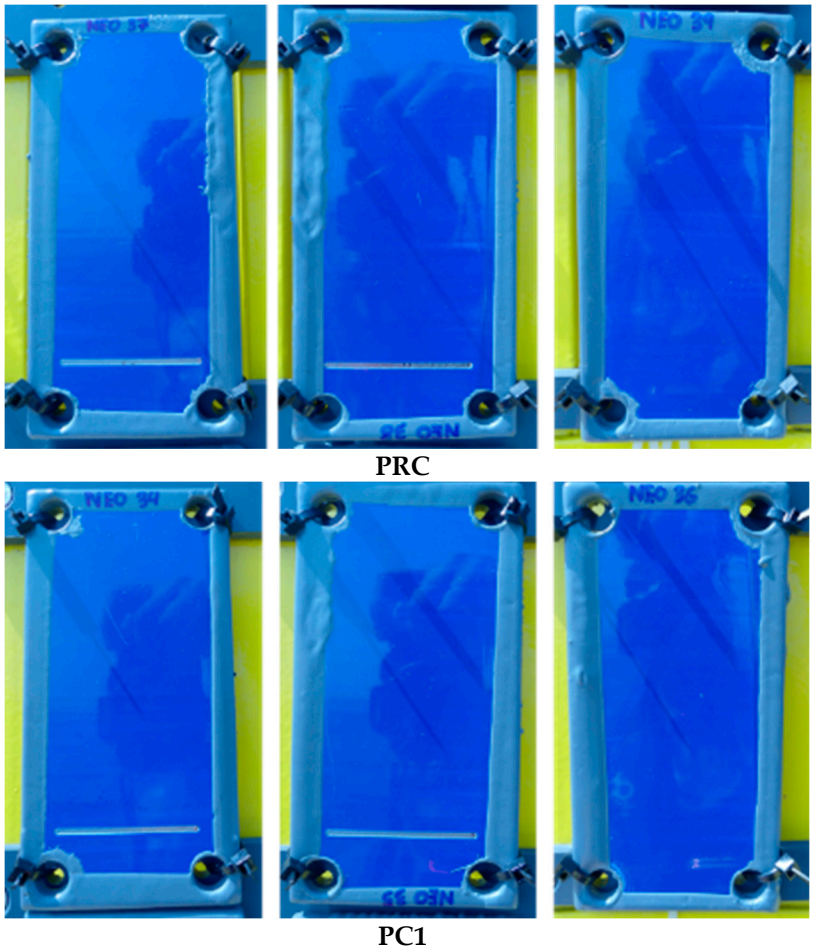


Figure 10. Pull-off adhesion images of different coating systems in this study: (**a**) PRC, (**b**) PC1, (**c**) PC2 after 1440 h NSST. Numbers 1 and 2 below the images indicate number of dollies.

3.3.2. Field Exposure

After the promising results obtained in the laboratory testing, field testing of the three systems in aggressive offshore conditions was performed. For this purpose, the coated panels with the complete three-layer systems were exposed at the HarshLab testing facility for 10 months in the period July 2022–May 2023. The samples were exposed to the atmospheric zone of the floating laboratory, which is one of the most aggressive and corrosive environments [1,3,13]. It is also worth mentioning that the standard which deals with protection coatings for this coating category (ISO 12944-9) clearly states that the minimum primer thickness for this zone should be no less than 40 μm for zinc-rich primers and no less than 60 μm for other primers. For this purpose, PC2 does not seem to be suitable for this corrosivity category since its thickness (Table 5) is far below the recommended one for such a harsh environment. Nevertheless, the PC2-based system was included in the field exposure experiment to gather valuable information on its performance, assessing various coating parameters under real conditions. To the best of the authors' knowledge, this type of primer is not yet widely used in the industry and there are limited reports on the performance of such coatings in a real environment.

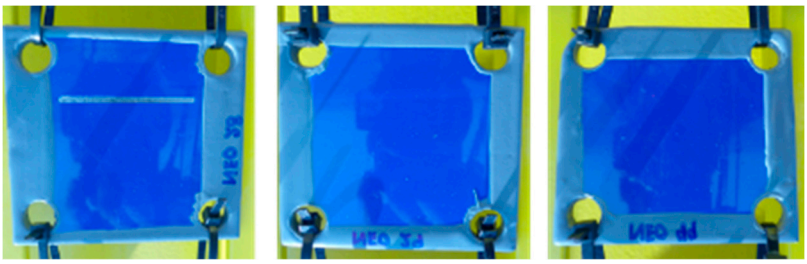
The visual appearance of the samples before exposure can be seen in Figure 11 and after 10 months exposure in Figure 12. Apart from the scribe line, where a high amount of corrosion product can be observed, there are no additional signs of blisters, rust, cracking, or flaking. For all systems, the rusted area is 0% and the degree of rusting is Ri 0, according to ISO 4628-3.



PRC

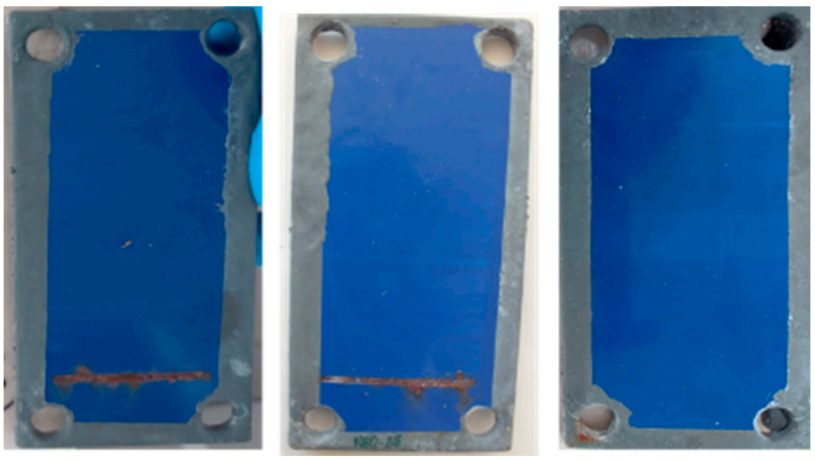
PC1

Figure 11. *Cont.*

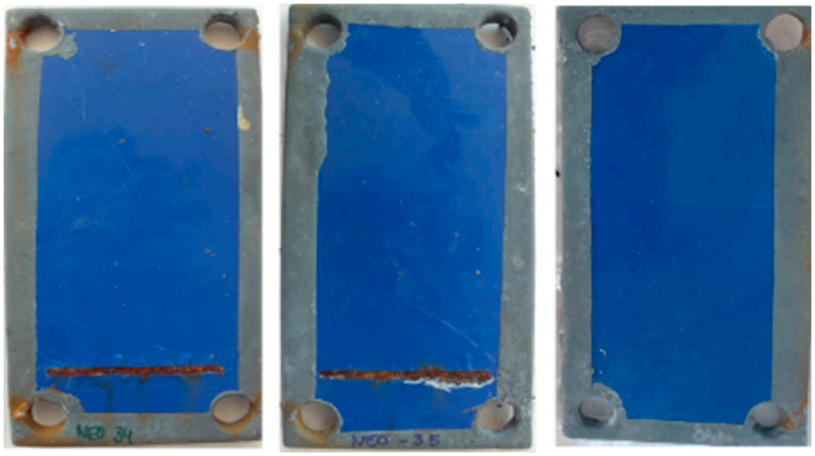


PC2

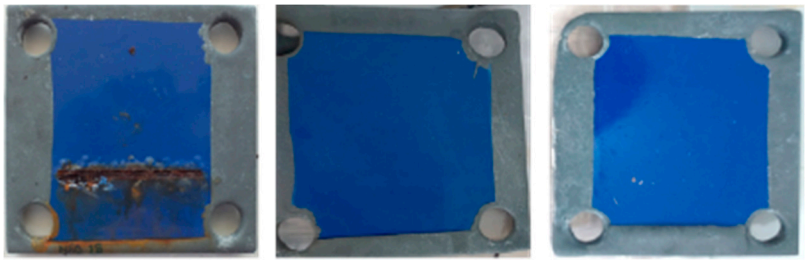
Figure 11. Samples before being exposed at HL (15 July 2022).



PRC



PC1



PC2

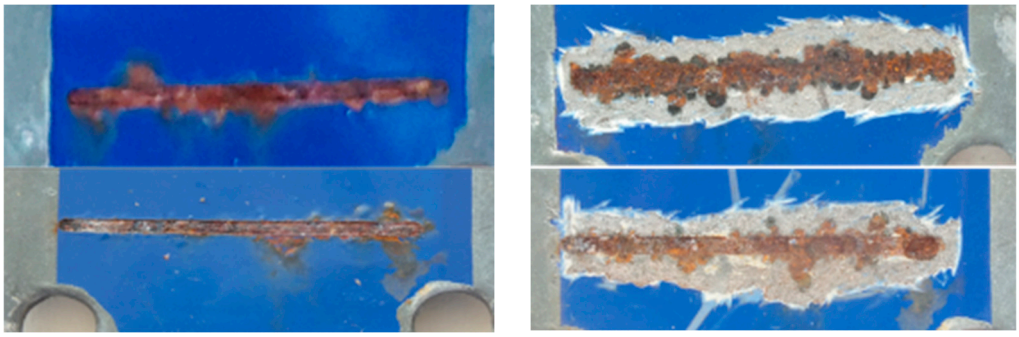
Figure 12. Samples after 10 months at HL (2 May 2023).

The coating around the scribe lines was removed and the penetration of the corrosion over the carbon steel substrate was measured. Figure 13 shows the scribe lines before and after the removal of the paints. The corrosion penetration was calculated following

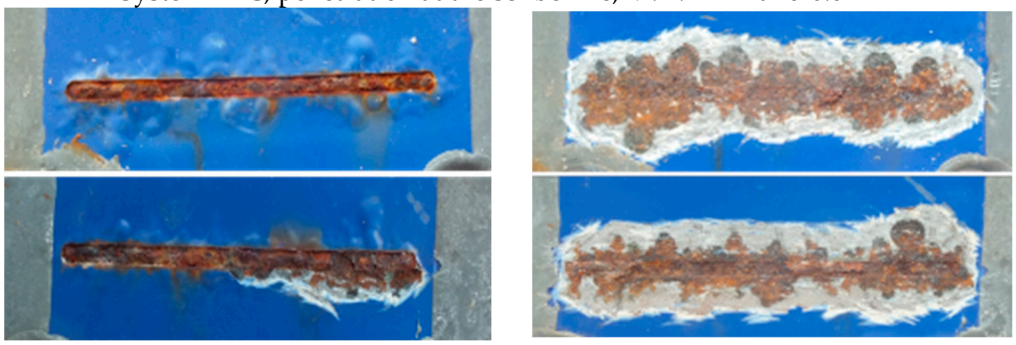
Equation (1). The systems PRC and PC1 show similar behaviour in the NSST and under field exposure, while the corrosion penetration is slightly higher in the case of PC2.

As expected, for PC2, the corrosion penetration is higher, just above 3 mm. Given the very low thickness of the new primer, PC2, and the fact that the total thickness of the system is only 193 µm, these results were expected. Nevertheless, the authors believe that these results are encouraging, and further investigation will help to improve the performance (even at a lower thickness) of hybrid organic–inorganic coatings developed by the sol–gel method for marine applications.

The adhesion after 10 months of field exposure was also assessed; the results are shown in Figures 14–16 and Table 7. In this type of ageing, all systems behave very similarly, with high pull-off values of in the range 14–15 MPa. In addition, the nature of the pull-off break is, in most cases, cohesive on the top-coat, except for some dollies from the system PC1. This means that the replacement of a BPA-based resin with a partially bio-based one does not negatively affect the adhesion of the system. Furthermore, the substitution of a ~75 µm Zn-rich primer with a ~5 µm hybrid sol–gel primer shows a slight improvement in the pull-off values, which is in agreement with the laboratory study and confirms the good adhesion properties provided by hybrid organic–inorganic coatings developed by the sol–gel method.



System PRC, penetration at the scribe line, *M*: 1.4 mm and 0.6 mm



System PC1, penetration at the scribe line, *M*: 3.0 mm and 2.2 mm



System PC2, penetration at the scribe line, *M* = 3.2 mm

Figure 13. Images of the panels before and after removing coating around the scribe line.

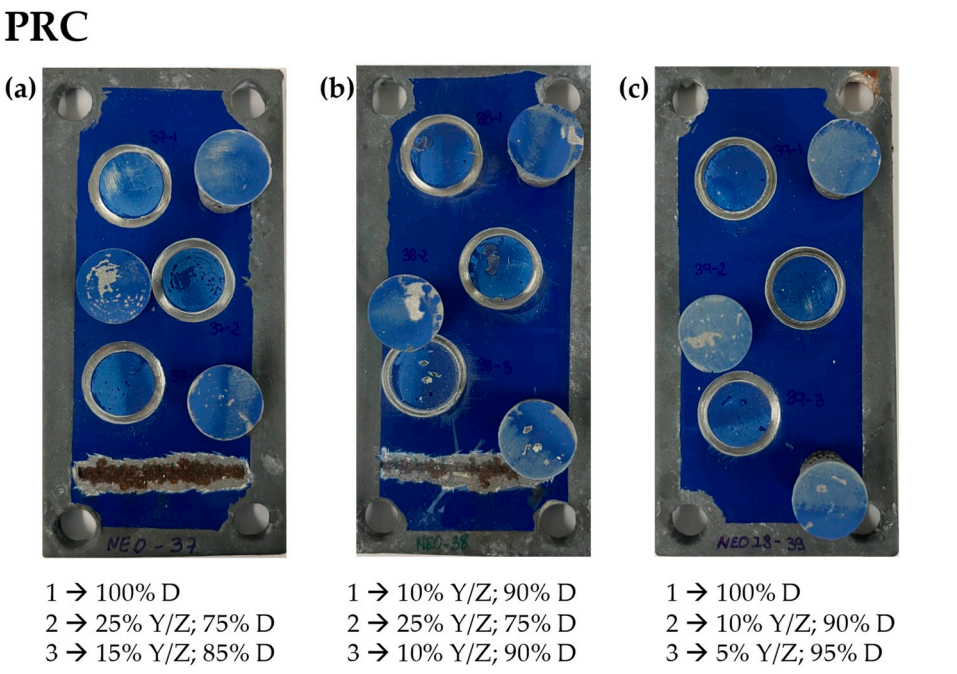


Figure 14. Pull-off adhesion images of the three test panels (**a**–**c**) of PRC coating system after field exposure. Numbers 1, 2 and 3 below the images indicate number of dollies.

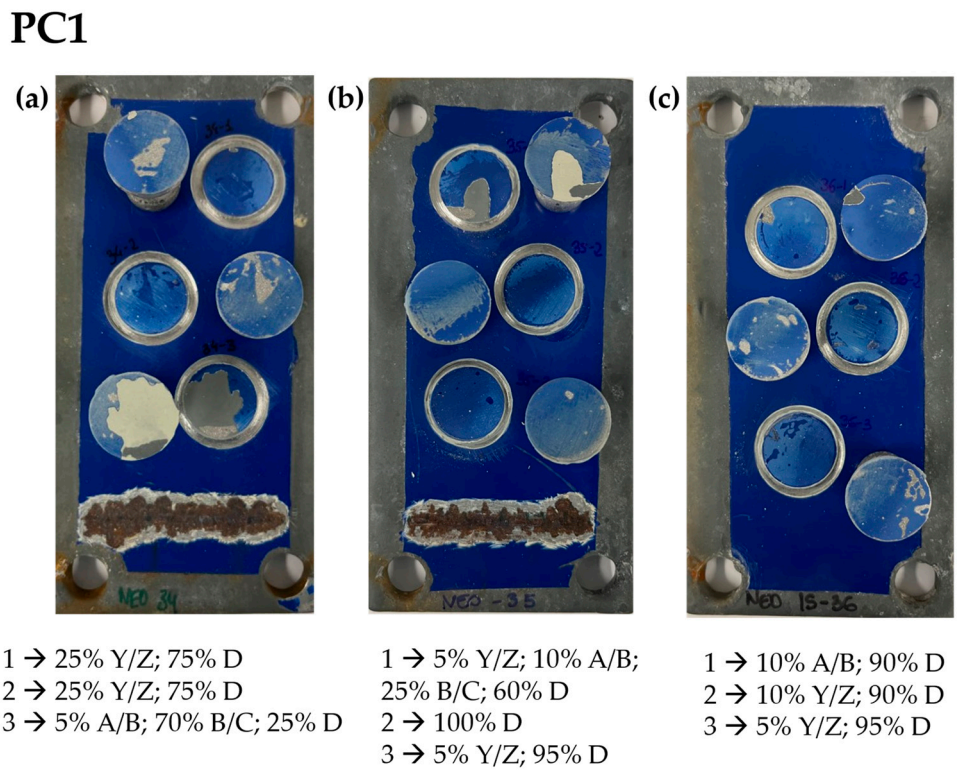


Figure 15. Pull-off adhesion images of the three test panels (**a**–**c**) of PC1 coating system after field exposure. Numbers 1, 2 and 3 below the images indicate number of dollies.

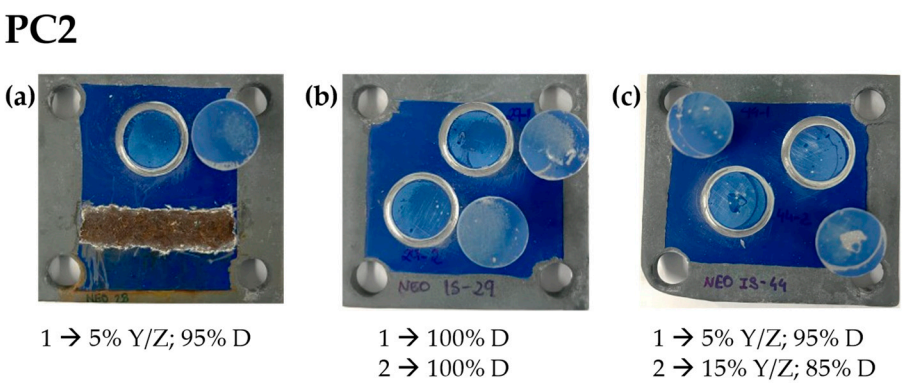


Figure 16. Pull-off adhesion images of the three test panels (**a**–**c**) of PC2 coating system after field exposure. Numbers 1,2 and 3 below the images indicate number of dollies.

4. Conclusions

In this work, a traditional Zn-rich epoxy primer (PRC) used for the protection of carbon steel against corrosion in a complete three-layer coating system was replaced with two novel types of primers: a Zn-rich 30% bio-based epoxy primer (PC1) and a sustainable hybrid siloxane coating with very low thickness developed by the sol–gel method (PC2). The complete coating systems were compared in two different types of ageing tests: laboratory studies and a real-environment study. In both cases, promising results were obtained.

The lab studies revealed that after the 1440 h NSST, none of the 3 systems under study showed any kind of degradation on the surface of the coatings. In addition, the corrosion penetration at the scribe line was very similar in the three systems. Furthermore, in the field tests, the new primers demonstrated encouraging results after 10 months of exposure in a highly corrosive environment. None of the panels subjected to this test showed any blistering or cracking on the surface. However, the penetration of corrosion at the scribe line was higher in PC1 and PC2 when compared to PRC. Nonetheless, due to the extreme conditions at which these samples were exposed, these results are considered very positive. To the best of the authors' knowledge, there are not yet any results reported regarding a primer coating being replaced by a hybrid siloxane coating (PC2) with such low thickness. Lastly, the pull-off adhesion tests of both primers, performed before and after the ageing tests, showed very high adhesion of the coatings not only to the metal substrate, but also to the coatings on top, demonstrating that substituting a petro-based resin with a partially bio-based one and a hybrid siloxane coating not only does not decrease the pull-off strength, but, in some cases, slightly improves it.

The outcomes reported here are very promising, considering that the novel primers show significantly improved sustainability: PC1 has a 30% bio-based content and PC2 is more sustainable, not only due to the use of more environmentally friendly raw materials, but also because of its lower thickness (~5 vs. 70 μm), which reduces the possibility of microplastic contamination and reduces costs, since less paint is needed to provide very similar corrosion protection. These results are a step forward towards replacing thick organic primers with sol–gel-based hybrid coatings for the corrosion protection of carbon steel subjected to marine environments.

Author Contributions: Conceptualization: A.S.-V. and G.B.; Methodology: A.S.-V. and G.B.; Validation: A.S.-V., G.B., A.U., D.M., A.S., M.F., N.M. and R.C.; Formal Analysis: A.S.-V., G.B. and A.U.; Investigation: A.S.-V. and G.B.; Writing—Original Draft Preparation, A.S.-V. and N.M.; Writing—Review and Editing: A.S.-V., G.B., A.U., D.M., A.S., M.F., N.M. and R.C.; Visualization: A.S.-V., G.B., A.U., D.M., A.S., M.F. and N.M.; Supervision: N.M. All authors have read and agreed to the published version of the manuscript.

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