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Review

Natural Polyphenols and the Corrosion Protection of Steel: Recent Advances and Future Perspectives for Green and Promising Strategies

Rossella Sesia, Silvia Spriano *, Marco Sangermano and Sara Ferraris

Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca Degli Abruzzi 24, 10129 Torino, Italy; rossella.sesia@polito.it (R.S.); marco.sangermano@polito.it (M.S.); sara.ferraris@polito.it (S.F.)
* Correspondence: silvia.spriano@polito.it

Abstract: Corrosion is recognized as an unavoidable phenomenon and steel, particularly carbon steel, is strongly susceptible to corrosion. Corrosion damages cause serious material, energy, and economic losses as well as negative impacts on the environment. As a result, research interest has been focused on the development of effective corrosion prevention strategies. However, some of the most commonly used corrosion inhibitors, such as chromates and pyridines, are harmful to human and environmental health. Polyphenols are natural, non-toxic, and biodegradable compounds from plant sources or agricultural by-products. Polyphenols' chelating capacity has been acknowledged since the 1990s, and tannins, in particular, have been widely exploited as green rust converters in phosphoric acid-based formulations to recover rusty steel. Polyphenolic compounds have recently been investigated as a method of corrosion prevention. This review overviews not only the polyphenolic rust converters, but also the application of green anticorrosive coatings containing polyphenols. Moreover, polyphenols were discussed as an active component in corrosion-inhibiting primers to also promote strong adhesion between the steel surface and the topcoat layer. Finally, an overview of the use of polyphenolic additives in coatings as sustainable systems to improve corrosion resistance is provided.

Keywords: steel; polyphenols; tannins; tannic acid; corrosion protection; coating; environmental sustainability

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Citation: Sesia, R.; Spriano, S.; Sangermano, M.; Ferraris, S. Natural Polyphenols and the Corrosion Protection of Steel: Recent Advances and Future Perspectives for Green and Promising Strategies. *Metals* **2023**, *13*, 1070. https://doi.org/10.3390/met13061070

Academic Editor: Sebastian Feliú, Jr.

Received: 24 April 2023
Revised: 22 May 2023
Accepted: 30 May 2023
Published: 3 June 2023

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1. Introduction

Steel is the most widely diffused structural material in a variety of different fields, such as industrial pipes, open-air structures, or automotive, to cite some examples, due to its reasonable cost and good mechanical properties [1–4]. In the cited applications, steel can be subjected to corrosion related to carbon dioxide, hydrogen sulfide, and chlorides [1–4].

The real impacts of the corrosion of steel structures also include the loss of productivity, safety concerns, impacts related to eventual failures, and environmental impacts, such as CO_2 emissions associated with steelmaking for the replacement of the corroded structures [5]. The World Bank estimated that the cost of corrosion was about 6 trillion US dollars in 2021, while the global GDP was approximately 96.1 trillion US dollars [6]. Considering the global impact of corrosion, several strategies have been developed to limit the corrosion of steel. Thereby, researchers believe that between 14 and 33% of the costs could be avoided [6].

The use of corrosion inhibitors is the simplest and cheapest method to limit steel corrosion in working environments. Corrosion inhibitors are substances that, added in a proper amount to the aggressive solutions that can cause metal corrosion, can prevent and/or slow down corrosion phenomena without causing a significant alteration of the solution composition, as indicated in ASTM GIS-2018 and ISO8044-2020 standards [7,8]. Corrosion inhibitors are chemically or physically adsorbed on the surface of the metal to

form a protective film that can limit the redox reactions on the surface. There are many different types of corrosion inhibitors currently used, such as inorganic corrosion inhibitors (preferred in almost neutral environments and at high temperatures) and organic corrosion inhibitors (generally preferred in acidic environments). Organic corrosion inhibitors usually contain polar functional groups, with atoms including O, S, and N, with unshared electron pairs or π electrons, able to interact with the metallic surfaces and organic hydrophobic moieties able to limit the surface reactions with corrosive media [1,7–9]. Examples of organic corrosion inhibitors are fatty amides, pyridines, polymers, and imidazolines, while chromates, dichromates, phosphates, and arsenates can be cited among the most diffused inorganic corrosion inhibitors [7,8]. The toxicity of these substances for humans and the environment makes urgent the need for alternative solutions for the protection of steel from corrosion.

Green corrosion inhibitors should have no bioaccumulation, very limited marine toxicity, and biodegradability [8,9]. Natural molecules within plant extracts satisfy the above-cited requirements, can be obtained from natural resources or by-products, with a circular economy approach and low costs, and have chemical moieties suitable to work as effective corrosion inhibitors. Due to these reasons, plant extracts are gaining increasing interest as green corrosion inhibitors, as demonstrated by recent works [7–11]. Their effectiveness in the protection of metallic substrates from corrosion has been demonstrated in several corrosive environments, such as HCl, H_2SO_4, Na_2SO_4, NaCl, NaOH, Na_2CO_3, H_3PO_4, aqueous, CO_2, citric acid, biodiesel, geothermal fluid, trichloroacetic acid, and artificial saliva. However, some issues are still open, such as variability in composition and properties, dependence on the source and extraction technique, degradability, poor knowledge of the mechanisms responsible for corrosion protection, and commercial availability [7–9].

The protection of metallic surfaces from corrosion by means of the application of protective coatings is another effective and widely diffused strategy. Differently from corrosion inhibitors, coatings are directly applied on the metallic surface and can protect it in different critical working situations, not limited to a corrosive bath. Moreover, better surface coverage and consequently more uniform and stable protection can be guaranteed by corrosion protection coatings. Many different polymeric [12,13], ceramic (oxides, nitrides, and diamond-like coatings) [14], superhydrophobic [15], nanocomposite [16,17], and even smart [18,19] or bioinspired [20] coatings have been proposed in the scientific literature and were recently reviewed. The service temperature, eventual UV exposition, and presence of porosity can limit the application of polymeric coatings. Some limitations can be overcome by the introduction of proper additives [12,13], while ceramic coatings should be preferred in the case of components working at high temperatures or in aggressive chemical environments. The possibility of uniformly covering complex shapes is another issue to be faced. Dip-coating procedures and chemical/electrochemical routes can be advantageous from this standpoint, even if specific surface pre-treatments can be requested in some cases (e.g., PEO ceramic coatings on steel substrates [14]). Analogously to traditional corrosion inhibitors, some environmental concerns can also be evidenced for corrosion protection coatings, such as the use of toxic reagents, nanoparticles, and petroleum-derived materials. Despite the increasing attention to environmental and health protection, the research on green corrosion protection coatings, based on natural polymers and environmentally friendly procedures, is still at the beginning.

The development of corrosion protection coatings with natural polyphenols is gaining increasing interest [21]. Moreover, polyphenols' non-toxicity, biodegradability, ease of extraction at reduced costs, availability, low cost, anti-microbial and anti-oxidant actions, and high affinity for metallic surfaces are their main advantages [22–24].

Polyphenols are a large class of natural and ubiquitous molecules in all plant organs. They exhibit a wide range of chemical structures, but all share a basic group: a hydroxyl-substituted benzene ring [25,26]. The polyphenols family includes compounds with different molecular weights [27], degrees of oxidation, hydroxylation, methylation,

and glycosylation [28]. Therefore, there is discordance concerning polyphenols' classification. The most adopted classification implies the subdivision of polyphenolic compounds into phenolic acids, flavonoids, and non-flavonoids [28–32]. Figure 1 schematically depicts the different polyphenols classes and their subclasses. The non-flavonoids class includes stilbenes, lignans, and tannins as subclasses [28,32], although some works reported in the literature consider tannins in the flavonoid class as flavanol polymers [26,33]. In detail, tannins are strictly referred to as plant polyphenols with molecular masses between 500 and 3000 Da [34], and they are conventionally classified into two main groups according to their chemical structures: hydrolysable and condensed tannins (Figure 1). On one side, hydrolysable tannins are subdivided into gallotannins, which produce gallic acid during hydrolysis, and ellagitannins, which form ellagic acid when hydrolyzed. On the other side, condensed tannins are oligomers and polymers of the flavonoid repetition unit, and are classified as proanthocyanidins, prodelphinidins, profisetinidins, and prorobinetinidins [34–38].

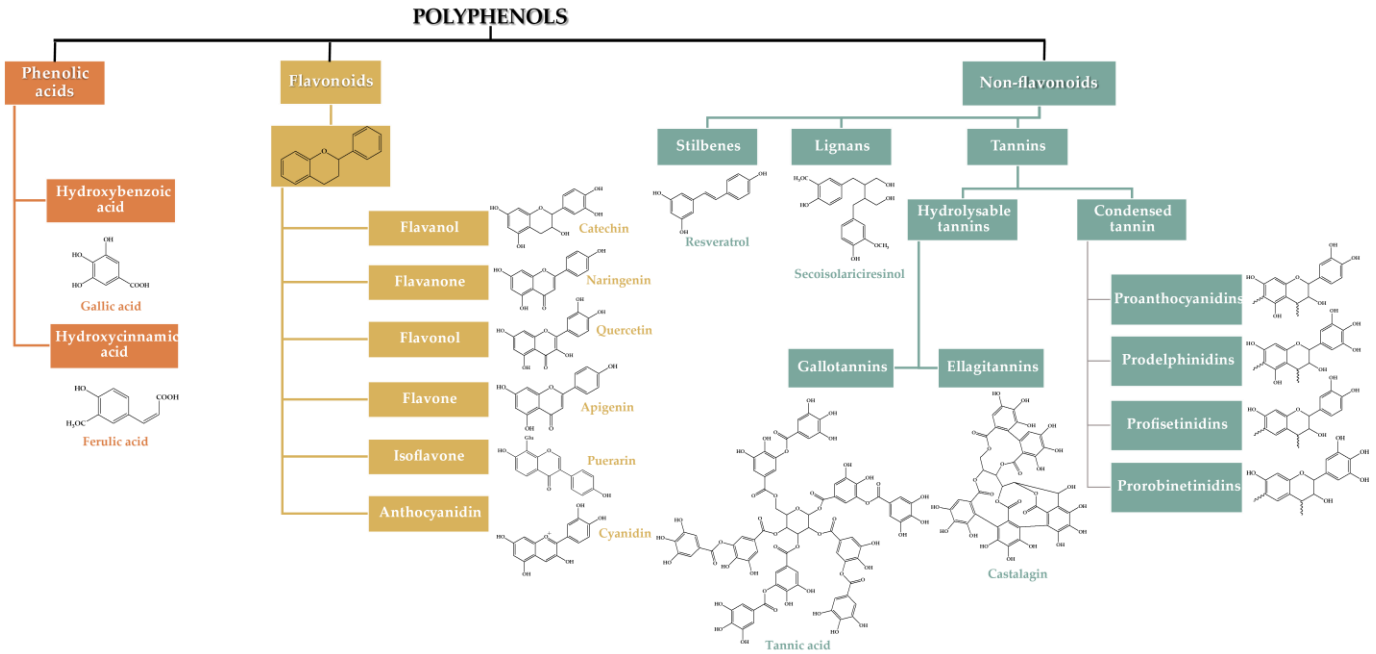

Figure 1. Scheme of the classes and subclasses of polyphenols with some examples of chemical structures.

Tannins are the most studied polyphenols for the corrosion protection of metals. Both hydrolysable and condensed tannins have been considered for this purpose due to their ability to scavenge oxygen radicals and form corrosion protection films on metallic surfaces [39]. Moreover, the bacteriostatic/antibacterial properties of these molecules can also protect metals from microbial corrosion [39].

The present review is focused on recent advances in the exploitation of natural polyphenols as corrosion protection coatings and covers the literature in the range from the 1990s to nowadays. The use of polyphenols as rust converters on the surface of steels, the application of polyphenols as primers and adhesion promoters on steel substrates, the deposition of corrosion protection coatings, the inclusion of polyphenols as an additive in polymeric coatings, and the realization of coatings with polyphenols for corrosion protection have been investigated in the scientific literature and discussed. The focus of the work is on the use of polyphenols directly on the material surface with the purpose of preparing, improving, or developing green corrosion protection layers.

2. Polyphenols as Rust Converter Layers on Steel Substrates

Rust converters react with surfaces covered by iron oxides (rust) to produce a harmless and stable surface layer on which paint coatings can be effectively deposited. This strategy

is essential when it is not possible to completely remove the rust before painting, for example, in the cases of components with complex shapes [40]. Furthermore, the rust conversion technique is particularly useful for vast areas where traditional rust removal processes, such as sandblasting and acid solutions methods [41], take a long time and damage the ecosystem [42].

The risk of rusty steel is the possible unceasing development of rust even under the applied painting film due to the presence of moisture and contaminants [43]. Consequently, the rust converter must show two main functions: removing the rust and reducing the corrosion rate of the metal when covered by a primer or additives [44]. Therefore, the features of the rust on the metal surface (thickness, structure, composition, age of formation, etc.), as well as the chemical characteristics of the used rusting compound (chemical structure, concentration, pH, solubility, and chelation ability towards iron) affect the rust conversion treatment and its achievement. An efficient rust converter must show water solubility, non-toxicity, non-corrosiveness, non-flammability, applicability to a wide range of metal surfaces, and ease of application [42].

The rust converter formulations consist of an active component that reacts with the rust to produce more inert compounds than the original iron oxo-hydroxides, and a polymeric one capable of forming a continuous film [45–47]. Since the early 1990s, mixtures of phosphoric and tannic acids have been used as possible rust converter formulations [40,48,49] due to their ability to form iron phosphates and tannates upon reaction with the surface of rusted steels. More recently, gallic acid is exploited as an active component [50–52]. These tannin-based rust converters are low cost, have a low toxicity, are environmentally friendly, and obtained from renewable resources [40]. The polyphenol concentrations studied in the formulations of rust converters extend from 0.2 to 25 wt% [40,48,51].

The mechanism of the rust conversion performed by tannins is widely investigated [53–56]. The reaction between the rusty iron surface and tannins quickly occurs and the polyphenolics moieties from the tannin-based compound establish interactions with iron oxides and oxyhydroxides. The polyphenolic compounds can directly complex Fe(III) to produce ferric tannates or the Fe(III) ions are reduced to ferrous complexes, due to the tannins' reducing properties (Equations (1) and (2)), and they are subsequently oxidized by the atmospheric oxygen into ferric tannates (Equation (3)) [52,54].

$$FeOOH + 3H^+ \rightarrow Fe^{3+} + 2H_2O \quad (1)$$

$$nFe^{3+} + \text{tannins} \rightarrow (Fe^{2+})_n\text{tannate} + nH^+ \quad (2)$$

$$(Fe^{2+})_n\text{tannate} + \frac{1}{4}\,nO_2 + nH^+ \rightarrow (Fe^{3+})_n\text{tannate} + \frac{1}{2}\,nH_2O \quad (3)$$

After coating the rusted steel surface with a 15% aqueous ethanolic oak tannin solution, Gust and Suwalski studied the reaction products of polyphenols and iron ions via the Mossbauer spectroscopy. They have reported that the reaction between the rust phase and natural tannins forms mono-complexes (Figure 2a) and bis-complexes (Figure 2b) [57]. The produced iron tannates appear as an amorphous blue/black layer on the surface, and their highly crosslinked network [42] explains their sparing solubility and, therefore, their ability to inhibit corrosion [54].

The efficiency of the rust conversion by the tannins can be enhanced by the synergic effect of phosphoric acid. As far as it concerns the reaction mechanism, the mixture of Fe(III) oxide-hydroxide and Fe(II, III) oxide and the steel substrate react with the phosphoric acid to produce iron phosphates (Equations (4) and (5)) [54,55,58]. Therefore, iron phosphates are formed together with iron tannates as a result of the chemical rust conversion, and the steel is covered by these insoluble conversion products in order to prevent further corrosion.

$$FeOOH + H_3PO_4 \rightarrow FePO_4 + 2H_2O \quad (4)$$

$$2H_3PO_4 + 3Fe_3O_4 + 8H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O + 6FeOOH \quad (5)$$

However, the effectiveness of the protection is highly controversial due to the wide range of parameters. For instance, Gust demonstrated that the composition of the converted rust by the mixture of tannic acid and phosphoric acid is dependent on the different phases of the original rust, which is influenced by the environment [59,60]. Indeed, the conversion reaction is fastest with the lepidocrocite phase than with the magnetite and goethite phases [61]. The work of Rahim et al. confirms this result and also suggests that the formation of ferric tannates occurs predominantly in the lepidocrocite outer layer and less in the magnetite inner layer, which is unaltered by the tannins addition (Figure 2c) [62]. Moreover, the performance of the rust converter was examined by Zhao et al. in relation to temperature variations between 2 and 60 °C, and a decrease was observed in the conversion film's protectiveness at elevated temperatures [58]. Both hydrolysable and condensed tannins show the ability to convert rust into iron tannates, although the concentrations of their solutions and the pH affect the final result [56,59,63,64] as well as the concentration of phosphoric acid [65]. Rahim et al. evaluated the rust conversion efficiency as a function of phosphoric acid concentration and the pH, and demonstrated that at a pH of 5.5, the addition of phosphoric acid in a mangrove tannins solution increases the inhibition efficiency of the rusty mild steel [65].

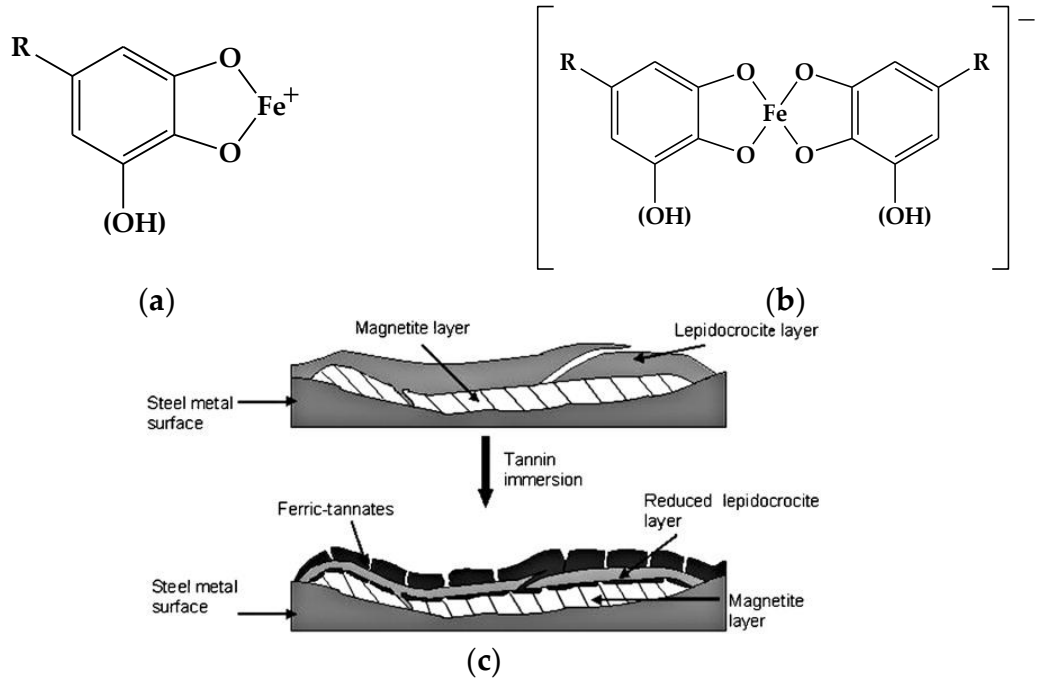

Figure 2. (**a**) Iron tannate as a mono-complex, known as catecholate mode; (**b**) iron tannate as a bis-complex; (**c**) profile of rust conversion into ferric tannates after immersion of steel in a tannin solution. Reprinted with permission from [62], copyright 2011, Taylor & Francis.

Lastly, the rust conversion agents have to maintain their corrosion resistance even after the overlaying of a topcoat [42]. The application of a phosphoric and tannic acid-based rust converter significantly improves the corrosion resistance of steel bars coated with a zinc rich organic coating in simulated alkaline solutions containing concrete [66]. In this last example, the release of the unreacted rust converter, through the zinc-based coating, helps maintain the pH in the range of 11–13, in which the corrosion protection of the zinc layer is maximized. An experimental demonstration of the enhancement of the adhesion of an epoxy top coating after the tannic converter treatment was carried out by Li et al. in 2014. An adhesion improvement from 1.93 to 5.97 MPa could be ascribed to a micro-cracked tannic conversion layer (which reinforces the anchoring of epoxy coating through a pinning

effect) and the rise in the rust layer compactness [67]. However, Ocampo et al. reported no significant improvement in the corrosion protection of steels treated with a phosphoric and tannic acid-based rust converter after epoxy-mastic coatings [40]. An improvement was confirmed by a study by Wang et al., which also suggests that a layer of unreacted rust between the substrate and rust conversion film negatively affects the epoxy resin adhesion strength, limiting the anticorrosion performance [52]; this could be a critical issue which could explain some of the failures of this approach.

3. Coatings for Corrosion Protection with Polyphenols

Thanks to their capability to coordinate iron, polyphenols have also been explored as the main constituents of corrosion protection coatings for steel substrates (Table 1), without the use of paints on it. Coatings were obtained by means of cyclic voltammetry [68,69], electropolymerization [70], dip-coating [71,72], or sponge rolling on various steel substrates mainly degreased [73] or grinded and degreased [68,69].

As summarized in Table 1, different types of coatings were tested on different steels: multilayer coatings of polypyrrole and polyphenol [68,69] or branched polyethylenimine (PEI) and tannic acid (TA) [71], as well as coatings with phenol, o-methoxyphenol, and o-nitrophenol [70], or containing silane and metal-polyphenol networks [72] or phosphorylated polyphenols [73]. Silanes were used as final hydrophobic layers obtained by CVD deposition on polyphenolic coatings [72], or as agents for the obtainment of silane-phosphorylated-polyphenol hybrids by chemical reaction [73].

Polyphenols layers improved the corrosion protection properties of polypyrrole coatings, making the whole coating less porous and acting as a barrier to corrosion [68,69].

A strong adhesion and homogeneous surface coverage are key factors to guaranteeing effective corrosion protection. In fact, coatings with O-methoxyphenol, despite having a good adhesion, presented inhomogeneous surface coverage and subsequent sub-optimal corrosion protection [70]. On the other hand, the layer-by-layer deposition of tannic acid and polyethylenimine resulted in a strong electrostatic interaction and substrate adhesion, with uniform coverage and excellent corrosion protection [71].

Table 1. Anticorrosive performance of coatings with polyphenols on different types of steels.

Substrate	Coating	Application Strategy	Main Results	Reference
Mild steel (composition—wt.%—0.098 C, 0.35 Mn, 0.031 S, 0.017 P, and 99.334% Fe). Pre-treatment of the surface: polishing abrasive papers up to 1200, degreasing with 1:1 ethanol/acetone mixture, washing with bi-distilled water, and drying with warm air	Polypyrrole (PPy) and polyphenol (PPhe) films	Electrochemical synthesis by cyclic voltammetry technique	The synthesis of a thin PPhe coating on PPy one increased the corrosion protection, acting as a barrier able to block the solution penetration in the PPy pores.	[68]
Mild steel (composition—wt%—0.098 C, 0.35 Mn, 0.031 S, 0.017 P, and 99.334% Fe) polished with abrasive papers up to 1200 grit, degreased with 1/1 ethanol/acetone mixture, washed with distilled water, and dried	Polypyrrole (PPy) and polyphenol (PPhe)	Cyclic voltammetry technique. Deposition of PPhe in acidic conditions	The thin PPhe coating on top of the PPy one increased the corrosion protection in an acid environment. The PPhe coating covered the PPy pores, increasing the protection ability.	[69]
Carbon steel	Phenol, o-methoxyphenol, and o-nitrophenol	Electropolymerization by cyclic voltammetry	O-methoxyphenol resulted to be the most effective in the synthesis of a corrosion protection coating. The coating adhered well to the carbon steel, but was non-completely homogeneous and continuous; consequently, the corrosion protection was not complete.	[70]
Carbon steel and corroded carbon steel by exposure to air for 6 months	Branched polyethylenimine (PEI) and tannic acid (TA)	Alternating steps of dipping in a TA and PEI solution to obtain a layer-by-layer deposition (TA/PEI multilayer coating)	TA/PEI multilayer assembly presented long-term corrosion resistance. Negatively charged TA and positively charged PEI joined to form a very thin multilayer coating. The high water stability was due to ionic bonding and strong adhesion to the steel surface and, as a result, outstanding corrosion resistance was proved.	[71]
Several substrates, including iron sheets and stainless steel	Metal-polyphenolic network-based (MNP) coatings and silane-MNP coatings prepared by proanthocyanidin and iron(III) nitrate nonahydrate	Dipping of the substrates in a reactor for the coatings' preparation	Substrates with MNP coatings showed lower values in water contact angle compared to the original substrates, while silane-MNPs coatings increased the surface hydrophobicity. The silane-MNP coating was more stable than MPN coatings under strong acid conditions, showing excellent resistance to acid corrosion.	[72]
Galvanneal steel degreased with degreasing solution (20 wt.% cetylctrimethylammonium bromide mixed with demineralised water)	Coating based on phosphorylated polyphenol and organic–inorganic silane compounds with different additives	Application by sponge roller	The silane-phosphorylated polyphenol coating enhanced the corrosion resistance, and 0.5 wt.% of manganese phosphate as an additive in a silane-phosphorylated polyphenol coating improved the corrosion resistance and lubricant properties.	[73]

4. Polyphenols as Adhesion Promoters/Primers for Anticorrosion Coatings

The protection of the steel substrate provided by the paint finish can be significantly enhanced by the application of an anticorrosive primer before the main paint [74].

Steel substrates are often only degreased [75–79] before primer application, but degreasing followed by abrasive paper grinding [80,81] and blasting [82–84] have been reported as surface pre-treatments. Moreover, the pickling process is used to superficially clean steel substrates [81,85].

A multilayered and hybrid coating system is achieved (Figure 3 [86]) and is composed of the interfacial or primer layer and a topcoat, that acts as a barrier to external corrosion, against the diffusion of oxygen, water, and corrosive compounds, such as chloride ions, to the metal surface. Primer layers play a key functional role because they markedly contribute to the efficiency of corrosion prevention [86]. Moreover, primers should have high cohesion towards the metal surface and ensure superior adhesion to the subsequent paint layers [87].

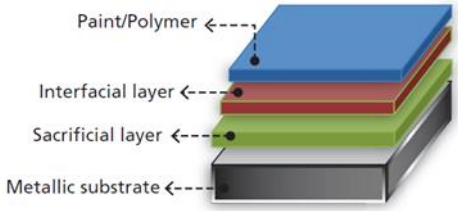

Figure 3. Scheme of the state-of-the-art multilayered coating system. Adapted with permission from [86], copyright 2013, ICE Publishing.

A large number of compounds could be used as primary protection against oxidation corrosion. Up to the present time, inorganic and organic–inorganic hybrid types of primer coats are used due to their ease of processing and application versatility [86]. However, the usage of inorganic and synthetic corrosion inhibitors, such as chromium, arsenic, and phosphate derivatives, raises much concern as they negatively impact the health of human beings and the environment [88–91]. In order to overcome this issue, the research interest has been focused on the application of low-cost, green, and harmless anticorrosive primers, such as organic compounds obtained from natural plant extracts [89,92]. Therefore, the well-known anticorrosion characteristic of polyphenols, especially tannins, has been exploited to prevent corrosive phenomena and tannin-based primers, which were commercially used in England since the 1950s [74].

In 1994, the authors demonstrated the possibility to apply pine tannins-based formulation on clean metal substrates [82]. In this work, anticorrosive tests in a salt fog chamber according to ASTM B 117-73 and potentiodynamic scanning measurements in a solution of sodium chloride were performed on steel samples previously treated with a tannin-based primer and then paint coated. The results show that corrosion resistance is significantly increased by the application of a tannin primer under a polymeric topcoat layer, and natural tannins-based primers outperformed traditional primers, which were formulated with $ZnCrO_4$ in an H_3PO_4 medium, by 300%, in terms of the corrosion rate with the same thickness of the dry film. Moreover, paint adherence is distinctly improved thanks to the tannin-based primer contribution, suggesting that natural tannins can be used as adhesion promoters for the topcoat. Lastly, Matamala et al. proposed a corrosion inhibiting mechanism based on the initial oxidation of the metallic iron in the acid environment, due to the pH of 3.2 of the used tannin formulation (Equations (6) and (7)), and following reactions involving polyphenolic groups and iron ions according to Equations (8)–(10).

$$2Fe + 4H^+ + O_2 \rightarrow 2Fe^{2+} + 2H_2O \quad (6)$$

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \quad (7)$$

$$\text{Tannin-OH} + Fe^{3+} \rightarrow (\text{Tannin-O-}Fe^{3+})^{2+} + H^{+} \quad (8)$$

$$\text{Tannin-2OH} + Fe^{3+} \rightarrow (\text{Tannin-2O-}Fe^{3+})^{+} + 2H^{+} \quad (9)$$

$$\text{Tannin-2OH} + (\text{Tannin-2O-}Fe^{3+})^{+} \rightarrow (\text{Tannin-4O-}Fe^{3+})^{-} + 2H^{+} \quad (10)$$

Thus, black iron tannates are produced and acidify the reaction system, making the re-action between polyphenols and the metal substrate self-catalyzed.

Pine tannins (condensed) have been extensively studied as active compounds in primer formulations [82,83,93]. The second most employed tannins for this purpose are the tara ones [75,76,80], which are hydrolysable. Moreover, different condensed (black acacia, black wattle barks, and quebracho [81,83,84]), and hydrolysable (chestnut [77,78]) tannins were also tested as active components in primers/adhesion promoter formulations. Tannins from different natural sources could exhibit different corrosion-inhibiting properties. For instance, a study compared two types of natural tannins as steel primers: pine bark tannins and black acacia ones [83]. The best anticorrosive efficacy of the pine tannin-based primer over that of the black acacia primer was evaluated by rusting tests in a salt fog chamber and polarization analyses. Furthermore, the application of a primer layer of pine tannins over steel leads to less blistering and topcoat adhesion enhancement, thus increasing the corrosion resistance of the painted steel.

As discussed in the following and summarized in Table 2, tannins are rarely used alone as primers or adhesion promoters [84]. The preparation of a primer or adhesion promoter layer often foresees the combination of tannins with phosphoric acid [77,78] or a polymer such as polyvinyl butyral [75,76,82,83], epoxy [93], or acrylic [77,78] resins and their application on the substrates by brushing [75–78,82,84], spraying [80], or bar coating [79].

The research interest has been recently focused on corrosion protection by the combination of natural polyphenols and metal oxides within formulations to be applied as a primer layer on the steel. The introduction of metal oxide nanoparticles, such as ZnO, Fe_2O_3, and TiO_2, in epoxy resin-based coatings provides a more uniform distribution and thus, a better protection performance against corrosion [94]. In this framework, Ramírez et al. successfully incorporated tannins from Pinus radiata barks into an epoxy-based primer enriched by zinc oxide nanoparticles to improve the functionality of the coating system, such as the resistance against aggressive agents, mechanical response, and film adhesion [93].

Zinc oxide is a good inorganic corrosion inhibitor. For this reason, it is used as one of the major additives in the phosphating baths, an industrial process to protect steel from rust formation. However, phosphate coatings do not guarantee corrosion protection as they are highly porous and could be attacked by electrolytes [95]. Therefore, tannins could be exploited as additives to phosphating solutions to improve corrosion resistance and subsequently epoxy paint adhesion due to the zinc phosphate crystals' reduction by tannins. Indeed, tannins adsorption by steel surface can modify the active sites of the substrate and, as a result, this phenomenon can affect the crystals' size and distribution on the metal surface [81]. The addition of a natural polyphenol compound to a zinc phosphating bath can be a more environmentally friendly and low-cost strategy to enhance the durability of a coating system on steel.

Table 2. Anticorrosive and adhesion promotion performances of polyphenols-based primers under the topcoat on different types of steels.

Substrate	Adhesion Promoter/Primer	Corrosion Protective Coating	Application Strategy	Main Results	Reference
Sandblasted SAE 1010 steel panels degreased with toluene	Two commercial tannins from tara: T40 and T80	An anticorrosive alkyd paint pigmented with zinc molybdenum phosphate and titanium dioxide, and an alkyd topcoat containing titanium dioxide	Preparation in a two-pack system of tara tannins primer (TT40 and TT80) and lanthanum tannates (LT40 and LT80) in a polyvinyl butyral resin-based formulation and a subsequent application by brushing	LT40 highly reduced the steel corrosion rate, and its efficiency was 95%, while an efficiency of 86% was assessed for LT80. TT40 and LT40 had similar steel corrosion rates, whereas the anticorrosive performance of LT80 was better than TT80. The ionic resistance was increased by the use of tannin-based primers and in particular, TT40 and LT40 showed ten times higher resistance than TT80 and LT80. The anticorrosive performance of a complete painting system was enhanced by the primer application. LT40 performed as the one with zinc tetroxychromate (ZTC) in accelerated tests and had better behavior than the other tannin-based primers formulations.	[75]
SAE 1010 steel degreased with isopropyl alcohol	Tannins from tara (T40, INDUNOR, abbreviated as T) and quebracho (UNITAN CROWN ATO, abbreviated as Q)	-	Preparation in a two-pack system of tannins primers (T and Q) and lanthanum tannates (TL and QL) in a polyvinyl butyral resin-based formulation and a subsequent application by brushing	Results from humidity chamber experiments proved that tara-based primers and quebracho-based ones had good adhesion to a steel substrate at the beginning of the test. In detail, after 5 days, the adhesion of T and TL primers was better than Q and QL, while the rusting degrees were similar (T and Q were more protective than TL and QL). T-coated panels had ionic resistance with an order of magnitude greater than steel without primer, and steels with a TL primer layer showed 2–4 times higher values. Q and QL primers on steels presented 3–4 times higher ionic resistance values than the metal without primer. Tannin-based primers had similar adhesion to the zinc tetroxychromate (ZTC) one and better barrier properties than ZTC.	[76]

Table 2. *Cont.*

Substrate	Adhesion Promoter/Primer	Corrosion Protective Coating	Application Strategy	Main Results	Reference
SAE 1010 steel panels degreased with toluene	Tannins from chestnut	An alkyd paint pigmented with zinc molybdenum and/or an alkyd topcoat pigmented with titanium dioxide	Mixing of filtered tannins with a 40% aqueous solution of an acrylic resin, Texanol, and 10% ammonium molybdate solution, and brush application of the primer	The water permeation was not considerably influenced by the primer treatment. Impedance data showed a significant corrosion delay due to the iron tannates' formation. The corrosion protection provided by the tannin primer was limited to a short immersion period in non-aggressive electrolytes (the tannin primer layer was more effective in NaCl than in $NaClO_4$).	[77]
SAE 1010 steel panels degreased with toluene	Tannins from chestnut	An anticorrosive alkyd paint pigmented with zinc molybdenum phosphate and with a 0.8 PVC/CPVC ratio, and an alkyd topcoat pigmented with titanium dioxide	Mixing of filtered tannins with a 40% aqueous solution of an acrylic binder, Texanol, and 10% ammonium molybdate solution, and brush application of the primer	The anticorrosive performance was improved by a complete paint system (tannin primer + anticorrosive coating + topcoat). The tannin treatment prevented the formation of oxides on the scratch marks, where the corrosive process was more intense. The tannin-based primer on the steel showed high adhesion (20 ± 5 kg/cm^2) and good paint adhesion promotion even after the salt fog chamber test.	[78]
Low-carbon steel and aluminum plates degreased with acetone	Acrylated tannic acid	A UV curable resin containing Irgacure 1173 (photoinitiator), polyester acrylate (DR-E524), tetrahydrofurfuryl acrylate (THFA), standard bisphenol-A epoxy acrylate (G500), and a leveling agent (BYK333)	Addition of the adhesion promoter to the resin formulation and application of the mixture on the substrate by bar coating	Tannic acid-based adhesion promoters significantly increased the adhesion of the polymeric coating to the metallic substrates and their corrosion protection ability. An optimal acrylation degree was identified.	[79]

Table 2. *Cont.*

Substrate	Adhesion Promoter/Primer	Corrosion Protective Coating	Application Strategy	Main Results	Reference
JIS G3141 mild steel (composition—0.15% C, 0.60% Mn, 0.05% S, 0.10% P) polished using a grinder, manually with an emery paper no. 100, and then degreased with ethanol	Zinc tannate pigment prepared with tara powder and zinc oxide	Isopropanol-based wash primer	Spray gun application of two coats of a wash primer containing zinc tannate (WTZ)	WTZ, alone and with a topcoat of a synthetic, commercial, and white alkyd paint, exhibited an anticorrosive property that was similar to primers containing zinc phosphate. However, the zinc chromate-based primer had the best corrosion protection capacity and higher adhesion to steel.	[80]
Carbon steel (composition—wt.%—0.103 C, 0.46 Mn, 0.013 P, 0.096 S, 0.01 Cu, 0.18 Cr) degreased with an acetone/chloroform mixture and polished with sandpaper up to grade #1200	Condensed tannin from black wattle barks	Epoxy coating (Intergard 269) as a finish paint for adherence tests	Addition of different black wattle tannin concentrations (0, 2, 4, and 8 g L^{-1}) to a zinc phosphating bath and 0.5 g L^{-1} of tannin to an iron phosphating bath. Dipping of a steel sample in the bath for 10 min at 80 °C after an acid pickling treatment	The tannin addition affected the zinc phosphate crystals' orientation and size over the steel surface, modifying the substrate's active sites. The grain size reduction was confirmed in iron phosphating. From EIS analysis, better corrosion resistance was found when the tannin concentration in the zinc phosphating bath was 2 g L^{-1}.	[81]
Plain or shot-blasted plates of AISI 1010 steel	Tannins from radiata pine bark	Three anticorrosive top coatings: alkyd, vinylic, and epoxy paint systems	Application of a 5 μm thick layer of a tannin-based primer containing polyvinyl butyral as a ligand element by brush and the use of spraying topcoats	The difference in rusting kinetics indicated the tannin primer's corrosion inhibitor capacity over the anticorrosive alone. Particularly, no rusting or color change occurred when a 25 μm-thick anticorrosive epoxy coating was applied over a tannin primer layer. The corrosion current of the steel treated with the tannin primer stabilized at 2.7 μA/cm^2 against 8.5 μA/cm^2 of the steel protected by a chromated conversion coating. The adherence test on the epoxy paint applied in combination with a tannin primer achieved values of up to 35 kg/cm^2.	[82]

Table 2. *Cont.*

Substrate	Adhesion Promoter/Primer	Corrosion Protective Coating	Application Strategy	Main Results	Reference
10 × 15 cm plain or shot-blasted plates of AISI 1010 steel	Tannins from radiata pine bark and from black acacia	Three anticorrosive top coatings: alkyd, vinylic, and epoxy paint systems	Application of a 5 µm thick layer of tannin-based primer containing polyvinyl butyral as a ligand element and the use of spraying topcoats	During the salt spray chamber exposure, the percentage of the rusted steel area was notably decreased by the use of pine tannin under the topcoat compared to samples without a primer layer and samples with an acacia tannin primer layer. Both types of tannins acted as adhesion promoters, although the acacia tannin-based primer slightly decreased paint adherence.	[83]
Sandblasted SAE 1010 steel panels, previously degreased with toluene	Tannins from quebracho	Anticorrosive alkyd paint and finish alkyd topcoat	Brush application of a wash-primer composed of quebracho tannin (QT) or lanthanum "tannate" (LT), which was obtained as a precipitated mass from a mixture of tannin, potassium nitrate (KNO_3), and lanthanum(III) nitrate ($La(NO_3)_3$)	Results from steel corrosion potential measurements in pigment suspensions in 0.025 M NaCl showed that LT was the best inhibitor for steel corrosion. LT significantly decreased the steel corrosion rate with an efficiency of about 94%. LT in a primer formulation inhibited the development of globular oxides as zinc tetroxychromate (ZTC) did. The electrochemical evaluation revealed that the presence of a primer in the paint system delayed the corrosion, and the LT primer showed a similar anticorrosive property to a traditional ZTC primer.	[84]
ASTM A36 Steel	Tannins from radiata pine	Topcoat containing Poliol 112, BYK 333, BYK 425, additives (BYK 333, Purmol 333, Antiterra), zinc oxide nanoparticles (ZnO-NPs), thinner, and crosslinking agents	Application of a mixture of tannins with an epoxy resin formulation containing zinc oxide nanoparticles (PT-ZnO NPs) and a topcoat by an air gun.	After accelerated corrosion chamber experiments, no type of failure occurred for the PT-ZnO NPs primer according to ISO 4628: better adhesion and excellent interlay adhesion than commercial coatings (polyurethane and transurethane paints). The PT-ZnO NPs coating showed similar or superior mechanical properties than commercial coatings, except for the impact resistance. The impedance modulus of PT-ZnO NPs was measured at 6.7×10^8 Ω cm^2, which indicated high resistance against aggressive agents. Therefore, the functional properties (film, mechanical, and corrosion) were improved by the addition of tannins in the primer formulation.	[93]

In addition, tannates can be used as additives in the coating formulation for several applications, resulting in organometallic compounds from the interaction between tannins and metallic salts or oxides [54,96,97]. Hence, a safer coating for humans and the environment can be produced with improved anticorrosive and adhesion promoter properties. A study by Hadzich et al. aimed at evaluating the inhibitory efficiency of primers formulated with zinc tannates [80]. These complexes were prepared by using tara tannins and zinc oxide, and their properties were compared to zinc chromate and zinc phosphate modified with molybdenum, which are commercial, well-known anticorrosive pigments. The results showed that primers with zinc tannates or formulated with conventional inhibitors exhibited similar behaviors [80]. Therefore, the replacement of zinc chromate or zinc phosphate by tannates is possible, and can positively contribute to the health of humans and the environment.

The research attention has been recently focused on rare-earth metal compounds as an alternative to common corrosion inhibitors that are toxic and environmentally un-friendly, such as zinc tetroxychromate. Among the rare-earth metals, lanthanum salts demonstrated good cathodic inhibition effectiveness [98,99]. In the literature, works about lanthanum incorporation in coatings are reported [100,101]. D'Alessandro et al. proposed an ecofriendly formulation of a primer immobilizing lanthanum ions by tannin macromolecules [84]. The outstanding protective action of primers containing lanthanum tannates is due to two contributions. On one side, tannins complexes with iron ions produce their typical crosslinked anticorrosive network. On the other side, modest amounts of lanthanum are slowly released, resulting in the precipitation of slightly soluble compounds of $La(OH)_3$ on the metal cathodic areas, that are alkalinized in corrosion conditions [84].

As commercial anticorrosive coatings are solvent-based coatings and release volatile organic compounds (VOCs), UV-curable coatings present many advantages, such as a high-speed cure, energy saving, and no VOCs emission [102–105]. However, the adhesion of UV-curable coatings to metal surfaces is limited, so UV-curable coatings need an underlying primer layer [106]. Acrylated tannic acid is a good bio-based adhesion promoter because it acts as a bridge between the steel surface and the coating (Figure 4, [79]) during the resin photo-crosslinking. The pull-off strength measured on a low-carbon steel plate with a tannin primer and UV-curable resin was 1.65 MPa, while it was measured at 0.44 MPa for a coated steel sample without the tannin primer [79]. Consequently, the adhesion improvement is associated with a significant enhancement of the corrosion protection property of the coating system.

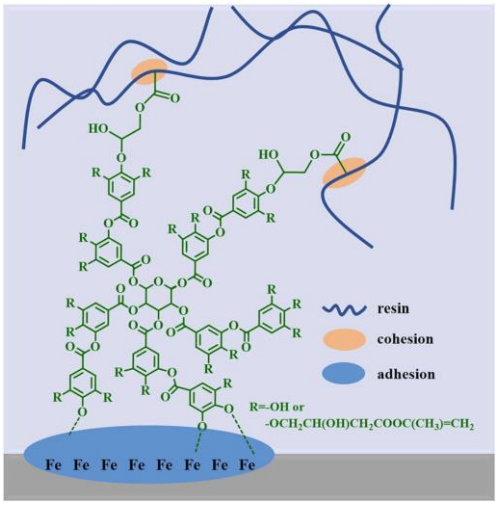

Figure 4. Scheme of the adhesion mechanism between steel surface and UV-curable coating through the contribution of the acrylated tannic acid. Reprinted with permission from [79], copyright 2022, Elsevier.

The ability of tannins to chelate iron (or zinc) ions is at the basis of their efficacy as anticorrosion coatings or primers. General rules for a rational selection of tannins based on their chelation ability are not easily identified. The availability of the catechol (with two adjacent OH groups) and pyrogallol or galloyl (with three adjacent OH groups) groups is for sure of great importance both for metal chelation and grafting to surfaces [107]. A larger chelant efficacy of pyrogallol is claimed somewhere and is correlated to the better behavior of some hydrolysable tannins [83] within coatings on steel rather than condensed ones. Chelation can also occur through the chetonic and adjacent OH group in condensed tannins, while the eventual glycosylation of OH groups can negatively affect the chelation ability. Another critical feature of tannins for the chelation ability is the molecular weight and polymerization degree [83,108]. An extract that contains higher molecular weight molecules shows greater chelating activity.

Film-forming ability is another critical requirement. Tannin coatings without a polymeric matrix or phosphoric acid are sometimes reported to be non-homogeneous and spot-like [88]. When a water solution is used to create thin coatings of polyphenols, partial oxidation followed by oligomerization decreases the solubility of polyphenols and, because of their grafting ability to surfaces, ultimately leads to surface deposition. A pH close to 8 and certain ionic strength (NaCl) favor this process.

On the other side, the high water solubility of tannins is related to the insolubility in apolar solvents and induces a higher film forming ability when they are dispersed into organic polymer formulations.

Table 2 summarizes the works on the exploitation of polyphenols as adhesion promoters and primers for the corrosion prevention of different types of steels and their main findings.

5. Polyphenols as Additives to Corrosion Protection Polymeric Coatings

The application of polymeric coatings provides an efficient way to protect metal surfaces from unwanted corrosion through the formation of an impermeable barrier to corrosive species or solutions [109–111]. Nevertheless, the prolonged exposure of the coating to the environment can develop "under coating corrosion" and lead to delamination, which is caused by the separation at the coating/metal interface [112].

Several surface pre-treatments have been tested for the steel substrates before corrosion protection coating deposition: degreasing and grinding [80,113,114], degreasing and blasting [115–117], grinding and etching [118], rusting [119], or surface preparation according to SSPC-SP5 and SP1 standards [88,120]. As specified by SSPC-Surface Preparation (SP)-1, a solvent is used to remove soluble substances from steel, such as oil, dirt, and drawing or cutting compounds [121]. Instead, SSPC-SP5 describes white metal blast cleaning as a method of achieving, by abrasive blasting media, a white or gray appearance steel surface that is uniformly free of all foreign matter [121].

The direct addition of corrosion inhibitors to polymeric coating formulations plays an important role in achieving high anticorrosive performance and extending the lifetime of coated metals [122]. Indeed, once the coating is damaged, the corrosion inhibitor additive can mitigate the corrosion process by decreasing its rate [123,124]. Therefore, anticorrosive additives have to be homogeneously dispersed in the polymeric coating to achieve a substantial enhancement of the protection by a barrier effect, cathodic protection, and inhibitory effect [125,126].

The inhibiting efficiency, toxicity level, and price are the specific parameters to assess the commercial value of anticorrosive additives [127]. Among the different types of synthetic anticorrosive additives, such as sulfonates, heterocyclic nitrogen compounds, chromates, and nitrites, a large number of corrosion inhibitors are expensive and, above all, toxic to human beings and environmentally unfriendly [128]. Hence, biodegradable, non-toxic, and ecological natural polyphenolic compounds can be employed as green additives to enhance the corrosion protection properties of coatings [129,130].

In the literature, many works about the incorporation of vegetal polyphenols are reported, and Table 3 schematically describes the type of steel, the kind of anticorrosive polyphenolic additive, the coating matrix used, and the main findings.

Montoya et al. studied two fractions extracted from Pinus radiata bark as additives to a two-component epoxy-polyamide resin [88]. The total phenol contents of the water-soluble fraction (WSF) and water-insoluble fraction (WIF) are similar, but the WSF is composed of a higher amount of flavonoid monomers than the WIF. Due to the greater percentages of catechin and taxifolin in the WSF, this polyphenolic fraction showed approximately 69% of antioxidant activity, while the antioxidant power of the WIF was measured at just over 21%. Moreover, the WSF presented a higher ability to form films on the metallic substrates compared to the WIF. The resulting significant difference suggested that the greater effectiveness of the WSF as an inhibitor, and the confirmation of better achievement in anticorrosive performance by the addition of WSF into coatings, came from EIS analysis and an accelerated corrosion test.

As can be seen in Table 3, many studies were conducted considering polyphenols-metal complexes as additives for polymeric corrosion protection coatings. For instance, zinc tannates are discovered to be appropriate pigments for replacing chromate or modified zinc phosphates in alkyd paints, thanks to their superior anticorrosive behavior [76,80].

Moreover, zinc oxides were used in combination with tannins as additives in corrosion protection polymeric coatings, showing improved corrosion resistance [102,105]. However, a certain reduction in the abrasion resistance was noticed in the presence of ZnO nanoparticles [102].

Other metal complexes have been investigated as alternative sustainable corrosion inhibitors to replace zinc and zinc compounds that are dangerous to the aquatic environment [131]. In order to reduce the zinc content in coatings formulations, Lamprakou et al. tested calcium tannates as an inhibitive pigment, added to epoxy organic coatings for steel protection [132]. Potentiodynamic polarization tests indicate the anodic reaction inhibition by calcium tannate due to the film formation on the steel, which was distinctly observed in SEM images (Figure 5b, [132]). In Figure 5a [132], the steel surface without the anticorrosive pigment, after dipping in a 3.5 wt.% NaCl solution, showed an increased surface porosity due to the iron oxides' formation, indicating the occurrence of corrosion. On the contrary, in the SEM image (Figure 5b, [132]) of the steel sample with calcium tannate, the protective film upon the surface is visible (blue circle pointed by blue arrow). Figure 5c [132] represents the mechanism of corrosion inhibition by calcium tannate as an additive to epoxy coatings, as proposed by Lamprakou et al. [132]. Briefly, the produced iron tannates efficiently protected the steel, anodically suppressing the corrosion, while calcium oxides and hydroxides were formed on the steel surface to provide further protection towards the cathodic regions and a barrier for the corrosive species transportation.

Cerium tannate [113] also resulted as a promising pigment to increase the corrosion protection of polymeric coatings. On the other hand, poor results were obtained with magnesium tannate [114], probably due to its scarce stability at neutral and acidic pH.

The presence of corrosion inhibitors in the polymeric coatings, such as tannins [120], tannin-based pigments (cerium tannate) [113], tannic acid in a proper carrier (mesoporous silica) [133], or cerium montmorillonite [134], can confer self-healing properties to a corrosion protection coating. In fact, the corrosion inhibitor can be released in the case of coating damage, allowing continuous metal protection.

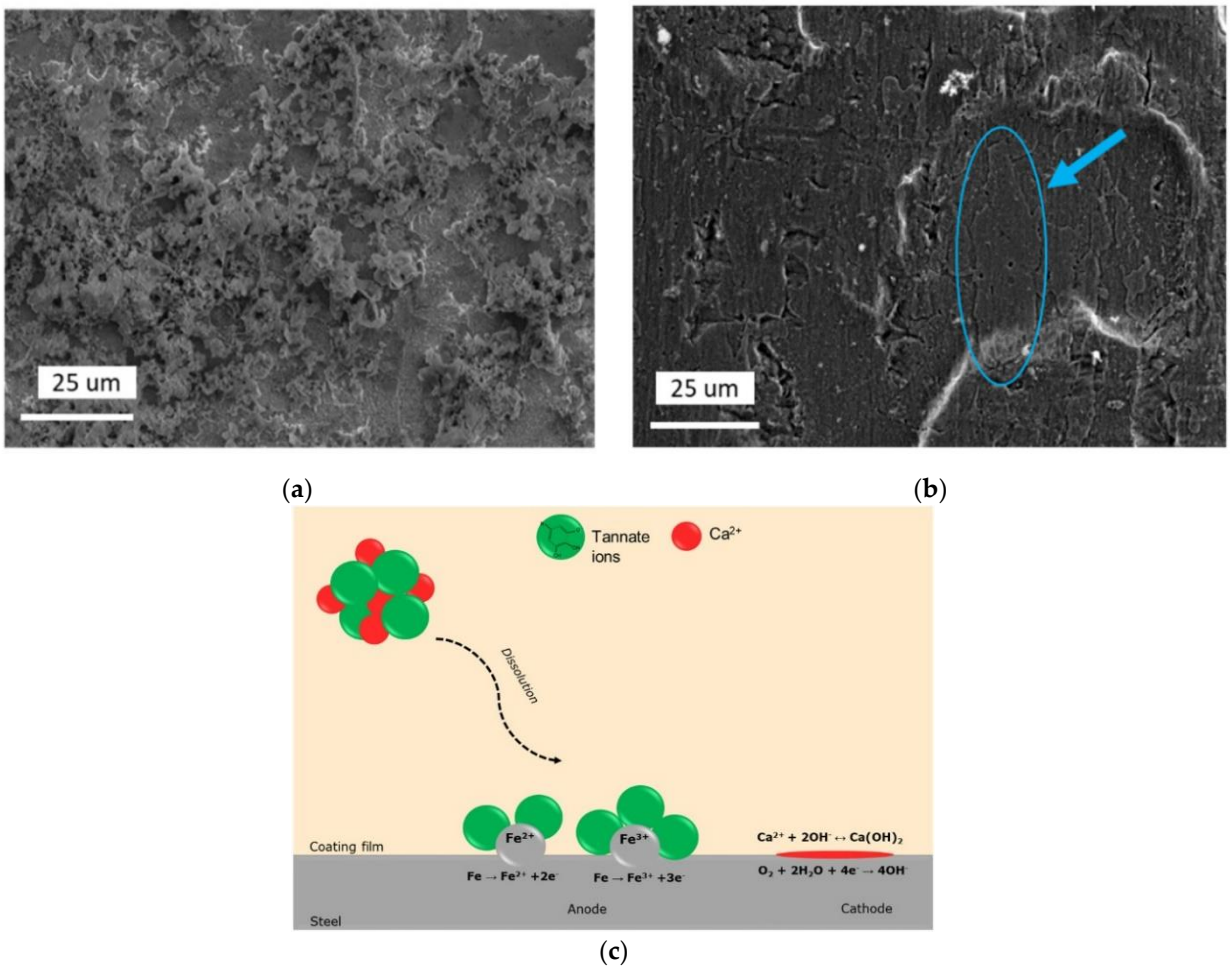

Figure 5. (**a**) SEM image of steel surface without inhibitive pigment after immersion in 3.5 wt.% NaCl solution for 2 h. Adapted under the terms of the CC−BY license from [132], copyright 2022, the authors, published by Elsevier; (**b**) SEM image of steel surface with calcium tannates after immersion in 3.5 wt.% NaCl solution for 2 h. Adapted under the terms of the CC−BY license from [132], copyright 2022, the authors, published by Elsevier; (**c**) Mechanism of corrosion protection by calcium tannates. Reproduced under the terms of the CC−BY license from [132], copyright 2022, the authors, published by Elsevier.

Tannic acid is the most widely used additive [113,119,133,134] together with tannins from different sources, such as tara [80], Pinus radiata [90,120], mangrove bark [135], quebracho [115], black wattle [114], and even tannins recovered from the wastewater of the vegetable tanning process [118]. In addition, acetylated kraft lignin [116] and tea polyphenols [117] have also been considered for these purposes.

The addition of polyphenols to polymeric formulations resulted in corrosion protection that is at least comparable with one of the coatings doped with a traditional corrosion inhibitor, improved adhesion, self-healing ability, and the possibility to add specific properties, such as UV protection, to the coating [116].

Table 3. Corrosion resistance and adhesion properties of coatings with polyphenols additives on different types of steels.

Substrate	Polymeric Coating	Additive	Application Strategy	Main Results	Reference
JIS G3141 mild steel (composition—0.15% C, 0.60% Mn, 0.05% S, 0.10% P) polished using a grinder and then manually with an emery paper no. 100, and then degreased with ethanol	Alkyd paint	Zinc tannate pigment prepared with tara powder and zinc oxide	Spray gun application of 2 coats of alkyd paint pigmented with zinc tannate (ATZ)	Results from salt spray tests proved that samples covered by ATZ paints had outstanding anticorrosive behavior compared to those with paints containing conventional pigments. The system with the ATZ paint and the topcoat of a synthetic, commercial, and white alkyd paint showed similar degrees of rusting and blistering to a system with zinc chromate. The adhesion was significantly increased by using ATZ paints.	[80]
1020 Steel with a surface preparation according to the SSPC SP5 and SP1 standards	Bisphenol A solvent-based epoxy resin, amide-based hardener, acrylic diluent as a solvent, R1 titanium dioxide, mica, calcined aluminum silicate, pigment dispersant, fumed silica, and a film leveling agent	The water-soluble fraction (WSF) and water-insoluble fraction (WIF) from industrial by-products of Pinus radiata	Pure tannins applications followed by drying in an environmental chamber at 25 °C, with a relative humidity of 60% and pH of 7, for periods of 12 h, 24 h, and 48 h. Tannins addition to an epoxy resin and spray coating (100 µm)	Polyphenols formed a protective film on steel, and the WSF fraction was more effective at this purpose and also at increasing the corrosion protection of epoxy-resin coating.	[88]
Steel grinded (600, 1200 grit) and degreased with acetone	Epoxy-ester resin (EER) (type EE-430CS, solid content: 60 wt%) and driers/accelerators, including cobalt (57%, as primary drier and autoxidation catalyst), lead (72%, as a secondary drier which activates the crosslinking steps of the coating), and calcium (41%, as an auxiliary drier)	Ce-TAA pigment obtained by the formation of a complex between the tannic acid and cerium nitrate	Introduction of the additive into the resin before curing, and resin application on the steel substrate.	The corrosion protection was increased. The release of the active inhibitor (Ce-TAA pigment) after the coating damage guaranteed corrosion protection.	[113]

Table 3. *Cont.*

Substrate	Polymeric Coating	Additive	Application Strategy	Main Results	Reference
Carbon steel samples (composition—0.108% C, 0.42% Mn, 0.12% Cr, 0.053% S, 0.016% P) degreased with acetone and polished with #150 sandpaper	Araldite® GZ 7071 × 75 epoxy resin and Aradur® 450 curing agent	Zinc tannate prepared by mixing black wattle tannins and 1 M $Zn(NO_3)\cdot 6H_2O$ solution. Magnesium tannate prepared by mixing black wattle tannins and 1 M $MnSO_4$ solution.	Brush-application	From pull-off test, no influence on the coating adherence by the introduction of zinc tannate and magnesium tannate pigments was proved. Results of EIS analysis and salt spray tests indicated the resin with zinc tannate as an excellent anticorrosion agent.	[114]
SAE 1010 steel panels degreased with toluene and sandblasted	Polyvinyl chloride (PVC) water-based anticorrosive system	Quebracho tannin-based pigment containing zinc oxide	Application of two coats of anticorrosive paints and then two coats of a topcoat white paint (PVC as a paint matrix and titanium dioxide as a unique pigment) by brushing	The best adhesion values were obtained for samples with the tannin-based coating. No brushing and rusting phenomena and no adhesion losses were noticed for samples coated with a paint pigmented with tannin after the humidity cabinet test as well as the salt fog test. The zinc tannate pigment was the most efficient in corrosion protection together with zinc phosphomolybdate.	[115]
SAE 1020 carbon steel blasted and degreased	DGEBA epoxy resin	Acetylated Kraft lignin	Addition of acetylated lignin to an epoxy resin before curing and coating application by paintbrush	The presence of lignin (7.5 and 15%) did not alter the curing process. Lignin added UV adsorption ability to the coating conferring UV protection of the resin. The corrosion protection of the coating was comparable with conventional coal tar epoxy.	[116]
Q235 steel pre-treated with a sandblasting machine	Epoxy matrix	Graphene nanosheets functionalized by tea polyphenols (TP/GE)	Addition of TP/GE (0.1, 0.3, and 0.6 wt.%) in an epoxy matrix (EP/TPG) and coating process on steel samples by immersion	TPG additive in an epoxy resin improved the coating barrier properties. The addition of 0.3 wt.% TP/GE widened the impedance arc, indicating the enhanced impenetrability and corrosion resistance of the coating. EP/TPG (0.3 wt.%) showed the lowest value of corrosion current density due to its excellent anticorrosive ability and it had the fewest corrosion products and bubbles after the spray test.	[117]

Table 3. *Cont.*

Substrate	Polymeric Coating	Additive	Application Strategy	Main Results	Reference
Mild steel cleaned by mechanical buffing and dilution with HCl	Phenol-formaldehyde matrix (PF)	Recovered tannins from wastewater from the vegetable tanning process	Application of a PF-recovered tannin resin (PFT) above mild steel	The introduction of tannins into a PF matrix enhanced the coating adhesion property. Thus, the PFT resin showed great resistance to alkali and acid conditions.	[118]
Rusted carbon steel	Epoxy resin E51	Tannic acid, limonene, and nano-ZrO_2	Tannic acid used, at first, as rust converted and also added to the resin together with limonene and nano-ZrO_2	The rust conversion layer protected the substrate and improved coating adhesion, tannic acid increased the stability of the coating, acting as a crosslinker and forming ferric tannates, limonene was able to adsorb to both steel substrate and tannic acid, improving coating performances, and finally, nano-ZrO_2 was effectively able to bind to tannic acid and limonene and fill the pinholes of the coating, improving the corrosion resistance.	[119]
ASTM A36 steel, surface preparation in accordance with SSPC SP5 and SP1 standards	Araldite GY 9513 (resin derived from Bisphenol-A) crosslinked with a polyamine Versamid®	Tannins from Pinus radiata and zinc oxide nanoparticles bare or silanized with 3-aminopropyltriethoxysilane (APTES)	Addition of Pinus radiata tannins and zinc oxide nanoparticles bare or silanized with 3-aminopropyltriethoxysilane (APTES) to the resin. Coating application by spray painting (150–200 μm)	Tannins increased the abrasion resistance of the coating while the ZnO nanoparticles were detrimental to this property. Functionalized ZnO nanoparticles increased the contact angle. Composite coatings improved steel corrosion resistance and exhibited self-healing properties.	[120]
Mild steel panels (Q panels from TQC sheen)	Epoxy resin-based coating	Calcium tannate obtained by the filtration of a mixture of commercial hydrolysable tannin and 1 M calcium nitrate ($Ca(NO_3)_2$)	Application of a calcium tannate 10 wt.% epoxy coating (CTE) by using a draw-down film applicator	In potentiodynamic polarization tests, a corrosion potential shift to more positive values was observed for the CTE-coated steel, suggesting the efficient anodically inhibition of the corrosion by calcium tannates. No adhesion losses for the CTE coating after 21 days of exposure to the salt spray chamber.	[132]

Table 3. *Cont.*

Substrate	Polymeric Coating	Additive	Application Strategy	Main Results	Reference
Q235 steel	Alkyd varnish coatings	Tannic acid loaded to silica mesoporous nanoparticles attached to Ti_3AlC_2 powder as an additive of the polymeric coating	Inclusion in the coating mixture and deposition on the substrate	The corrosion resistance was improved, and self-healing ability occurred due to the tannic acid released in the case of coating damage.	[133]
Q235 steel sheets	Waterborne polyurethane coating	Tannic acid functionalized cerium montmorillonite nanocomposites (TA@Ce-MMT)	Uniformly coating on steel surface at room temperature for 24 h and drying step at 50 °C for 2 days	The release of tannic acid and Ce^{3+} ions increased as the pH decreased and allowed a positive corrosion resistance to steel, producing TA-Fe^{3+} complexes. The TA@Ce-MMT markedly enhanced the long-term protection against corrosion due to the synergistic effect of tannic acid and Ce^{3+} ions.	[134]
Mild steel (composition -wt.%—0.22 C, 1.30 Mn, 0.035 S, 0.35 silicone, 0.035 phosphate)	Paralux P268HS, an epoxy high solid zinc phosphate primer (Paralux P268HS)	Tannin extracted from Rhizophora apiculate mangrove bark	Zinc tannates (TZn) were produced by mixing 1 M zinc nitrate and tannin solution at pH 4 for 24 h. Five paints with different amounts of TZn were obtained by stirring for 1 h and cured in an oven at 35 °C for 3 h after their application on the steel samples	Weight loss measurements in 3.1 wt.% NaCl in 20 L of artificial seawater for 45 days showed that paint with tannin exhibited an excellent corrosion inhibition effect. The efficiency of the corrosion protection increased along with the tannin content in the paint (93.9% for paint with 6 g of TZn). EIS results demonstrated the improvement of coating barrier properties and layer strengthening due to the TZn addition to the paint. A decrease in the damage of TZn-epoxy coated steel was observed through SEM analysis.	[135]

6. Conclusions and Future Perspectives

Steel, especially carbon steel, is significantly affected by corrosion phenomena which can hamper its functionalities with important consequences in terms of costs and environmental impacts. For these reasons, the individuation of suitable strategies to prevent steel corrosion is a critical need in many application fields.

The direct protection of metallic surfaces can be obtained by means of several kinds of surface treatments and coatings, starting from rust converters to multi-layer coatings for corrosion protection. All these strategies are key research topics in which the role of green corrosion protection substances, such as polyphenols, is gaining increasing interest.

Polyphenols are promising substances for the preparation of surface treatments and coatings for the corrosion protection of steels because of their corrosion protection properties and high affinity for metallic surfaces. Moreover, polyphenols are non-toxic substances that can be easily obtained from many by-products of agri-food industries with a circular and environmentally friendly approach.

Polyphenols-based rust converters are mainly based on tannins and phosphoric acid. The reaction with rust produces insoluble iron tannates that are able to protect steel from corrosion. These compounds can treat complex surfaces and large areas where conventional rust removal is not applicable. Performances that are at least comparable with conventional rust converters are obtained with the polyphenol-based ones. A certain variability in the effectiveness of this strategy is, for all kinds of rust converters, related to the type of rust, incomplete removal of it, and operating conditions (e.g., temperature).

The use of polyphenols as the active constituent of corrosion protection coatings based on the coordination bonds' formation is, actually, the less explored strategy. However, some encouraging results have been obtained, suggesting that further research should be performed for the obtainment of green and environmentally friendly corrosion protection coatings.

Adhesion promoters and primers act as barrier layers in contact with the metallic surface, and are able to protect the metal and improve the compatibility between the metal itself and the corrosion protection coating. The polyphenols' presence provides protection, even in the case of coating damage. Tannins, or more often, metal tannates, have been used in combination with polymeric matrices or phosphoric acid as effective primers for corrosion protection.

Polyphenols have been successfully used as additives to polymeric corrosion protection coatings in order to substitute polluting and toxic additives for the improvement of coating performances, such as greater continuity and a lower porosity of coating film, and to confer the self-healing ability to them. Upon the coating damage, in fact, polyphenols can be released (instead of chromates, as an example) to act as corrosion protection agents. Moreover, specific functionalities, such as UV protection or self-healing ability, can be added to the coating by the polyphenols' addition.

Author Contributions: Writing—original draft preparation: R.S. and S.F.; writing—editing: R.S., S.S. and S.F.; writing—review: S.S. and M.S.; visualization: R.S.; supervision: S.S. and M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Acknowledgments: MUR is acknowledged for funding R. Sesia's fellowship (MUR—D.M.1061/2021—Dottorati di ricerca su tematiche green e dell'innovazione: nuove risorse dal PON Ricerca e Innovazione). Silvateam S.p.a. is acknowledged for the collaboration.

Conflicts of Interest: The authors declare no conflict of interest.

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