

Article

The Influence of Organic Modifiers on the Formation and Anticorrosion Properties of Phosphate Coatings on Steel

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Highlights

What are the main findings?

- Catechol acted as the most effective dihydroxybenzene modifier of phosphate coatings on St20 steel.
- Catechol-modified coatings showed higher resistance than coatings without the accelerator or with NaNO_2 , confirmed by static and flow-through electrochemical tests.
- Raman and electrochemical data suggest that catechol reduces effective coating porosity and modifies the phosphate layer.

What are the implications of the main findings?

- Low-molecular-weight phenolic compounds can be promising alternatives to conventional phosphating accelerators.
- Catechol-modified phosphate layers can serve as effective pretreatments for subsequent acrylic paint coatings.
- Combining static and flow-through corrosion tests allows for a comprehensive evaluation of phosphate coating stability.

Abstract

The formation of phosphate conversion coatings on St20 low-carbon steel was studied in order to evaluate the effect of organic accelerators on coating formation and protective performance. The influence of pH, temperature, treatment time, and stirring rate on coating formation was studied by gravimetry and SEM-EDS, the influence of accelerators was studied by Raman spectroscopy, salt spray testing, polarization measurements, EIS, and dynamic LPR monitoring. Efficient coating formation was achieved at an initial pH of 3.0, elevated temperature, and intensive stirring; the process showed diffusion-controlled behavior with an apparent activation energy of 28 kJ/mol. Sodium nitrite accelerated coating formation but did not increase the limiting coating mass. Among the organic additives, catechol provided the most pronounced improvement in corrosion resistance, which was attributed to lower effective porosity and possible incorporation of catechol-derived oxidized fragments into the phosphate layer. The catechol-modified coating also improved electrochemical resistance and did not impair the adhesion of subsequent acrylic paint. These results indicate that catechol is a promising organic modifier for zinc phosphate intermediate pretreatment layers.



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1. Introduction

Phosphate conversion coatings remain one of the most widely used methods for the chemical pretreatment of steel surfaces owing to the technological simplicity of the process, its relatively low cost, and its ability to improve the corrosion resistance of metals and enhance the adhesion of subsequent functional layers, including paint coatings [1–3]. Despite their long history of application, interest in phosphate systems has not decreased, since the requirements for coating uniformity, density, and protective ability are becoming increasingly stringent, while phosphating processes themselves are being modified in view of environmental and technological restrictions.

In recent years, considerable attention has been paid to clarifying the mechanism of zinc phosphate coating formation on iron-based substrates. In general, this process is associated with electrochemical dissolution of the metal in an acidic phosphating medium, hydrogen evolution at cathodic sites, a local increase in pH near the surface, and subsequent crystallization of zinc and iron phosphates [3,4]. Jiang et al., in their study of phosphate coatings on alloy steel, showed that layer formation can be described as a sequence of stages: electrochemical dissolution of the substrate, the formation of an amorphous phase, and phosphate crystallization and growth, followed by the establishment of a dynamic equilibrium between coating formation and partial dissolution [3].

The structure and phase composition of the coating are substantially affected not only by the composition of the phosphating solution, but also by the substrate microstructure, pH, and process temperature [2–5]. Alinezhadfar et al. investigated the formation of zinc phosphate coatings on steel and ferritic iron at different pH values and temperatures and showed that increasing the temperature accelerates the growth of phosphate crystals, whereas pH determines the balance between surface coating growth and bulk precipitation of the phosphate phase [4]. These data emphasize that the performance properties of phosphate coatings are largely determined at the early stages of layer formation and depend on the balance between substrate dissolution, local pH changes, and crystallization of the phosphate phase. Therefore, phosphating should be considered as a process of phosphate precipitation from the solution that is sensitive to the microstructure, defectiveness, and electrochemical activity of the steel.

In parallel with mechanistic studies, research is being developed toward the search for more efficient and environmentally acceptable phosphating accelerators and modifiers. Nitrites, nitrates, chlorates, molybdates, as well as metal cations, are traditionally used to accelerate the process [1–3]; however, environmental restrictions stimulate the search for alternative additives [6,7]. Recent studies show that changing the nature of the additive allows us to control the coating formation rate, crystal size, layer density, and electrochemical behavior [6–10]. For instance, Wang et al. introduced black phosphorus nanosheets into the phosphating solution and showed that, at an optimum concentration, a denser and more uniform coating is formed, while the corrosion rate decreases by an order of magnitude [6]. Tian et al. used α -zirconium phosphate as an accelerator for the phosphating of carbon steel, reducing the size of phosphate crystals, decreasing coating roughness, and also decreasing the corrosion rate [7]. In a later study, Tian et al. proposed the use of fly ash as an accessible and more environmentally acceptable phosphating accelerator. It was shown that the addition of fly ash promotes the formation of a denser and finer-crystalline

coating, reduces its porosity, decreases the corrosion rate, and sharply lowers the friction coefficient of the coating [8].

Particular attention is paid to two-dimensional and oxide nanoadditives, which can act as nucleation centers and simultaneously improve the barrier properties of the coating. Huang et al. showed that the introduction of boron nitride nanosheets into a zinc phosphate bath leads to a decrease in crystal size, the formation of a denser layer, and a reduction in corrosion current compared with an unmodified coating [9]. Bautin et al. studied the effect of graphene oxide on phosphate coatings of low-carbon steel and found that its effect depends on the testing medium: in neutral NaCl solution, the additive improved anticorrosion properties, whereas in an acidified sulfate medium, the deterioration of protective performance was observed [10]. In the work of Barsana et al., the incorporation of nanocrystalline CeO_2 and a CeO_2 –CuO nanocomposite into zinc phosphate coatings on steel promoted the formation of a more compact layer, reduced iron content in the coating, and substantially decreased the corrosion rate [11].

Along with inorganic and nanosized additives, organic modifiers of phosphate coatings have also been considered in recent years, since these modifiers may affect not only the deposition rate of the phosphate layer, but also steel dissolution, local redox processes, hydrogen evolution, and filling of coating defects. Their action is usually associated with the presence of functional groups capable of adsorbing on the steel surface, forming complexes with metal ions, and changing the nucleation conditions of the phosphate phase. Bold et al. studied the formation of phosphate coatings in the presence of nitrophenol, sodium *m*-nitrobenzenesulfonate, and hydroxylamine, showing that the nature of the nitrogen-containing accelerator substantially affects the protective properties, thickness, and adhesion of the coating [12]. Amini et al. investigated the addition of poly(vinyl alcohol) (PVA) to a phosphating solution and showed that this additive decreases the size of phosphate crystals, increases their population density, and reduces the corrosion rate due to the formation of Zn–PVA and Fe–PVA complexes [13]. In a related study, Ramezan-zadeh et al. used PVA as a “green” inhibitor in a zinc phosphate bath and found that such modification improves the adhesion of the subsequent epoxy coating and reduces cathodic delamination [14].

Another approach involves the use of organic compounds with surface-active or film-forming properties. Abd-El-Nabey et al. studied the effect of Tween-80 on zinc phosphate coatings on steel and showed that the introduction of this surfactant decreases coating porosity, increases charge transfer resistance, and improves protective efficiency [15]. Liu et al. investigated polyethylene glycol (PEG) as an additive to zinc phosphate coatings on carbon steel; the authors showed that PEG can act as a “precipitation substrate” for capturing metal ions, facilitate nucleation of coating crystals, and provide a dense and corrosion-resistant coating [16]. In a later study, Barsana et al. introduced poly(vinyl pyrrolidone) (PVP) into a zinc phosphate coating on mild steel and observed a decrease in crystallite size, reduced cracking, and a more than sixfold decrease in the corrosion rate in a neutral medium [17].

Thus, the available data indicate that organic additives can affect the formation and protective properties of phosphate coatings; however, the literature mainly focuses on polymeric compounds and surfactants, with lower-molecular-weight organic modifiers having been studied much less extensively. In this context, the use of hydroquinone (1,4-dihydroxybenzene) in phosphate coatings is of particular interest, since in phosphating solutions it can act simultaneously as an accelerator and as a reducing agent, i.e., an antioxidant [18,19]. Presumably, hydroquinone inhibits the oxidation of Fe^{2+} and also increases the hydrogen overpotential.

There exist three dihydroxybenzene isomers: hydroquinone (1,4-dihydroxybenzene), catechol (1,2-dihydroxybenzene) and resorcinol (1,3-dihydroxybenzene), and the different arrangement in hydroxyl groups in their structures may lead to markedly different behaviors in coating formation, affecting their redox behavior, complexing ability, and tendency toward oxidation or further polymerization. This is supported by voltammetric data: the oxidation peaks of hydroquinone, catechol, and resorcinol on a modified glassy carbon electrode were reported at 166, 277, and 660 mV vs. Ag/AgCl, respectively [20]. These values indicate pronounced differences in the redox activity of the three isomers: hydroquinone and catechol are oxidized at lower potentials than resorcinol. Therefore, their effect on interfacial redox processes during phosphating may be different. However, unlike hydroquinone, these compounds have practically not been systematically considered as modifiers or accelerators of phosphate coating formation, making their comparative study in phosphating systems of particular interest, since a systematic comparison of the effects of isomeric dihydroxybenzenes on the formation and protective properties of zinc phosphate coatings on steel is absent.

In this regard, the aim of the present work was to investigate the effect of organic modifiers, including isomeric dihydroxybenzenes, on the formation of zinc phosphate coatings on a steel surface and to compare their action with that of a traditional inorganic accelerator, sodium nitrite.

2. Materials and Methods

2.1. Synthesis of the Coatings

Steel plates of grade St20 (a low-carbon structural steel close in composition to AISI/SAE 1020) were used as substrates. According to elemental analysis, the steel contained 99.02 wt.% Fe, 0.38 wt.% Mn, 0.28 wt.% Si, and 0.32 wt.% Al.

The surface of the initial steel plates was mechanically treated using abrasive papers a belt grinder equipped with an 80-grit abrasive belt. Grinding was carried out for 5 min.

Phosphating was performed in an experimental setup consisting of a glass reactor used for preparing the phosphate solution and for carrying out the phosphating process by immersing the steel plates into the solution. Heating and temperature control were provided using an LOIP LT-200 liquid thermostat (LOIP Instrument, Saint Petersburg, Russia), while stirring was performed using an AREC Heating Magnetic Stirrer (VELP Scientifica, Usmate, Italy). The pH and temperature of the solution were measured and controlled using a pH-150MI pH meter (Izmeritelnaya Tekhnika, Moscow, Russia) equipped with a combined electrode and a temperature sensor. The obtained phosphate coatings were characterized by the change in sample mass using a Shimadzu AX200 electronic balance (Shimadzu, Kyoto, Japan) with a readability of 0.0001 g. The mass gain of the coatings was normalized to the total geometric surface area of the steel plates.

The phosphate solution contained ZnO (1.16 g/L), HNO₃ (0.614 mL/L), and H₃PO₄ (1.472 mL/L). The initial pH of the phosphate bath (pH₀) was adjusted to the required value by adding NaOH solution before immersion of the steel sample. Sodium nitrite or organic modifiers were added to the phosphate bath when required; the concentration of the modifiers used for comparative experiments was 0.15 g/L. This concentration was selected for comparative experiments and was not optimized in the present study.

2.2. Characterization and Performance Testing of the Coatings

The elemental composition and morphology of the coatings were studied using a JSM-6610LV scanning electron microscope (JEOL, Akishima, Tokyo, Japan) equipped with an energy-dispersive X-ray microanalysis system.

The chemical structure of the coatings was analyzed using a Solver Spectrum Raman spectrometer (NT-MDT Spectrum Instruments, Moscow, Russia). The spectra were recorded using laser excitation at 473 nm. A 600/600 diffraction grating was used for signal registration, providing a spectral resolution of 4 cm^{-1} .

The adhesion properties were evaluated via the cross-cut test using a BGD 502/2A adhesion tester (Biuged Precise Instruments, Guangzhou, China), with a grid of 49 squares of $1\text{ mm} \times 1\text{ mm}$.

The protective ability of the phosphate coatings was assessed using a visual drop test, in which the stability criterion was the time required for a drop of concentrated CuSO_4 solution containing NaCl (CuSO_4 , 82 g/L; NaCl , 33 g/L; HCl , 13 mL/L) to change color from blue-green to red, caused by the corrosion of the steel substrate through defects and pores of the coating, followed by the reduction of Cu^{2+} ions from the test solution and deposition of metallic copper on the exposed steel surface.

The anticorrosion properties of the samples were also evaluated in a salt spray chamber (Dongguan Tianshuo Testing Equipment, Dongguan, China) in accordance with ISO 7523–2001 at $35\text{ }^\circ\text{C}$ using a 50 g/L NaCl solution for different exposure times.

2.3. Electrochemical Measurements

Electrochemical studies were carried out using a Metrohm Autolab PGSTAT302N potentiostat-galvanostat (Metrohm Autolab, Utrecht, The Netherlands) in a standard three-electrode corrosion cell. Steel samples with and without phosphate coatings were used as working electrodes. An Ag/AgCl electrode in 3 M KCl was used as the reference electrode, a graphite rod served as the counter electrode.

Measurements were performed under stationary conditions. Before recording polarization curves, the working electrode was kept in the solution until a stable open-circuit potential (OCP) was established. Polarization measurements were performed within a potential range of ± 10 – 20 mV relative to OCP at a potential scan rate of 0.1 mV/s .

Electrochemical impedance spectra (EIS), presented as Nyquist plots, were recorded using an AC signal amplitude of 10 mV over a frequency range from 10^{-3} to 10^4 Hz . Quantitative analysis of the impedance spectra was carried out using an equivalent electrical circuit consisting of the solution resistance R_s , the charge transfer resistance R_p , and a constant phase element (CPE), which accounts for the non-ideal capacitive behavior of the electrical double layer and surface heterogeneity of the studied samples.

The corrosion current density i_{corr} (A/cm^2), was calculated using the Stern–Geary equation according to ASTM G59–23 and ASTM G102–23:

$$i = \frac{B}{R_p} \quad (1)$$

where $R_p \approx R_{ct}$ is the charge transfer resistance (Ω), and B is the Stern–Geary constant, calculated as follows:

$$B = \frac{\beta_c \beta_a}{2.303(\beta_c + \beta_a)} \quad (2)$$

where β_c and β_a are the cathodic and anodic Tafel slopes, respectively, obtained from the Tafel plots (V/dec).

The corrosion rate CR (mm/year), was calculated according to ASTM G102–23 using the standard relationship accounting for the equivalent weight and density of steel:

$$\text{CR} = \frac{K \cdot i_{\text{corr}} \cdot \text{EW}}{\rho} \quad (3)$$

where $K = 0.00327$ for CR expressed in mm/year, EW is the equivalent weight of steel, taken as 28.25 g/equiv (mass of metal corresponding to one equivalent of electrochemical dissolution of iron to Fe^{2+} , taking into account the composition of steel), and ρ is the steel density, taken as 7.85 g/cm³.

The protective efficiency of the coatings was evaluated using the degree of protection Z (%), and the corrosion inhibition coefficient γ , calculated according to the following equations:

$$Z = \frac{\text{CR}_0 - \text{CR}}{\text{CR}_0} \times 100\% \quad (4)$$

$$\gamma = \frac{\text{CR}_0}{\text{CR}} \quad (5)$$

where CR_0 is the corrosion rate of the reference sample series in the electrolyte without inhibitor (mm/year); CR is the corrosion rate of the sample series in the electrolyte with inhibitor (mm/year).

Additional measurements of the corrosion rates were performed using a laboratory flow-through electrochemical setup, based on a Monikor-2M corrosion monitoring unit (Akrus-M, Ufa, Russia) operating by the linear polarization resistance (LPR) method. The system included a circulation loop with a pump providing a controlled flow rate of the test medium of 10 L/min. The measuring unit was connected to a flow cell consisting of four cylindrical stainless-steel blocks, into which cylindrical steel electrodes (grade St20) were mounted. The geometry of the cell and electrodes, with an internal cylindrical working surface, was selected to reproduce corrosion processes occurring on the inner walls of pipelines. The electrodes were electrically isolated from each other using transparent inorganic glass sleeves, allowing for visual observation of the processes occurring in the flowing medium.

Signals from the sensors and the Monikor-2M measuring unit were recorded using a computerized data acquisition system with automated processing, including calculation of the corrosion rate. The degree of protection, Z (%), and the protection coefficient, γ , were calculated in accordance with Equations (4) and (5).

A model saline electrolyte was used as the test medium for all electrochemical studies. Its composition was as follows (g/L): CaCl_2 , 11.66; NaCl , 6.27; MgCl_2 , 5.64; K_2HPO_4 , 0.314; KCl , 0.068; and NaBr , 0.05.

3. Results and Discussion

3.1. Effect of Phosphating Conditions on Coating Formation

The optimal conditions for phosphate coating deposition were determined by studying the effects of the phosphating parameters, including solution pH, temperature, treatment time, and stirring rate.

According to the literature, the optimal pH range for immersion phosphating is usually reported to be 2.7–3.2 [1–3]. In the pH range of 2–4, the phase composition of the solution and the solid phases in equilibrium with it change substantially. At $\text{pH} < 2.2$, regardless of the Zn^{2+} concentration in the solution, the solvated undissociated H_3PO_4 form predominates. An increase in pH leads to its dissociation with the formation of H_2PO_4^- anions. A further increase in pH to 3–4 results in bulk precipitation of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Classical crystallization theory considers two nucleation mechanisms: homogeneous and heterogeneous nucleation [21]. In both cases, the parameter determining the possibility of precipitate formation is the Gibbs energy of nucleation:

$$\Delta G_{\text{nuc}} = \frac{4\pi}{3} \sigma r_{\text{cr}}^2 \quad (6)$$

where σ is the surface tension, J/m^2 , and r_{cr} is the critical nucleus radius, m.

In the case of homogeneous nucleation, occurring in the bulk solution, σ refers to the surface tension of the forming nucleus. In the case of heterogeneous nucleation, it corresponds to the interfacial tension. Thus, during phosphating, this parameter is related to the surface tension of the steel plate on which the coating is deposited. In general, $\sigma_{\text{het}} < \sigma_{\text{hom}}$ and, consequently, $\Delta G_{\text{het}} < \Delta G_{\text{hom}}$ [21]. For this reason, the actual pH of phosphate coating deposition is lower than the corresponding equilibrium pH for homogeneous precipitation; therefore, zinc phosphate formation on the metal plate occurs at $\text{pH} < 3\text{--}4$.

Increasing the temperature changes the system such that the pH range in which $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ precipitates becomes narrower. From the standpoint of phosphating, this is important because the actual pH of coating formation increases, and therefore, the real process conditions must be adjusted accordingly. To verify this assumption, a series of phosphating experiments were carried out at 70°C , 1000 rpm, and different initial pH values. The experimental results are shown in Figure 1.

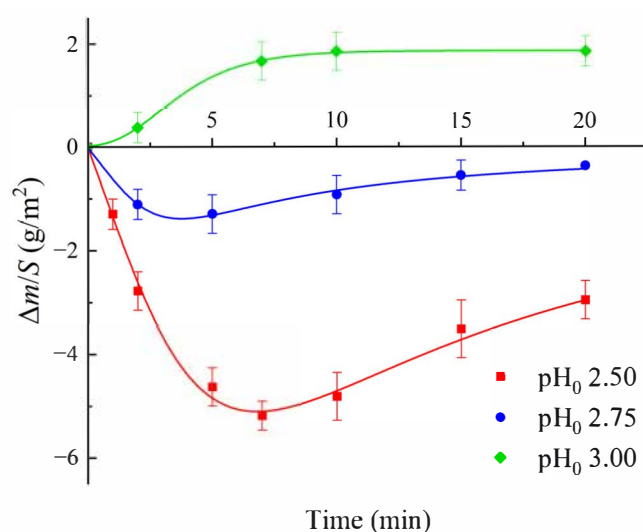


Figure 1. Time profiles of the specific mass change of phosphate coatings depending on the initial pH of phosphating: experimental data (symbols), standard deviations (error bars), smoothing curves drawn (lines).

A positive final mass change of the sample was observed only at an initial pH of 3.00 ($\text{pH}_0 = 3.00$). At lower initial pH values, etching of the sample surface occurred, presumably due to an excess of free H^+ ions in the bulk solution. This was confirmed by intense bubble formation on the surface of the samples, observed throughout the experiment under these conditions, most likely according to the following reaction:



The presence of iron ions in the solution after phosphate treatment was confirmed qualitatively using a reaction with potassium hexacyanoferrate, $\text{K}_4[\text{Fe}(\text{CN})_6]$. This observation supports the assumption that partial dissolution of the steel surface occurs during phosphate coating formation.

Therefore, it can be concluded that at excessively low pH values, etching dominates and coating growth becomes inefficient; at the selected pH range, dissolution and phosphate precipitation are balanced, resulting in the formation of a protective conversion coating.

The pH was also monitored during phosphating at an initial pH of 3.00. A typical time profile of pH variation recorded at 70°C and 1000 rpm is shown in Figure 2.

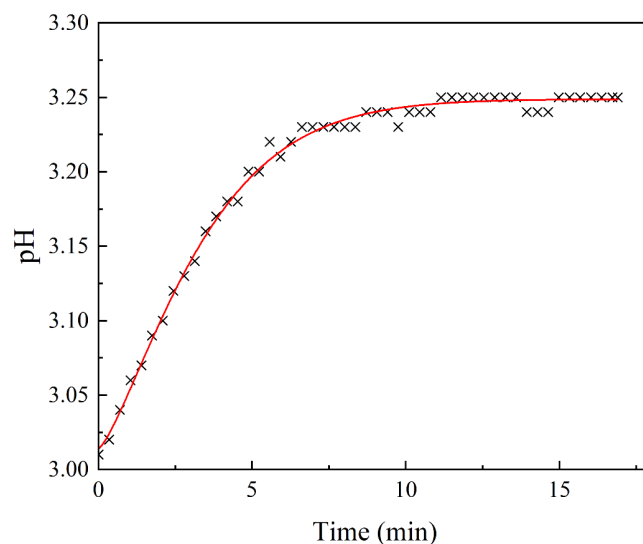


Figure 2. pH variation during the phosphating process: experimental data (cross symbols) and smoothing curve (red line).

The pH variation curve generally coincides with the corresponding mass change curve of the coating (Figure 1, $\text{pH}_0 = 3.00$). After 10 min of phosphating, both the pH and coating mass values were nearly stabilized, and further treatment resulted only in minor changes. Therefore, it can be assumed that a phosphating time of approximately 5–10 min is sufficient under these conditions.

Another important feature observed in Figure 2 is the final pH value of the phosphating solution, which reached 3.25. Evidently, a further increase in the initial pH leads to the precipitation of the $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ phase in the solution bulk via a homogeneous crystallization mechanism. Thus, coating formation proceeds until bulk precipitation begins. This determines the rational pH range for phosphating under these conditions as not higher than 3.0–3.2, which is in good agreement with the literature data [1–3].

To study the effect of process temperature on phosphating, a series of experiments was carried out at $\text{pH}_0 = 3.00$, 1000 rpm, and temperatures of 50, 60, and 70 °C. The obtained results are shown in Figure 3.

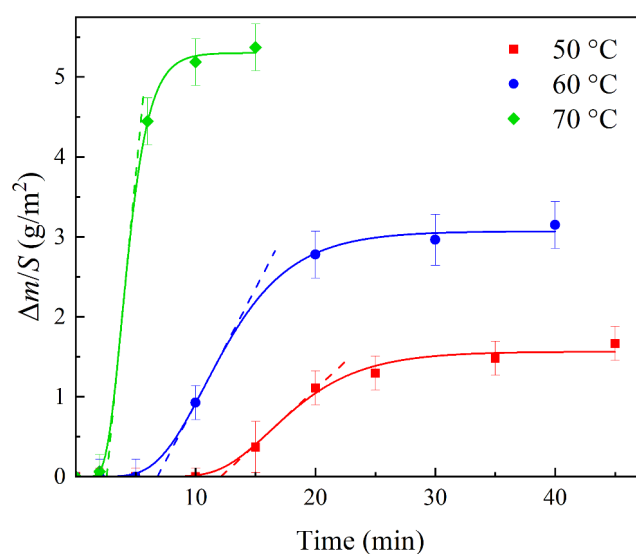


Figure 3. Time profiles of the specific mass change of phosphate coatings depending on the phosphating temperature: experimental data (symbols), standard deviations (error bars), smoothing curves drawn (lines) and linear approximations used to estimate the coating formation rate (dashed lines).

As can be seen from Figure 3, increasing the temperature simultaneously increases both the phosphating rate, estimated from the slope of the main part of the sigmoidal mass change curve, and the final limiting value of the specific mass change, from 1.9 g/m² at 50 °C to 5.7 g/m² at 70 °C. At the same time, the duration of the initial induction period preceding the exponential growth region decreases with increasing temperature. These observations indicate a significant acceleration of phosphate coating formation with a relatively small increase in temperature from 50 to 70 °C.

To further clarify the coating formation mechanism, the activation energy of the process was calculated under the studied conditions. To estimate the growth rate constants, k (s^{−1}) the values of the half-conversion time, $\tau_{50\%}$ (min) were used without accounting for the induction period. The rate constant was calculated according to the following equation:

$$k = \frac{\ln 2}{60 \cdot \tau_{50\%}} \quad (8)$$

The calculated k values were $1.97 \times 10^{-3} \text{ s}^{-1}$ at 50 °C, $2.15 \times 10^{-3} \text{ s}^{-1}$ at 60 °C, and $2.69 \times 10^{-3} \text{ s}^{-1}$ at 70 °C. These rate constants were then plotted in Arrhenius coordinates, $\ln k$ versus $1/T$ (Figure 4).

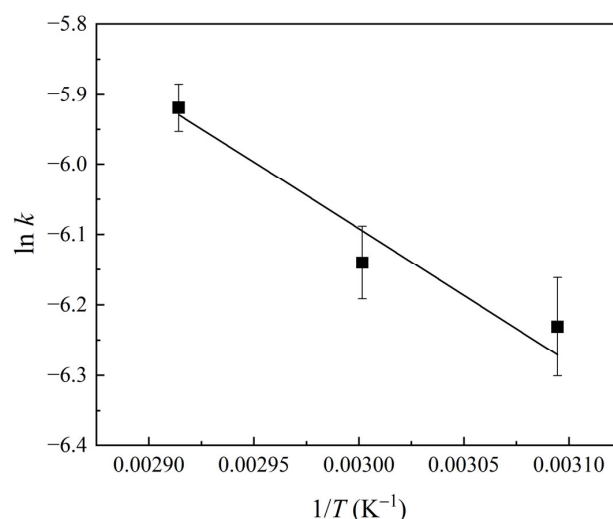


Figure 4. Temperature dependence of phosphate coating formation rate constant: experimental values (black squares), standard deviations (error bars) and linear fit (line).

The activation energy was found to be 28 kJ/mol. This value indicates a diffusion-controlled character of the process; that is, under the studied conditions, phosphate coating formation is limited by ion transport through the porous layer already formed on the surface. These results are in good agreement with similar literature data [4,5].

SEM was used to study the effect of temperature on the morphology of the formed coatings. Representative micrographs of phosphate coatings obtained at 50 and 70 °C, pH₀ = 3.00, and 1000 rpm are shown in Figure 5, while the elemental composition of the coatings is given in Table 1.

Table 1. Elemental composition of steel plates after phosphating at different temperatures according to SEM-EDS analysis.

Temperature, °C	Element Content, wt.%					
	O	Al	P	Mn	Fe	Zn
50	18.26	0.29	6.28	0.14	62.74	12.28
70	33.13	0.30	12.15	0.12	38.94	15.36

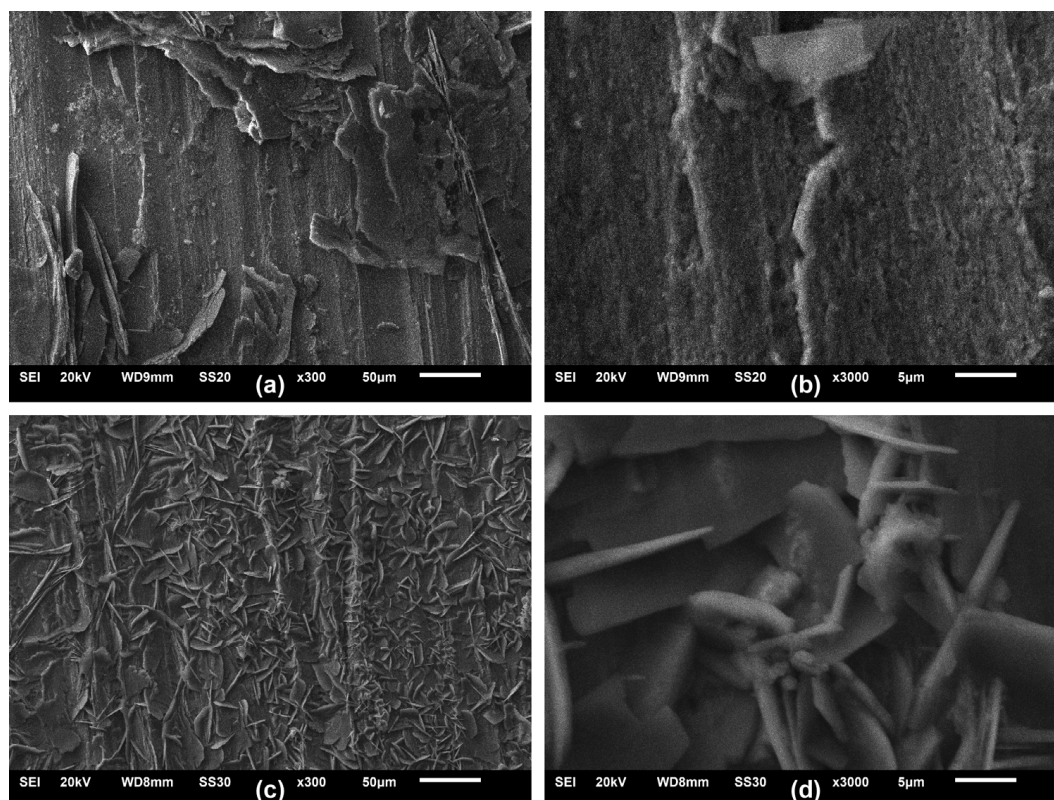


Figure 5. SEM micrographs of the sample surface after phosphating at 50 (a,b) and 70 °C (c,d), at magnifications 300× (a,c) and 3000× (b,d).

For the sample phosphated at 50 °C (Figure 5a,b), thin multilayer platelets were observed. This indicates that the coating was formed predominantly through crystal growth; that is, the rate of heterogeneous crystal nucleation was lower than the crystal growth rate, consistent with classical crystallization theory [21].

The elemental composition (Table 1) indicates that the formed coating mainly contains Fe, Zn, P, and O; therefore, it is most likely composed of iron and zinc phosphates. The substrate is observed beneath the crystals, which is confirmed by elemental mapping data (Figure 6).

Increasing the temperature to 70 °C (Figure 5c,d) leads to the formation of a continuous sponge-like layer without clearly distinguishable crystals or platelets. This indicates rapid and nearly complete reaction progress. The characteristic rounded channels reflect the course of the reaction and can be regarded as residual “craters” formed after the detachment of hydrogen bubbles evolved during phosphating. The absence of clearly expressed crystal morphology and the continuity of the layer indicate that the nucleation rate was higher than the crystal growth rate. Therefore, elevated temperatures are favorable for phosphate coating formation using this composition; in particular, temperatures not lower than 60–70 °C are preferable for obtaining a continuous coating.

It should also be noted that, even at elevated temperatures, analysis of the solution using potassium hexacyanoferrate, $K_4[Fe(CN)_6]$, indicated the presence of Fe^{3+} cations. This suggests partial etching of the surface even under conditions favorable for coating deposition.

To study the effect of stirring rate on phosphate coating formation, an additional experiment was carried out at a lower stirring rate of 200 rpm, while keeping the other conditions unchanged: 70 °C and $pH_0 = 3.00$. The results are shown in Figure 7.

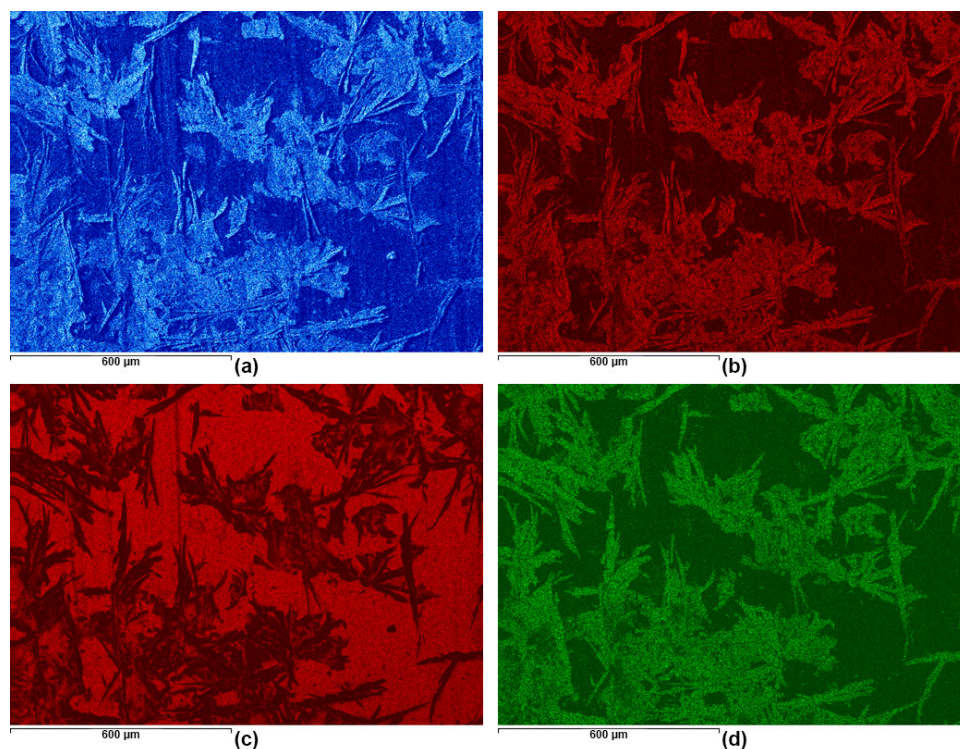


Figure 6. Elemental mapping results for the St20 steel sample after phosphating at 50 °C: (a) O; (b) P; (c) Fe; (d) Zn.

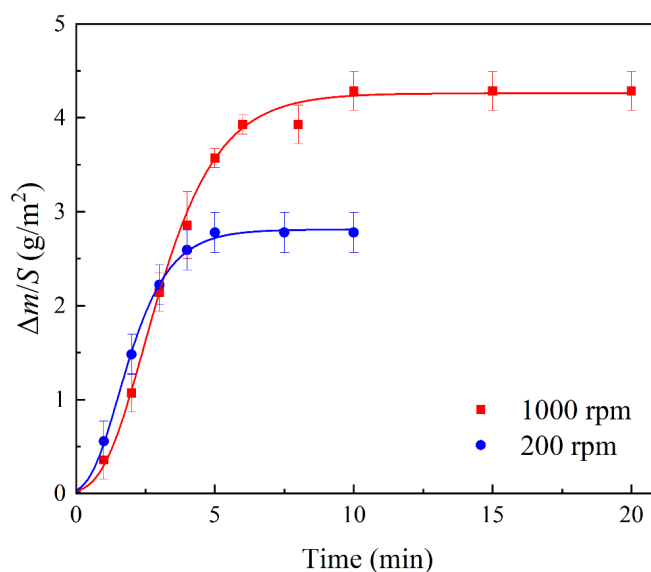


Figure 7. Time profiles of the specific mass change of the coatings depending on the stirring rate: experimental data (symbols), standard deviations (error bars) and smoothing curves drawn (lines).

Analysis of the curves (Figure 7) shows that decreasing the stirring rate during phosphating, while maintaining a similar mass change rate, leads to a significant decrease in the limiting specific mass change, from 4.7 to 2.9 g/m². This indicates a pronounced influence of external diffusion factors when the stirring rate is reduced.

It is known that, in stirred reactors, the mass transfer coefficient β (m/s) is a function of hydrodynamic similarity parameters [22]:

$$\beta = 0.43 \frac{D}{\delta_{b.l.}} \text{Re}_c^{0.7} \text{Sc}^{-0.33} \quad (9)$$

where D is the diffusion coefficient (m^2/s); $\delta_{b,l}$ is the thickness of the boundary diffusion layer (m); Re_c is the centrifugal Reynolds number; and Sc is the Schmidt number.

In Equation (9), Re_c is proportional to the square root of the stirring rate v_{st} (rpm) [22]:

$$\text{Re}_c = f(v_{\text{st}}^{0.5}) \quad (10)$$

Decreasing the stirring rate by a factor of 5 results in a decrease in β by approximately $5^{0.7 \cdot 0.5} \approx 1.6$, which agrees well with the observed change in the coating mass. Therefore, sufficiently high stirring rates, no less than 1000 rpm, should be used for efficient phosphating.

To determine the effect of accelerators on phosphating, a coating was deposited using an inorganic accelerator, NaNO_2 , at a concentration of 0.15 g/L. Sodium nitrite is a classical accelerator [1–3] that acts as an oxidizing and depolarizing agent. Its role is associated with oxidizing Fe^{2+} species, suppressing excessive hydrogen evolution, and accelerating phosphate nucleation on the steel surface. The obtained results are shown in Figure 8.

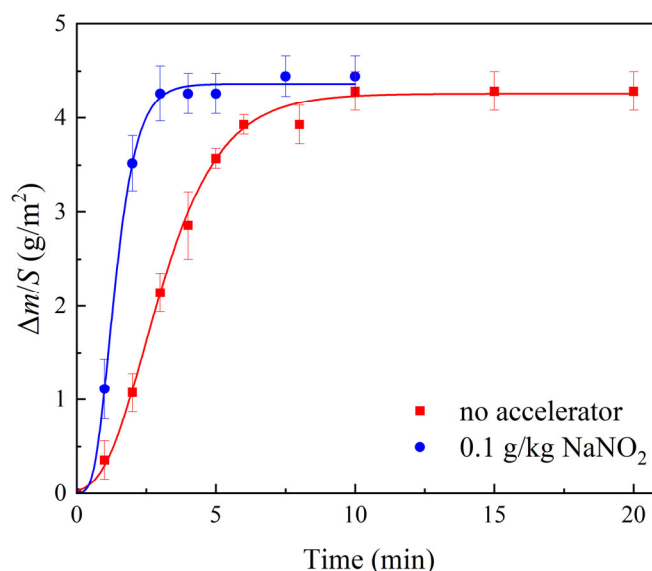


Figure 8. Time profiles of the specific mass change of the coatings depending on the presence of an accelerator: experimental data (symbols), standard deviations (error bars), smoothing curves drawn (lines).

Introduction of the accelerator does not increase the limiting value of the coating mass gain, but affects only the rate of coating formation, decreasing the characteristic formation time from approximately 10 to 3–5 min. The crystals formed during phosphating with sodium nitrite added to the solution formulation were significantly smaller in size, while their overall morphology remained unchanged. The decrease in crystal size can be explained by an increased nucleation rate, which predominates at the initial stages of the phosphating process [13].

3.2. Effect of Organic Accelerators on Phosphate Coating Formation

As noted above, both inorganic and organic materials have previously been considered as phosphating accelerators [6–17]. To evaluate the effect of organic accelerators, the stability of phosphate coatings synthesized under identical conditions was studied: 70 °C, $\text{pH}_0 = 3.00$, 1000 rpm, and 5 min treatment time. The phosphate solutions and coatings were prepared according to the procedure described above. The protective ability of the coatings was evaluated using the visual drop test, using concentrated CuSO_4 solution containing NaCl.

For the selected conditions of phosphating with different organic accelerators, the pH drift remained limited: at $\text{pH}_0 = 3.00$, the solution pH increased only to approximately 3.25 during treatment, as it did for the phosphating solutions without an accelerator. Therefore, no abrupt change in the bulk behavior of catechol is expected during the phosphating process.

The results obtained for samples prepared without an accelerator and with three dihydroxybenzenes as accelerators are summarized in Table 2.

Table 2. Mass change and protective ability of phosphate coatings after phosphating with different organic accelerators.

No.	Accelerator	$\Delta m/S, \text{g/m}^2$	Visual Drop Test Stability, s
1	—	4.6	88; 67; 46; 51; 64
2	0.15 g/L hydroquinone	5.4	82; 79; 76; 98; 104
3	0.15 g/L resorcinol	5.0	78; 63; 58; 84; 81
4	0.15 g/L catechol	4.3	139; 171; >600; 154; >600

The introduction of hydroquinone or resorcinol had only a minor effect on the corrosion rate during the test; hydroquinone provided only a slight improvement. In contrast, the addition of catechol resulted in coatings with substantially higher corrosion resistance: in some cases, the color change occurred after more than 2 min, while in others it took more than 10 min.

Figure 9 shows SEM images of the surface regions after the visual drop test for the coatings prepared without an accelerator and with catechol as an accelerator.

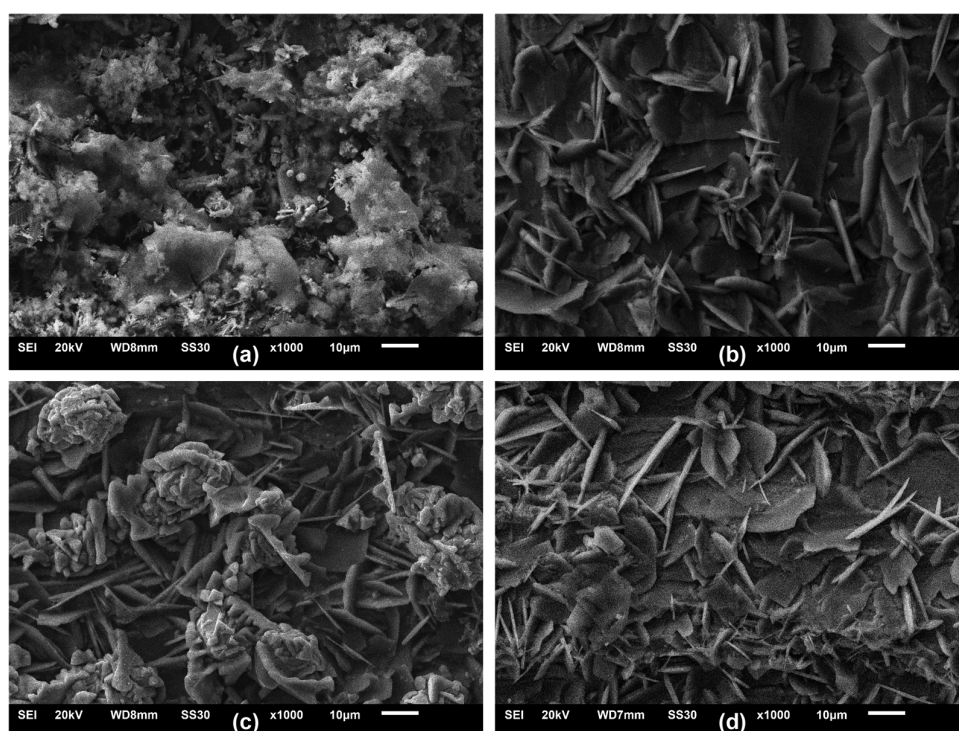


Figure 9. SEM micrographs of the sample surface after phosphating and the visual drop test, without an accelerator (a,b) and with a catechol accelerator (c,d), inside (a,c) and outside (b,d) the drop stain.

The data in Figure 9 indicate that, after the visual drop test, the surface becomes partially covered with copper crystals deposited as a result of corrosion. In the case of the less stable coating prepared without an accelerator, the phosphate layer was largely destroyed, and only loose aggregates of corrosion products were observed.

For the more stable coating obtained with catechol, characteristic petal-like features were observed, around which the original coating remained intact and was not destroyed. The copper crystals were large and well faceted. This can be explained by a smaller number of anodic sites at which corrosion occurs and, consequently, by the predominance of crystal growth over nucleation [4,5,21].

Further studies of coating stability were carried out using a salt spray chamber. Three types of coatings were synthesized: without an accelerator, with catechol, and with NaNO_2 . It was shown that the mass changes of the samples synthesized under the same conditions were of the same order of magnitude:

1. Without an accelerator: $(4.6 \pm 0.6) \text{ g/m}^2$;
2. With catechol: $(3.9 \pm 0.2) \text{ g/m}^2$;
3. With NaNO_2 : $(2.6 \pm 0.3) \text{ g/m}^2$.

For corrosion testing in the salt spray chamber, three samples of each type were loaded: uncoated steel sample and steel samples with coating 1 (without an accelerator), coating 2 (with catechol), and coating 3 (with NaNO_2). The change in the appearance of the samples during salt spray testing after 2, 4, and 24 h is shown in Figure 10.

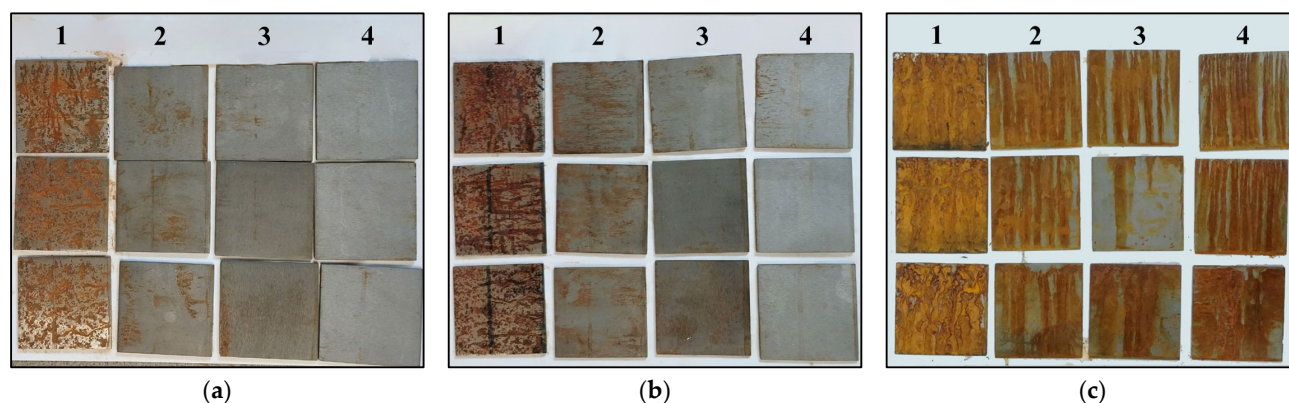


Figure 10. The appearance of the samples after salt spray testing: (a) after 2 h; (b) after 4 h; (c) after 24 h. Sample series: 1, uncoated; 2, phosphate coating without accelerator; 3, phosphate coating with catechol; 4, phosphate coating with NaNO_2 .

The photographs are used to illustrate the visual development of corrosion during salt spray exposure, whereas the quantitative comparison of corrosion damage was based on gravimetric mass changes after exposure.

As follows from Figure 10, the uncoated steel plates were covered with rust after only 2 h of exposure in the salt spray chamber, and further exposure led to a pronounced increase in corrosion damage.

The coated plates were corroded to a much lesser extent, although after 4 h corrosion was also observed on these samples, especially for the coatings obtained without an accelerator. After 24 h, almost all coated plates were at least partially covered with rust. The only exception was one of the samples synthesized with catechol.

Gravimetric calculations of mass changes caused by corrosion after 24 h of exposure in the salt spray chamber gave the following values:

- Uncoated plates: $(16.5 \pm 1.3) \text{ g/m}^2$;
- Plates with coating 1 (without an accelerator): $(2.5 \pm 0.3) \text{ g/m}^2$;
- Plates with coating 2 (with catechol): $(1.0 \pm 0.3) \text{ g/m}^2$;
- Plates with coating 3 (with sodium nitrite): $(2.0 \pm 0.3) \text{ g/m}^2$.

It can be seen that the catechol-containing coating was the most stable. This parameter was not directly related to the coating mass, since this sample did not show the highest

mass gain. Therefore, the protective effect of catechol is more likely associated with changes in the defect structure and barrier properties of the phosphate layer. Catechol contains an ortho-dihydroxy fragment capable of adsorption and coordination with Fe/Zn-containing surface centers. During phosphating, catechol may undergo partial oxidation with the formation of semiquinone or oligomeric derivative species. These products may become localized in pores and intercrystallite regions, decreasing the number of defects accessible to the electrolyte. Thus, it can be assumed that its addition changes both the deposition rate and the coating structure due to modification of interfacial and barrier properties of the phosphate layer.

To clarify whether the improved protective properties of the catechol-containing coating were associated only with morphological changes or also with changes in the chemical structure of the surface layer, Raman spectroscopy was used. The Raman spectra of the coatings are shown in Figure 11 and Table 3.

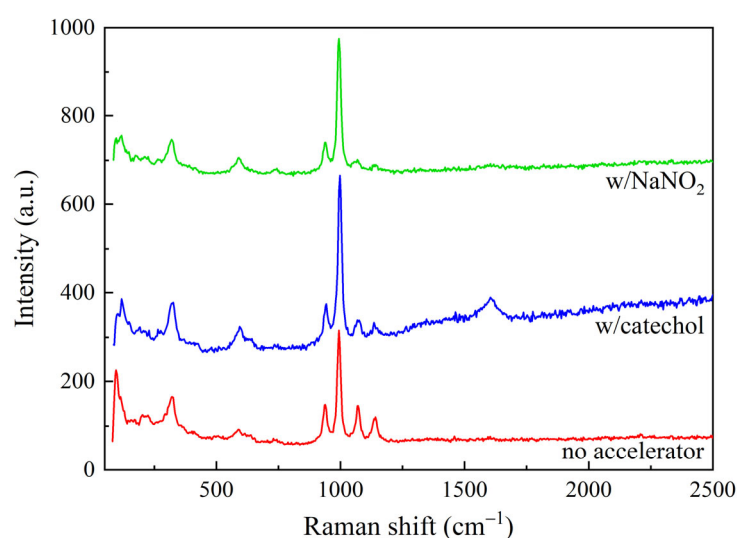


Figure 11. Raman spectra for St20 steel with different phosphate coatings.

Table 3. Reflections of Raman spectra for St20 steel with different phosphate coatings.

No.	Raman Shift, cm ⁻¹			Assignment
	No Accelerator	w/Catechol	w/NaNO ₂	
1	213	192	199	External lattice vibrations
2	323	327	319	$\nu_2(\text{PO}_4^{3-})$
3	409	427	416	$\nu_2(\text{PO}_4^{3-})$
4	597	594	590	$\nu_4(\text{PO}_4^{3-})$
5	639	643	643	$\nu_4(\text{PO}_4^{3-})$
6	744	748	744	Intraplane $\delta(\text{H}_2\text{O})$
7	939	943	940	$\delta(\text{P-O})$
8	994	998	994	$\nu_1(\text{PO}_4^{3-})$
9	1071	1068	1069	$\nu_3(\text{PO}_4^{3-})$
10	1141	1135	1142	$\nu_3(\text{PO}_4^{3-})$
11	—	1605	—	$\nu(\text{C=C})/\nu(\text{C-O})$

Note: A dash indicates the absence of the corresponding Raman shift in the spectrum.

The spectra of all phosphate-coated samples contained bands characteristic of phosphate groups, confirming the formation of a zinc–iron phosphate layer [23–25]. The main spectral features can be assigned to the vibrations of PO_4^{3-} groups in zinc phosphate phases, primarily hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, or phosphophyllite, $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; ac-

cording to Pawlig et al. [23], the Raman spectra of these phases are very similar, and therefore, their unambiguous separation is difficult.

At the same time, the spectrum of the coating obtained in the presence of catechol differed from those of the coatings prepared without an accelerator and with sodium nitrite. In particular, the catechol-containing sample showed additional broad spectral features in the region of approximately $1580\text{--}1720\text{ cm}^{-1}$. This region may correspond to overlapping vibrations of catechol-derived oxygen-containing organic fragments, including aromatic or quinoid ring modes. This assignment is consistent with literature data showing that catechol-containing systems exhibit an aromatic C=C stretching band near 1600 cm^{-1} , whereas quinone-type structures give C=O/conjugated double-bond contributions in the $1660\text{--}1690\text{ cm}^{-1}$ region [26]. Disordered or amorphous sp^2 carbon is also typically characterized by broad Raman bands, namely the D-band near $1320\text{--}1360\text{ cm}^{-1}$ and the G-band near $1560\text{--}1600\text{ cm}^{-1}$. In the present spectra, the high-frequency component may overlap with the G-band region; however, a well-developed D-band of comparable intensity near 1350 cm^{-1} was not observed for the catechol-modified coating. Therefore, the observed broad bands may reasonably be considered as evidence for the formation of a carbon-containing aromatic or conjugated phase associated with catechol transformation, although a contribution from disordered carbon-like species cannot be completely excluded.

This interpretation indicates that catechol is not simply removed from the surface during phosphating, but may undergo partial oxidative transformation and remain associated with the phosphate layer. The formation of such a mixed inorganic–organic surface layer may decrease the effective open porosity of the phosphate coating and hinder the penetration of aggressive species to the steel substrate.

3.3. Study of Phosphate Coatings Using Electrochemical Methods

The corrosion resistance of steel plates without and with different phosphate coatings (samples 1–3) was further evaluated in synthetic formation water using electrochemical methods. The measurements included potentiodynamic polarization with Tafel analysis, and electrochemical impedance spectroscopy (EIS). The polarization curves are shown in Figure 12, and the calculated electrochemical parameters are summarized in Table 4.

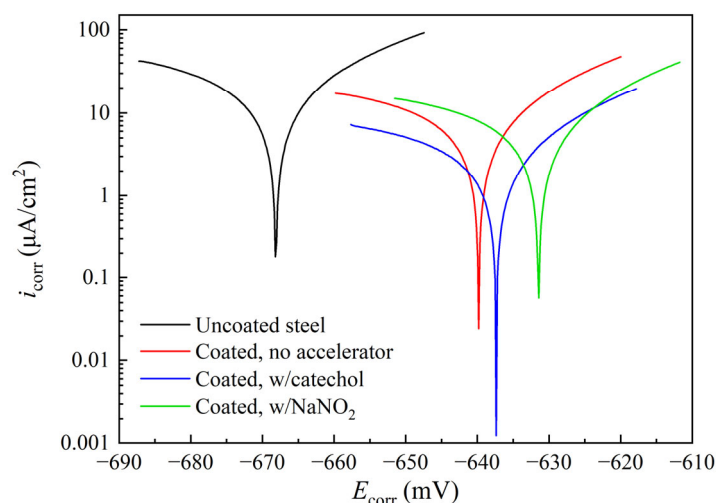


Figure 12. Potentiodynamic polarization curves for St20 steel without coating and with different phosphate coatings in synthetic formation water.

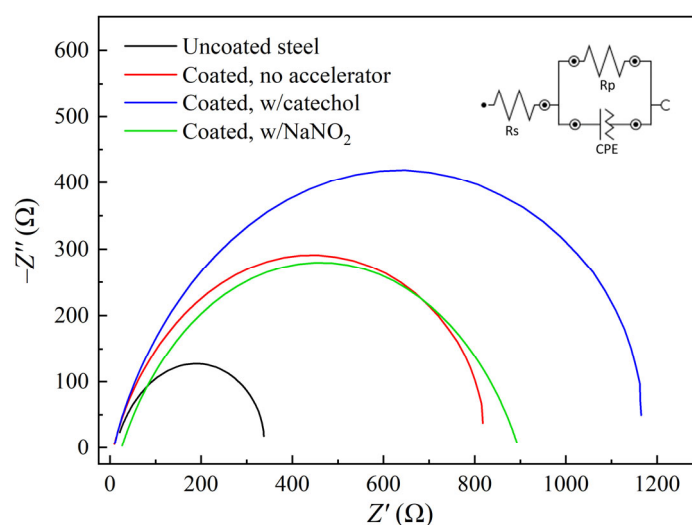
Table 4. Electrochemical corrosion parameters of St20 steel without coating and with phosphate coatings determined from potentiodynamic polarization measurements.

Sample	E_{corr} , mV	β_a , mV/dec	β_c , mV/dec	i_{corr} , $\mu\text{A}/\text{cm}^2$	CR, mm/year	Z_r , %	γ
Uncoated St20 steel	−669	49.4	235.8	59.4	0.70	—	—
Steel with coating 1 (no accelerator)	−640	47.3	531.3	28.2	0.33	52.6	2.1
Steel with coating 2 (with catechol)	−638	37.3	586.7	11.6	0.14	80.5	5.1
Steel with coating 3 (with NaNO_2)	−633	48.0	207.2	29.9	0.35	49.6	1.9

Note: A dash indicates that the parameter is not applicable.

The potentiodynamic polarization curves demonstrate a pronounced decrease in corrosion current density for the phosphate-coated samples compared with uncoated St20 steel, indicating that phosphating substantially suppresses the corrosion activity of St20 steel in synthetic formation water and confirming the formation of a protective surface layer. The most pronounced decrease in corrosion current was observed for coating with catechol, indicating the highest protective efficiency among the studied coatings. Coatings without an accelerator and with NaNO_2 accelerator also inhibit corrosion, but their effect is less pronounced.

To clarify the barrier properties of the coatings, EIS measurements were performed. The Nyquist plots are presented in Figure 13, and the fitted electrochemical parameters are summarized in Table 5.

**Figure 13.** Nyquist plots for St20 steel without coating and with phosphate coatings in synthetic formation water. The inset shows the equivalent electrical circuit used for fitting.

The Nyquist plots exhibit capacitive semicircles typical of corrosion processes controlled by charge transfer at the metal/electrolyte interface. Although phosphate conversion coatings are often represented by equivalent circuits containing two time constants associated with the porous coating layer and the metal/electrolyte interface, the impedance spectra obtained in the present work did not show a clearly resolved second relaxation process. The depression of the semicircle reflects the non-ideal capacitive response of the system and was taken into account by introducing a constant phase element (CPE). Therefore, the impedance data were fitted using the $R_s(R_p\text{CPE})$ equivalent circuit, which provided satisfactory agreement with the experimental data.

Table 5. Electrochemical corrosion parameters of St20 steel without coating and with phosphate coatings determined by EIS.

Sample	i_{corr} , $\mu\text{A}/\text{cm}^2$	CR, mm/year	R_s , $\Omega \cdot \text{cm}^2$	R_p , $\Omega \cdot \text{cm}^2$	$\text{CPE} \cdot 10^{-4}$	Z , %	γ
Uncoated St20 steel	53.4	0.63	13.2	335	134.1	—	—
Steel with coating 1 (no accelerator)	23.9	0.28	8.2	805	50.4	55.4	2.24
Steel with coating 2 (with catechol)	11.5	0.14	8.5	1350	62.3	78.9	4.65
Steel with coating 3 (with NaNO_2)	26.4	0.31	11.9	680	69.4	56.9	2.32

The uncoated steel exhibited the smallest semicircle diameter, corresponding to the lowest polarization resistance and the highest corrosion activity. After phosphating, the diameter of the semicircle increases, indicating higher charge transfer resistance and improved barrier properties of the surface layer. The largest impedance response was obtained for coating with catechol accelerator, which is consistent with the polarization measurements. The two other coatings also increase the impedance response relative to uncoated steel, but to a smaller extent.

Based on the electrochemical measurements data, the electrochemically active porosity of the coatings P (%) was estimated as an effective fraction of the substrate surface that remains accessible to the electrolyte through pores and defects, using the following formula [27]:

$$P = \frac{R_{p,s}}{R_p} 10^{-\frac{\Delta E_{\text{corr}}}{\beta_a}} \times 100\%, \quad (11)$$

where $R_{p,s}$ and R_p are the polarization resistances of the uncoated and coated samples, respectively; ΔE_{corr} is the difference between the corrosion potentials of the uncoated and coated samples; and β_a is the anodic Tafel slope of the uncoated steel.

Using the EIS-derived R_p values and the polarization parameters, the estimated effective porosity values were as follows:

- Plates with coating 1 (without an accelerator): 10.8%;
- Plates with coating 2 (with catechol): 5.8%;
- Plates with coating 3 (with sodium nitrite): 9.2%.

Thus, the lowest effective porosity was obtained for the coating containing catechol, which is consistent with its highest R_p value and the lowest corrosion current density. This supports the conclusion that the protective effect of the catechol-containing coating is associated not only with the presence of phosphate crystals on the surface, but also with a decrease in the number of open transport pathways for aggressive ions.

The agreement between the polarization and EIS results confirms the reliability of the observed trend. Both methods show that phosphate coatings decrease the corrosion current density and corrosion rate while increasing polarization resistance. Minor differences between corrosion rates calculated from polarization curves and EIS are expected, since potentiodynamic polarization involves external perturbation of the electrode potential, whereas EIS is performed close to OCP using a small-amplitude AC signal. Therefore, EIS is more sensitive to coating heterogeneity, pore structure, and non-ideal capacitive behavior, which are accounted for by the CPE element.

Additional dynamic corrosion tests were performed using a Monikor-2M setup. These measurements were used to evaluate the stability of the phosphate layer under flow conditions, with the protective layer exposed not only to the chemical action of formation

water but also to continuous hydrodynamic renewal of the electrolyte. The time profiles of the corrosion rates obtained by using this method for different samples are shown in Figure 14.

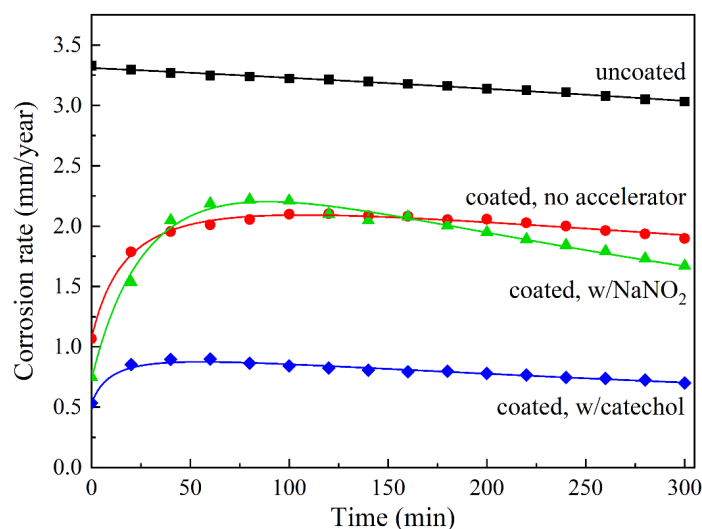


Figure 14. Time profiles of the median corrosion rates for different samples obtained under flow conditions.

For uncoated steel, the corrosion rate remained high throughout the experiment and decreased only slightly with time. This weak decrease may be associated with the gradual formation of a loose layer of corrosion products, which partially hinders further access of the electrolyte to the metal surface. However, under flow conditions and continuous contact with the salt solution, this layer does not provide sufficient protection.

The phosphate-coated sample showed a more complex, non-monotonic behavior. At the beginning of the test, its corrosion rate was noticeably lower than that of uncoated steel, confirming the initial barrier effect of the phosphate layer. During the first 60–90 min, however, the corrosion rate increased, which can be attributed to hydration of the coating, leaching of weakly bound surface components, and penetration of the electrolyte into pores and defects. This transient stage indicates that the phosphate coating is not an inert barrier, and that its electrochemical response changes during contact with the corrosive aqueous medium.

After reaching a maximum, the corrosion rate of the coated sample gradually decreased. This behavior may be related to secondary stabilization of the surface layer due to partial blocking of defects by corrosion products and products of interaction between the coating and the electrolyte. Thus, the coating passes through an adaptation stage in the electrolyte before reaching a more stable protective state.

It should be emphasized that this interpretation is based on the time-dependent electrochemical response. Direct identification of corrosion products or structural changes after flow-through exposure would require post-test surface characterization.

Overall, the flow-through LPR measurements confirm that the phosphate coating significantly reduces the corrosion activity of St20 steel in synthetic formation water. At the same time, its protective effect evolves with exposure time, which indicates that practical evaluation of phosphate coatings should include not only short-term electrochemical parameters, but also their stability under dynamic contact with the working medium.

3.4. A Study of the Protective and Adhesion Properties of Phosphate Coatings as Pretreatment Layers for Paint Coatings

To evaluate the applicability of the phosphate coatings as intermediate pretreatment layers for subsequent paint application, the phosphated steel plates were coated with a

white glossy acrylic aerosol paint (Tytan Professional, RAL 9003, Selena S.A., Wrocław, Poland). The paint was applied by spraying in two layers, with intermediate drying for 30 min between the layers, followed by final drying for 3 days.

The adhesion strength of the resulting paint coatings was evaluated by using the cross-cut test. The appearance of the samples after testing is shown in Figure 15.

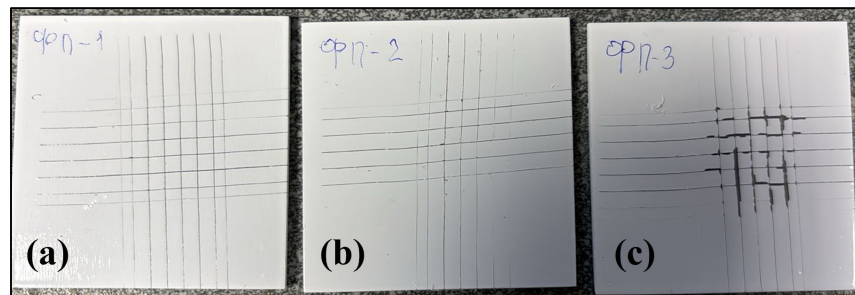


Figure 15. The appearance of the painted samples after the cross-cut adhesion test: (a) phosphate coating without accelerator; (b) phosphate coating with catechol; (c) phosphate coating with NaNO_2 .

The cross-cut adhesion test showed that the paint coatings deposited on samples with phosphate coatings prepared without an accelerator and with catechol passed the adhesion test without noticeable delamination. For the sample prepared using NaNO_2 as an accelerator, minor damage was observed along the cut edges. These results indicate that the use of catechol as an organic accelerator does not impair the adhesion properties of the final paint coating. Therefore, catechol-modified phosphate coatings can be considered suitable pretreatment layers for subsequent paint application.

The anticorrosion properties of the final paint coatings deposited on phosphated steel plates were evaluated in a salt spray chamber, similarly to the tests described above for phosphate coatings without an additional paint layer. Three types of pretreatment layers were used: a phosphate coating prepared without an accelerator, a phosphate coating prepared with catechol as an organic accelerator, and a phosphate coating prepared with sodium nitrite as an inorganic accelerator.

To assess the effect of coating defects on the overall corrosion resistance, X-shaped scratches were made on one representative painted sample from each group before exposure. During the test, the samples were periodically removed from the chamber to record changes in their appearance and mass. The initial appearance of the samples and their changes during salt spray exposure are shown in Figure 16, while corresponding mass change dynamics for the samples with X-shaped scratches are presented in Figure 17.

The mass change curves (Figure 17) show that the general corrosion behavior of all painted samples follows a similar pattern. At the initial stage, an induction period of approximately two days is observed, during which the mass change remains relatively small compared with the final value. This period is followed by a more pronounced increase in mass, which reflects the accumulation of corrosion products and/or penetration of the electrolyte through defects in the coating system.

For the painted samples deposited on the phosphate coating prepared without an accelerator, the mass increase was more pronounced. In contrast, the samples with phosphate pretreatment layers obtained in the presence of catechol or sodium nitrite showed an additional intermediate induction period of approximately 3–5 days, during which the mass change increased more slowly. This behavior may be related to the more complex corrosion process in the multilayer system, where electrolyte penetration, local corrosion at defects, and partial blocking of transport pathways occur simultaneously. This suggests

that the introduction of accelerators during phosphating promotes the formation of denser phosphate pretreatment layers.

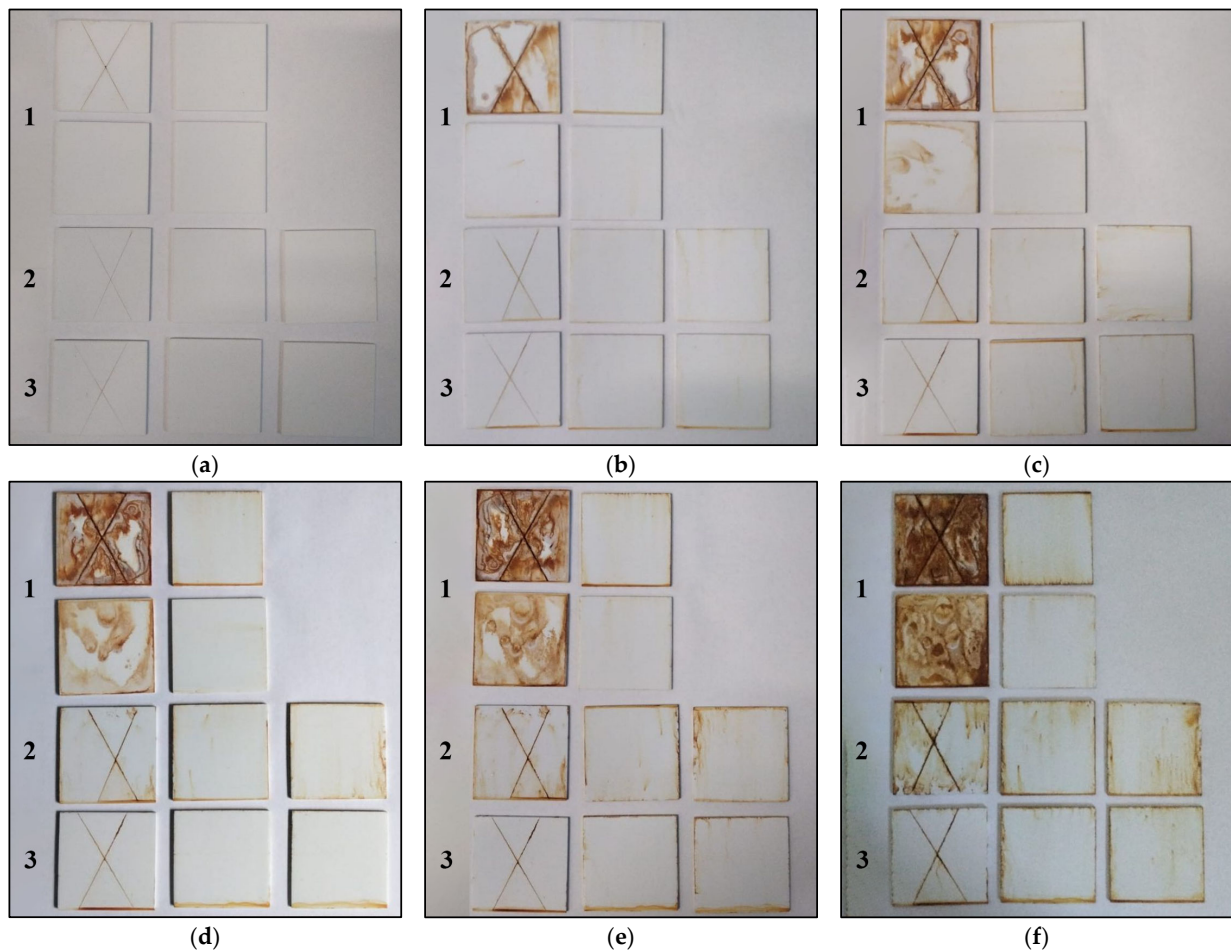


Figure 16. The appearance of the painted samples before (a) and during salt spray testing for (b) 1 day, (c) 2 days; (d) 3 days; (e) 4 days; and (f) 6 days. The numbers correspond to the series of paint coatings on phosphate intermediate coatings 1–3 described above.

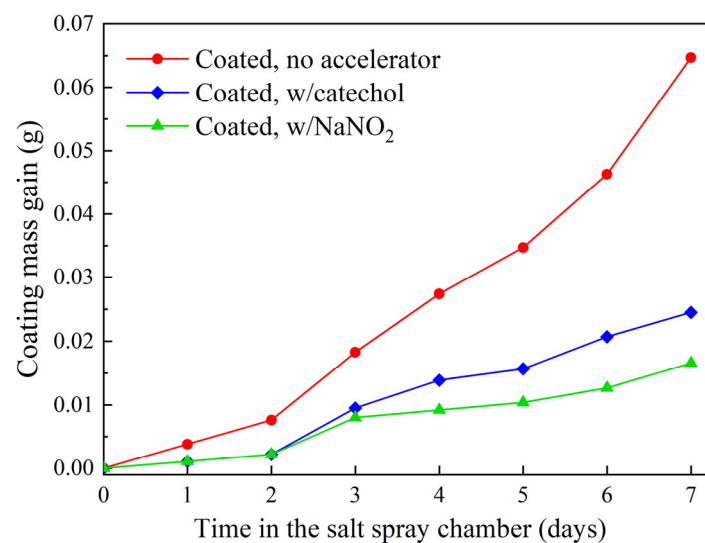


Figure 17. The mass change of painted samples with X-shaped scratches during salt spray testing for different types of phosphate pretreatment layers.

Together with SEM and optical microscopy data, these results indicate that the protective performance of the final paint coating is determined not only by the mass of the phosphate layer, but also by its morphology, continuity, and defectiveness. The use of catechol as an organic accelerator does not impair the adhesion of the paint coating and contributes to the formation of a phosphate pretreatment layer that provides stable anticorrosion behavior after paint application. Therefore, catechol-modified phosphate coatings can be considered promising intermediate layers for subsequent paint coating systems.

4. Conclusions

In the current work, the formation of zinc phosphate coatings on St20 low-carbon steel was studied as a function of phosphating conditions and the nature of accelerating, especially organic, additives. It was shown that efficient coating deposition requires a narrow pH range close to $\text{pH}_0 = 3.0$. At lower pH values, surface etching predominates, whereas a further pH increase favors bulk precipitation of zinc phosphate. Increasing the temperature from 50 to 70 °C accelerated coating formation, increased the final coating mass, and reduced the induction period. The activation energy (28 kJ/mol) indicates that, under the studied conditions, phosphate coating growth is controlled mainly by diffusion through the formed porous layer. A sufficiently high stirring rate is also required to provide effective mass transfer and obtain a continuous coating.

The use of sodium nitrite as a conventional inorganic accelerator significantly increased the rate of phosphate coating formation, but did not increase the limiting coating mass. Among the studied dihydroxybenzene isomers, catechol showed the most pronounced effect on the protective properties of the coating. In the visual drop test and salt spray experiments, the catechol-containing phosphate coating demonstrated higher resistance than both the coating prepared without an accelerator and the coating obtained with sodium nitrite. This effect was not directly related to coating mass, but was more likely associated with the changes in coating structure and lower effective porosity.

Raman spectroscopy confirmed the formation of phosphate phases of the hopeite/phosphophyllite type in all synthesized coatings. At the same time, the catechol-containing coating showed additional spectral features in the region characteristic of catechol-derived oxygen-containing organic fragments, including aromatic and/or quinoid structures. This supports the assumption that catechol may undergo partial oxidative transformation during phosphating and remains associated with the phosphate layer, presumably contributing to filling pores and channels in the coating and thus improving its barrier properties.

Electrochemical measurements in synthetic formation water confirmed that phosphate coatings reduce the corrosion activity of St20 steel and increase the resistance of the metal/electrolyte interface. The EIS data showed that the protective effect is related to the formation of a non-ideal capacitive surface layer with reduced access of the electrolyte to the steel substrate. Dynamic LPR measurements under flow-through conditions demonstrated that the coating behavior evolves with exposure time: after an initial protective effect, a transient stage is followed by presumable secondary stabilization of the surface.

The phosphate coatings were also evaluated as pretreatment layers for subsequent acrylic paint application. The catechol-modified intermediate phosphate layer did not impair paint adhesion and provided stable anticorrosion behavior of the final paint coating during salt spray testing. Thus, catechol can be considered a promising organic accelerator and modifier for zinc phosphate pretreatment layers on steel, offering improved protective performance without deterioration of the adhesion properties of the final coating.

Author Contributions: Conceptualization, A.S. and I.T.; methodology, A.N.; software, N.K.; validation, D.P. and A.N.; formal analysis, K.R. and G.K.; investigation, D.Z. and X.L.; data curation, N.K.; writing—original draft preparation, A.S. and I.T.; writing—review and editing, D.P.; visualization,

X.L.; supervision, M.Z.; project administration, N.K.; funding acquisition, D.P. and A.N. All authors have read and agreed to the published version of the manuscript.

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

Abbreviations

The following abbreviations are used in this manuscript:

ASTM	American Society for Testing and Materials
CPE	Constant phase element
CR	Corrosion rate
EDS	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
LPR	Linear polarization resistance
OCP	Open-circuit potential
PEG	Polyethylene glycol
PHB	Polyhydroxybutyrate
PVA	Poly(vinyl alcohol)
PVP	Poly(vinyl pyrrolidone)
SEM	Scanning electron microscopy
St20	Low-carbon structural steel close in composition to AISI/SAE 1020
XRD	X-ray diffraction
R_s	Solution resistance
R_p	Polarization resistance
R_{ct}	Charge transfer resistance

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