

Kinetic study on rapid phosphating compositions for eco-efficient corrosion protection in earth and environmental engineering

Maxsud Jumaniyazov, Sherzod Kurambayev*, and Surayyo Sapayeva

Urgench State University named after Abu Rayhan Beruni, 220100 Urgench city, Uzbekistan

Abstract. This paper presents a kinetic investigation of rapid phosphating compositions designed for corrosion protection in industrial environments. The formulations incorporate extraction phosphoric acid, furfuryl alcohol, hexamethylenetetramine, and lignin-hydrolysis industry waste with the following composition (wt.% relative to absolutely dry residue): C – 17.34, H – 6.43, O – 43.50, phenol groups (–OH) – 5.06, methoxy (–OCH₃) – 3.06, carboxyl (–COOH) – 1.18, total acidic groups – 6.24, ash – 4.12–2.74. Additionally, the natural mineral vermiculite was used (bulk density 70–180 kg/m³, water absorption 400–530%, pH 6.8–7.0, Mg content 10–14%, K 3–5%, Ca 1.2–2%, Mn 0.8–1%). The kinetic parameters obtained from this study elucidate the mechanisms governing the accelerated phosphating process. These results are significant for developing environmentally safer and more durable protective coatings, thereby extending the operational life of metal structures and reducing resource consumption.

1 Introduction

The issue of anticorrosion protection for various metal products and structures remains relevant to this day. From the perspective of cost-effectiveness, availability of raw materials, and ease of processing, chemical phosphating is considered highly important for preparing the surfaces of metals and alloys for paints, coatings, or lubricants.

Rapid phosphating compositions for corrosion protection form a protective phosphate layer on the metal surface, slowing down the corrosion process and improving the adhesion of paint coatings. The phosphating process is carried out by treating the metal surface with phosphoric acid or its salts. Traditional phosphating methods often involve heavy metals that are harmful to the environment. Therefore, the development of environmentally safe, rapid phosphating compositions is an urgent issue. In this regard, the trend of using non-toxic, eco-friendly reagents in the phosphating process is gaining momentum [1].

It is known that, compared to traditional methods, electrochemical phosphating is faster and more efficient, forming uniform and dense coatings on metal surfaces [2]. The effectiveness of zinc-based phosphating compositions against corrosion has been described

* Corresponding author: sherzod.k@urdu.uz

in numerous scientific sources [3, 4]. The processes of improving the properties of phosphate coatings by adding nanoparticles are being studied. For instance, in some sources, it has been investigated that phosphate coatings enriched with graphene oxide nanoparticles enhance corrosion protection on metal surfaces. Additionally, the addition of organic substances to phosphating solutions improves the adhesion and corrosion-resistant properties of the coatings [1, 5].

2 Methods

Gravimetric Method: In the gravimetric method, metal plates of various steel samples with dimensions of 3.0 x 0.1 cm are used. Before starting the experiments, the metal samples were cleaned with sandpaper and their dimensions were accurately measured. Then, they were washed with distilled water and acetone. The experiments were conducted in 10% HCl, 10% H₂S, and 1M NaCl solutions at different time intervals. Initially, the metal sample was immersed in the test solution for 3 hours, after which its mass was measured. Then, inhibitors of various concentrations were added, and the metal sample was weighed again. Before weighing, the metal samples were washed with distilled water and then with acetone, followed by weighing on a balance. Each experiment was repeated three times, and the obtained results were recorded.

The effectiveness of the modifier is determined using the following formula:

$$\eta\% = \frac{W_0 - W_i}{W_0} \times 100$$

Here, W_0 - and W_i - represent the mass loss (mg) without and with the addition of the modifier, respectively, and $\eta\%$ denotes the efficiency of the modifier.

The morphology of the modified metal surface was analyzed using a LaboMet-1 metallographic microscope. This microscope can magnify the metal surface up to 1000 times. The operating voltage range is between 5-15 kV. Using this microscope, images of the metal samples can be captured at various scales, accurately identifying structures up to 100 micrometers in size. Before starting the experiment, the metal samples were thoroughly washed with distilled water and acetone, then dried in a vacuum, and subsequently observed under the microscope [6-9].

3 Results and discussion

For the research, five samples were prepared with the compositions listed in Table 1 (Table 1).

Table 1. Compositions of rust modifiers.

№	In the modifier					
	Component Name	Component Amount, wt. %				
		Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5
1	Hydrolyzed Lignin	14	15	16	17	18
2	Orthophosphoric Acid	20	21	22	23	24
3	Furfuryl Alcohol	1	2	3	4	5
4	Vermiculite	3,0	3,0	3,0	3,0	3,0
5	Water	62	59	56	53	50
6	Total	100	100	100	100	100

The proposed agent can be used on metal surfaces regardless of the presence of rust products. Its composition includes Zn²⁺, Al, Ca, Mg, and Mn, which help to form a

concentration of hydroxyl ions on the metal surface, leading to the passivation of iron. An advantage of these minerals is their low toxicity. In contrast, compositions containing chromates and lead-based substances possess toxic properties and are therefore used less frequently. The inclusion of the above-mentioned compounds in the composition contributes to the formation of micro-coatings on the metal surface.

This, in turn, reduces the penetration of aggressive substances into the surface. To enhance the ion-exchange and adsorption mechanisms, vermiculite was included in the composition. The presence of organic inhibitors, such as urotropine, strengthens chemisorption and prevents rust formation on the surface. In this composition, the formation of chelate-type compounds explains the strong adhesion and high protective properties. The presence of polar functional groups (-OH, -COOH, -CHO₂, -COONH) enhances cohesive energy. These groups contribute to the formation of a coating that ensures strong adhesive bonding. Additionally, the inclusion of furfuryl alcohol provides barrier-type protection. The micronized thin layer of insoluble iron phosphate salts further enhances the protection. This complex composition not only prevents rust but also facilitates the formation of insoluble organic and inorganic compounds with the rust layer itself. By introducing 3% vermiculite mineral into the composition, compounds with high adhesion and anti-corrosion properties were achieved. A simplified setup was used in the production technology, maintaining the pH of the solution within the range of 4.5-5.0.

For the research, St3 grade structural steel materials were selected. The protective properties of the obtained phosphate coatings were controlled according to GOST 9.302-88 using Akimov's drop method. The insulating properties of the obtained coatings (films) were evaluated based on their dielectric strength. Measurements were performed using the UPU-10 device with a 0.5 N load and an electrode diameter of 25 mm. Chronopotentiometric measurements were conducted using an ANION 4154 combined device in a YASE-2 electrochemical glass cell equipped with a water thermostat. A silver chloride electrode was used for comparison, and potentials were referenced against the saturated silver chloride electrode [10-12].

To measure the thickness of the phosphate coatings, an electromagnetic thickness gauge "Konstanta-K5" calibrated with an ID sensor was used. In the studies, when the coatings were subjected to friction for 5 minutes, the average protective property of the phosphate films was 172 seconds. At the same time, for the samples treated for 10 minutes, this value decreased to 155 seconds (*Table 2*).

Table 2. Results of chronopotentiometric study of the phosphating process.

Processing Time, s	Changes in Potential Values During the Phosphating of Steel Samples			
	Potential Change During Phosphating at 70°C, E, mV (AgCl/Cl)		Potential Change During Phosphating at 90°C, E, mV (AgCl/Cl)	
60	-508	-550	-510	-480
120	-475	-462	-508	-487
180	-460	-470	-500	-480
240	-465	-464	-480	-440
300	-467	-460	-485	-450
360	-470	-460	-490	-445
420	-472	-462	-492	-430
480	-475	-458	-480	-430
540	-485	-465	-500	-443

When the phosphating time was increased from 5 minutes to 10 minutes, the average roughness of the obtained coatings decreased from 2.560 μm to 1.712 μm. The effect of the temperature range of 70-90°C on the deposition process of phosphate films on St3 grade steel was studied by analyzing the chronopotentiometric values obtained during the phosphating

process at different temperatures for each type of steel. As observed from Table 2 (in samples 3 and 4), the fastest shift towards positive potential values occurs during the deposition of the phosphate layer on the surface of the electrical steel at 90°C. At 240 seconds, the potential of the given sample shifts from -510 mV to -490 mV at 70°C and to -455 mV at 90°C, respectively.

Based on this, during the phosphating process at 90°C, the retention of electrical contact even after 10 minutes indicates that the process is not yet complete. Furthermore, the obtained data shows that, at 90°C, the exponential growth phase of the phosphate coating on electrical steel concludes after the first 5 minutes of the phosphating process. After this phase, the slowing phase of the process begins, during which the closure of pores associated with upward growth and the sealing of larger individual crystals in the phosphate coatings likely occur. Additionally, this phase may involve the restructuring of the coating as it stabilizes.

At the same time, increasing the temperature to 70–90°C during the phosphating of structural steel does not significantly affect the process rate. This is because, even at 70°C (as shown in samples 1 and 2 from Table 1), the active growth of the coating stops after 3 minutes from the start of the phosphating process. When the solution temperature was increased from 70°C to 90°C, the potential of the sample shifted towards positive values at 240 seconds, changing from -525 and -520 mV to -460 and -465 mV, respectively. This data indicates that at 70°C, it is possible to apply an adhesive phosphate coating on St3 grade steel within 3-4 minutes [13].

Extending the processing time to 10 minutes negatively affects the coating properties, as the potential of the sample shifts back towards negative values. The obtained results show that phosphating electrical steel with an area of up to 0.1 m² using 1 dm³ of solution causes insignificant changes in the chemical composition of the solution (Table 3).

Table 3. Dependence of the phosphating solution composition changes on the treated area of electrical steel.

Treated Surface Area in 1 dm ³ Solution, m ²	Total Acidity, points	Free Acidity, points	Phosphating Composition, g/dm ³	Mass of Sludge Formed from 1 dm ³ Solution, g
-	61,5	8	68,13	-
0,02	60,25	7,5	67,90	0,33
0,04	59	7,25	67,63	0,14
0,06	58,25	7,2	66,83	0,13
0,08	57,25	7,1	66,17	0,09
0,10	57	7	65,15	0,13

This confirms the insignificant changes observed in the obtained phosphate coatings (Figure 1, Curve 1). When the surface area of electrical steel samples up to 0.1 m² was treated with 1 dm³ of solution, the thickness of the resulting coating did not exceed 12-13 μm. The protective properties of the phosphate layer remained approximately at the same level (Figure 1, Curve 2). However, when phosphating an electrical steel surface area larger than 0.1 m² with the same solution volume, its protective value decreased sharply.

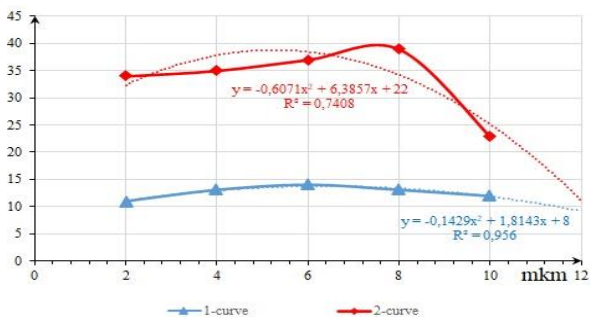


Fig. 1. Dependence of the phosphate layer thickness (1) and the protective properties of the layer (2) on the surface area of electrical steel treated with 1 dm³ of the proposed phosphating solution.

When treating an electrical steel plate with a surface area of no more than 0.1 m² in 1 dm³ of solution at a temperature of 90°C for 5 minutes, it is possible to obtain thin phosphate coatings with a thickness of 10-12 μm and a breakdown voltage of 300-500 V. Furthermore, this solution can be used for phosphating parts made of 08 KP steel at lower temperatures (70°C) following standard technological processes before applying the final lacquer-paint coatings.

The proposed technology allows for the phosphating of both electrical and structural steel in a single solution composition, reducing energy consumption and the need for additional equipment. This approach also minimizes the operational costs associated with maintaining phosphating baths. Traditionally, phosphate coatings for metals are formed in solutions at high temperatures, which leads to increased energy consumption and may limit the treatment of components susceptible to deformation. In our research, we investigated the kinetics of the phosphating process aimed at protecting metal surfaces from corrosion. For this purpose, St3 carbon steel was used. Before conducting the phosphating and electrochemical measurements, the steel electrodes were polished using fine abrasive skin, degreased with ethanol, and then washed with distilled water to ensure surface cleanliness.

The phosphating process was analyzed using a raw material containing various magnesium-based additives, including vermiculite. The process was conducted at a temperature of (25 ± 1)°C, using a solution based on 0.65M Mg²⁺ + 0.3M PO₄³⁻ with a pH of 1.95. The research began by developing a universal corrosion-resistant phosphate coating for St3 grade metals. Although the obtained phosphate coating provided sufficient protective properties at room temperature, its complex preparation process limited its technological applicability. To overcome this limitation, a phosphating composition was developed based on locally sourced raw materials.

The kinetics of phosphate coating formation on St3 steel at 25°C was studied. According to the data presented in Figure 2a, the formation of the phosphate coating begins from the first minutes of phosphating. This is evidenced by the changes in the mass of the dissolving alloy (m), the mass of the phosphate coating (p), and the shift of the potential (E) towards positive values. According to the modern theory of phosphating, initially developed for ferrous metals and later applied to some non-ferrous metals, when steel is immersed in the phosphating solution, electrochemical anodic processes occur on the metal surface. Simultaneously, the oxidizing agent present in the solution undergoes cathodic reduction, accompanied by the adsorption of hydrogen ions and an increase in pH around the electrode. This leads to reaching the solubility product necessary for the formation of sparingly soluble phosphates.

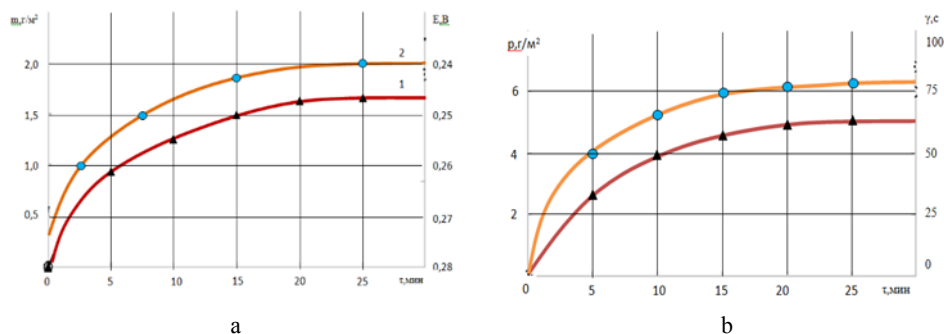


Fig. 2. Formation and Transformation of Phosphate Coating: a – Dissolved metal mass (1) and potential (2). b – Phosphate coating mass (3) and corrosion resistance (4) obtained when St3 grade steel is immersed in a zinc sulfate-phosphate solution.

The initial stage of steel phosphating is characterized by the synchronous change in both the growth rate of the phosphate coating and the dissolution rate of the metal in the phosphating solution. The electrochemical processes underlying phosphating play a crucial role in the formation and development of the phosphate layer structure, particularly in facilitating the crystallization process. However, the formation of primary passivating layers can also occur through surface mechanisms, such as the specific adsorption of phosphate ions and their interaction with the base metal.

It is important to emphasize that the increased content of alloying elements in steel significantly affects both the state of the steel during phosphating and the quality of the resulting coating. As noted earlier (*Figure 2*), during the phosphating of St3 steel in a basic phosphating solution, the corrosion resistance of the phosphate coating did not exceed 90 seconds. Under these conditions, altering the concentration of salt-forming ions (Zn^{2+} , PO_4^{3-}) did not result in an improvement in the properties of the phosphate coating formed on the St3 surface.

These additives may potentially influence not only electrochemical processes but also the crystallization process. According to accelerated corrosion tests conducted in a 3% NaCl solution, steel with phosphate coatings obtained under optimal conditions meets the requirements of GOST 9.302-88 in terms of protective properties.

4 Conclusion

This solution can be considered universal, as it allows the formation of corrosion-resistant coatings at room temperature for various steel grades, including St3, 20, and 08KP. Based on the specific characteristics of the cold phosphating kinetics of St3 grade steel, it is proposed to introduce 3% vermiculite into the composition to enable the rapid formation of phosphate coatings with the required functional properties within 15 minutes. Such phosphate coatings can be recommended as a base layer under various coatings and lacquer-paint applications to protect carbon steels from corrosion under different operating conditions.

References

1. R. Kumar, A. Singh, N. Gupta, “The Environmental Significance of Phosphating Compositions Based on Plant Extracts”, *Green Chemistry and Technology* **5(4)**, 321–328 (2019)
2. S. Wang, Q. Liu, T. Zhao, “Advantages of the Electrochemical Phosphating Process”, *Electrochemistry Acta* **67(2)**, 234–240 (2021)

3. Y. Zhou, X. Li, J. Wang, “Effectiveness of Zinc Phosphate Coatings Against Corrosion”, *Corrosion Science Journal* **12(3)**, 456–462 (2023)
4. H. Li, L. Zhang, Y. Chen, “Corrosion-Resistant Properties of Phosphate Coatings Enriched with Graphene Oxide”, *Nano Materials and Coatings* **8(5)**, 789–795 (2022)
5. D. Liu, T. Guo, G. Xu et al., “Modification Mechanism of Triethanolamine on Phosphating Coating with High Corrosion Resistance”, *Russ. J. Phys. Chem.* **97**, 3149–3155 (2023). DOI: 10.1134/S0036024423130071
6. J. Chen, P. Wu, M. Gao, “The Effect of Polymer Additives on the Efficiency of Phosphate Coatings”, *Journal of Coating Technologies* **15(1)**, 112–118 (2020)
7. H. Du, X. Ren, D. Pan et al., “Effect of phosphating solution pH value on the formation of phosphate conversion coatings for corrosion behaviors on AZ91D”, *Adv Compos Hybrid Mater* **4**, 401–414 (2021)
8. B. Liu, Y. Zheng, G. Xiao, C. Chen, Y. Lu, “Influence of Surface Post-Processing on Crystal Refinement and Characteristics of Hopeite Coating by Phosphating”, *Coatings* **11**, 541 (2021)
9. L. M. Monina, X-ray diffraction. Qualitative X-ray phase analysis (Prospekt Publishing House, 2017)
10. A. A. Ayoola, O. S. I. Fayomi, I. G. Akande et al., “Inhibitive Corrosion Performance of the Eco-Friendly Aloe Vera in Acidic Media of Mild and Stainless Steels”, *J Bio Tribo Corros* **6**, 67 (2020)
11. J. O. S. I. Akpoborie et al., “Electrochemical corrosion phenomenon and prospect of materials selection in curtailing the challenges”, in *IOP Conference Series: Materials Science and Engineering* 1107(1) (2021)
12. R. Yan, X. Gao, W. He et al., “A Simple and Convenient Method to Fabricate New Type of Phytic Acid Metal Conversion Coatings with Excellent Anti Corrosion Performance on the Iron Substrate”, *RSC Adv.* **7**, 41152–41162 (2017)
13. M. Dornbusch, *Corrosion Analysis* (CRC Press, Boca Raton, London, New York, 2018), p. 43