

# OPTIMIZATION OF LOW-TEMPERATURE CRYSTALLINE PHOSPHATIZATION OF STEEL SURFACES

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## Key words:

Low-temperature phosphate treatment, phosphatization activator, protective performance, corrosion protection, conversion coatings.

## ABSTRACT

Unique properties of phosphate coatings, a relatively low cost and a simple production process explain why phosphatization became widespread in many industries. Phosphatization involves multiple stages and a lot of energy, the temperature of conventional industrial phosphatization solutions can reach 85 °C. One of the processes involves surface activation of steel in phosphatization activator suspension.

This paper looks at the process of steel surface activation combined with phosphate coating. A conventional phosphatization process involves activation, i.e. a pre-treatment of the target surface in the suspension containing fine dispersed poorly soluble compounds. Due to surface adsorption, such compounds hinder the growth of phosphate grains thus increasing the coating consolidation. The authors also looked at the effect of fine dispersed SiO<sub>2</sub> and TiO<sub>2</sub> oxides introduced directly in the low-temperature phosphatization agent.

The authors developed a low-temperature steel surface phosphatization process that combines phosphatization with activation which take place in the suspension containing ZnO — 10 g/l, H<sub>3</sub>PO<sub>4</sub> — 19 g/l, HNO<sub>3</sub> — 8 g/l, FeCl<sub>3</sub>·6H<sub>2</sub>O — 0.3 g/l, Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O — 0.2 g/l, NH<sub>2</sub>OH — 2.0 g/l, SiO<sub>2</sub> or TiO<sub>2</sub> — 1 g/l at pH = 2±0.5. The paper shows that a 10-minute deposition at 30 °C produces phosphate coatings the corrosion resistance and protective properties of which would be comparable to those of the phosphate coatings produced with the help of pre-activation. Introduction of fine SiO<sub>2</sub> or TiO<sub>2</sub> particles would make it a simpler process because in this case no pre-activation bath is used. And the low-temperature regime helps reduce the energy cost.

## Introduction

Considerable popularity of phosphate treatment can be attributed to the fact that this process produces phosphate layers with a wide range of required functional properties (adhesion, anti-friction, insulation, anti-corrosion), the resultant coatings have stable characteristics and it is a simple coating process [1–5].

Crystalline phosphatization is a process that involves multiple stages and a lot of energy due to the high temperatures of process solutions (up to 85 °C). It comprises the following stages: degreasing, pickling, activation, phosphatization, inhibiting treatment, drying [6–12].

Having analyzed the conventional phosphatization processes, the authors wondered if they could reduce the energy consumption and optimize the required equipment if they reduce the temperature of the special phosphatization agent and exclude the surface pre-activation stage. Activation stands for surface treatment in the activator bath containing an aqueous suspension of a fine poorly soluble compound. During activation, microparticles of the poorly soluble compound adsorb on the treated surface and produce new crystallization centers, leading to refinement of growing phosphate grains and coating consolidation resulting in reduced porosity and enhanced protective performance. The most common activators

include suspensions of poorly soluble phosphates, such as manganese, calcium, titanium phosphates and others [10–11].

The authors' proposal is to get rid of the activation stage, optimize the process equipment, reduce the number of baths used, and thus save the need for constant maintenance of the special activation solution, which involves a daily replacement of 10% of the solution. The latter will also reduce the cost of waste water disposal.

In connection with the above, development of a crystalline phosphatization process based on the use of a special low-temperature solution and combining activation and phosphatization poses an important R&D problem.

## Experimental Technique

Phosphate coatings were installed on the 08ps grade of cold-rolled steel. 'Ch' and 'chda' chemical agents and distilled water were used for phosphatization solutions.

Protective performance of the coatings was evaluated based on the accelerated Akimov method [13].

X-ray fluorescence microanalysis was applied to study the chemical elemental composition of the specimens' surface. The analysis was carried out with the help of an INCA ENERGY+ analyzer (by Oxford Instruments, UK) installed on a JEOL JSM-6510LV scanning electron microscope (by JEOL, Japan).

The JEOL JSM-6510LV microscope was also used to study the surface morphology of the phosphate coatings.

The following formula was used to calculate the specific weight of the phosphate layer ( $m_{ph}$ ):

$$M_{ph} = (m_1 - m_2) / S,$$

where  $m_1$  — weight of the specimen after phosphate coating, g;  $m_2$  — weight of the specimen after the phosphate layer has been removed, g;  $S$  — phosphatization surface area, m<sup>2</sup>.

The specimens were weighed with the help of an AND GR-200 analytical balance.

The steel specimens with phosphate coatings were spray-painted with a polyester paint Ecocolor PE RAL 9016/P using a START-50 spray gun, followed by furnace melting at 180 °C for 5 minutes.

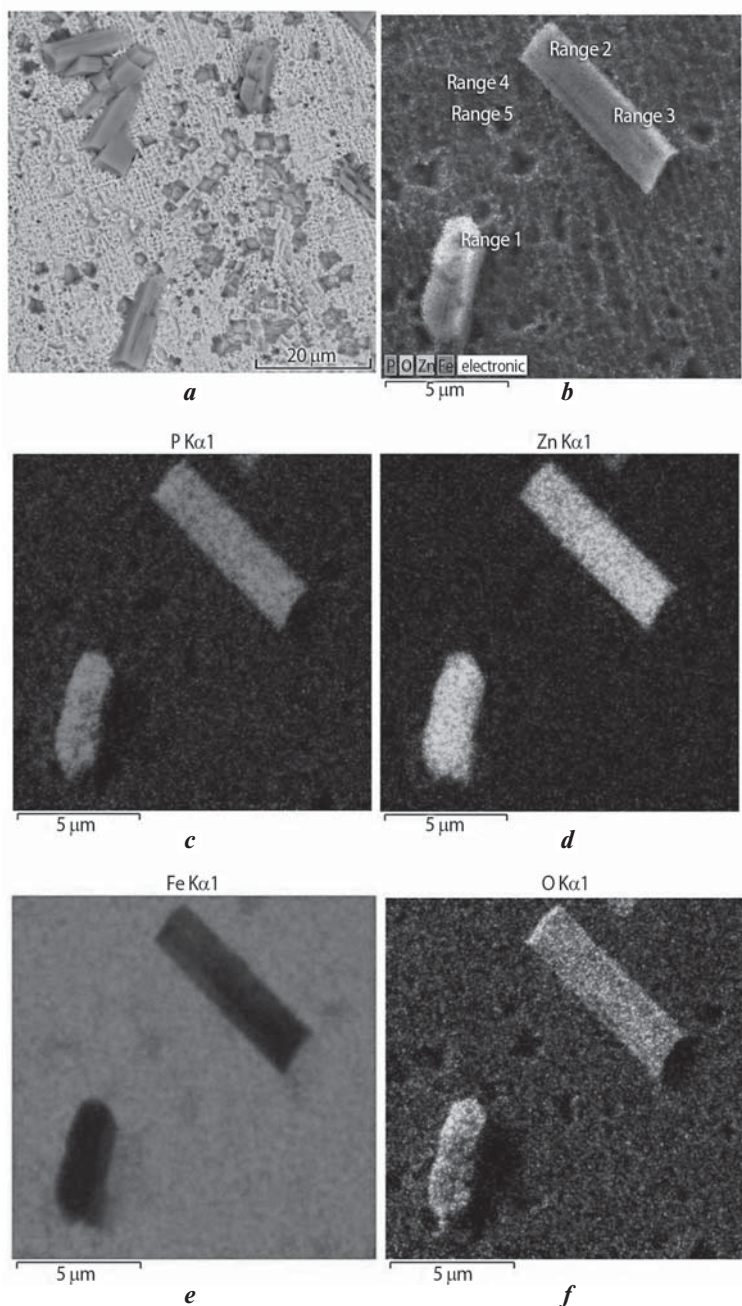
The surface of phosphatized and painted steel was then treated in an Ascott S120iP salt spray chamber and tested for corrosion resistance as specified by [14] and ASTM B117 (SCAB test). The authors measured the spread of underfilm corrosion from the cut h (mm). The adhesion of the RAL 9016/P paint was tested following ASTM D 3359 and [15] using an Elcometer 107 cross hatch cutter.

### Experimental Results and Discussion

The authors found that when cerium (IV) sulphate is added to a zinc containing solution, the process temperature drops to 30 °C, and when cerium sulphate is added simultaneously with hydroxylamine, their synergetic effect leads to faster phosphatization at low temperatures producing quality phosphate coatings. The authors developed a phosphatization agent with the following composition: ZnO — 10 g/l, H<sub>3</sub>PO<sub>4</sub> — 19 g/l, HNO<sub>3</sub> — 8 g/l, FeCl<sub>3</sub>·6H<sub>2</sub>O — 0.3 g/l, Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O — 0.2 g/l, NH<sub>2</sub>OH — 2.0 g/l. If the pre-activation stage is involved, crystalline phosphate layers with the specific weight of 7.2 g/m<sup>2</sup> can be produced in 10 minutes at 30 °C with the protective performance of 100 sec [16].

Figure 1 shows the results of X-ray fluorescence mapping done for the surface of steel specimens that were treated in a low-temperature phosphatization agent. The results were obtained with the help of a microprobe with optimum magnification. Figure 1 also shows the distribution of elements in the coating. This technique was used to analyze the coatings at different stages. The SEM image (Fig. 1, a) shows the morphology of the coating that was used for elemental spectroscopy. The general element distribution maps (Fig. 1, b), a result of overlapping separate spectral maps of each element (Fig. 1, c, d, e, f), characterize the average elemental composition of the coating surface. Analysis of the initial phosphatization stage, when the deposition lasted for 5 seconds, revealed a porous layer that formed on the surface together with the zinc phosphate crystals. The spectral maps of iron and oxygen (Fig. 1, e, f) indicate that these elements make the surface around the phosphate crystals, which is basically a coating made of iron oxides (Fig. 1, b, spectra 4 and 5).

When the phosphatization stage is almost completed (i.e. after 10 minutes of phosphate



**Fig. 1. X-ray fluorescence mapping of the phosphate coating produced at 30 °C in 5 s:**  
*a* — SEM image of the coating surface; *b* — general element distribution map; *c* — distribution of phosphorus in the coating; *d* — distribution of zinc in the coating; *e* — distribution of iron in the coating; *f* — distribution of oxygen in the coating

treatment), the completed coatings have all four layer-forming elements (P, O, Fe, Zn) evenly distributed across the phosphatized surface. The data on the elemental composition of the phosphate coatings obtained through X-ray fluorescence mapping indicate that cerium is not present in the phosphate coatings.

The authors also looked at the effect of  $\text{SiO}_2$  and  $\text{TiO}_2$  additives introduced in the low-temperature phosphatization agent on the properties of coatings. For this, the authors used the Aerosil A300 grade of silicon dioxide and titanium dioxide (pigment) with the particle size of 1.5–2.0  $\mu\text{m}$  [17].

The efficiency of the developed process was evaluated in comparison with the industrial phosphatization process, which takes place in a 70 °C solution and involves pre-activation, i.e. when the target steel surface is immersed in activator suspension containing fine dispersed titanium phosphate.

The experiments showed that the use of the solution that helps combine activation and phosphatization with bubble aeration simulating the industrial phosphatization environment helps avoid coagulation and sedimentation of particles for two hours.

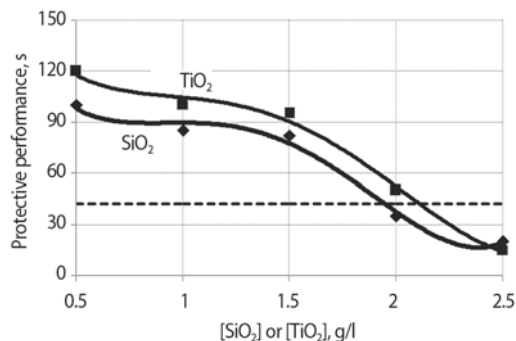
The digital photos show that the surface of phosphate coatings installed in the low-temperature solution containing  $\text{SiO}_2$  or  $\text{TiO}_2$  is very similar to the surface of coatings produced in the industrial solution following pre-activation with the help of standard activator.

It was established that the protective performance of the phosphate layers produced in a 30 °C solution with fine dispersed  $\text{TiO}_2$  or  $\text{SiO}_2$  oxides are comparable to the protective performance of the phosphate layers installed in the industrial phosphatization solution at 70 °C after pre-activation (Fig. 2). The protective performance of the coatings is 100 and 85 s, respectively (it is 100 s for the coatings produced from the same solution but without the use of disperse phases and with pre-activation). The protective performance of the layers produced from the industrial solution with pre-activation are considerably inferior — 45 s.

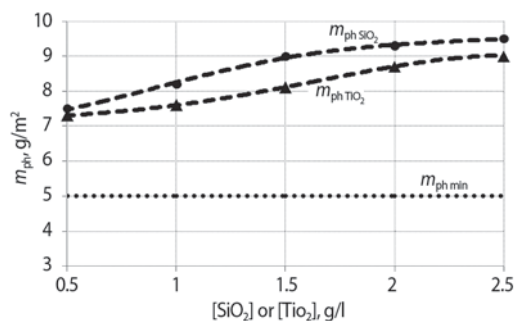
Phosphate coatings of acceptable quality can be obtained when 1.0–1.5 g/l of titanium and silicon oxides are introduced in the low-temperature solution. Coatings produced in the presence of  $\text{TiO}_2$  microparticles demonstrate maximum protective performance. This value is considered the optimum concentration of particles in the low-temperature phosphatization solution.

It is shown that the specific weights of the phosphate layers in view tend to be a little higher in comparison with the phosphate coatings produced from the low-temperature solution with pre-activation (7.2 g/m<sup>2</sup>) and are as follows: 7.8–8.2 g/m<sup>2</sup> and 7.3–7.6 g/m<sup>2</sup>, respectively, in the presence of  $\text{TiO}_2$  and  $\text{SiO}_2$  (Fig. 3).

The increased specific weights of the phosphate layers can probably be attributed to the increased deposition rate on the dispersed  $\text{TiO}_2$  and  $\text{SiO}_2$  particles adsorbed by the surface and their inclusion in the coating composition. When any of the disperse phases is present in the solution,



**Fig. 2. Relationship between the protective performance of the phosphate coatings and the concentration of the  $\text{TiO}_2$  and  $\text{SiO}_2$  disperse phases in the solution with the following composition (g/l):**  
 $\text{ZnO}$  — 10.0;  $\text{H}_3\text{PO}_4$  — 19.0;  $\text{HNO}_3$  — 8.0;  
 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  — 0.3;  $\text{Ce}(\text{SO}_4)_2$  — 0.2;  $\text{NH}_2\text{OH}$  — 2.0;  $\text{pH} = 2 \pm 0.5$ ;  $t = 30$  °C; treatment time — 10 min



**Fig. 3. Relationship between the specific weight of phosphate coatings  $m_{\text{ph}}$  and the concentration of the  $\text{TiO}_2$  and  $\text{SiO}_2$  disperse phases in the solution, (g/l):**  
 $\text{ZnO}$  — 10.0;  $\text{H}_3\text{PO}_4$  — 19.0;  $\text{HNO}_3$  — 8.0;  
 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  — 0.3;  $\text{Ce}(\text{SO}_4)_2$  — 0.2;  $\text{NH}_2\text{OH}$  — 2.0;  $\text{pH} = 2 \pm 0.5$ ;  $t = 30$  °C

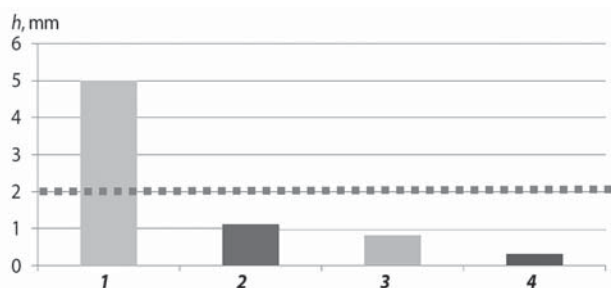
the low-temperature phosphatization time is always the same — 10 min.

It was established that, for the developed process, additional activation in the titanium phosphate suspension before phosphatization produces no positive effect on the protective performance or the specific weight of phosphate layers.

The salt spray chamber tests of steel specimens treated in a combination low-temperature solution and coated with the Ecocolor PE RAL 9016/P paint revealed that the spread of corrosion from the cut (h) does not reach 2.0 mm after 240 hours, which complies with ASTM B117 (Fig. 4).

Cross hatch cut test was conducted to evaluate the adhesion between the paint and the phosphatized surface before and after the salt spray chamber test. The coatings produced in the combination low-temperature phosphatization solution have good adhesion, and it did not deteriorate after the tests.





**Fig. 4. Spread of corrosion h after salt spray chamber testing of painted steel specimens with phosphate coatings produced in the solution, g/l:**

- 1: steel with no coating;  
 2: ZnO — 10.0; H<sub>3</sub>PO<sub>4</sub> — 19.0; HNO<sub>3</sub> — 8.0;  
 FeCl<sub>3</sub>·6H<sub>2</sub>O — 0.3; Ce(SO<sub>4</sub>)<sub>2</sub> — 0.2; NH<sub>2</sub>OH — 2.0;  
 3: ZnO — 10.0; H<sub>3</sub>PO<sub>4</sub> — 19.0; HNO<sub>3</sub> — 8.0;  
 FeCl<sub>3</sub>·6H<sub>2</sub>O — 0.3; Ce(SO<sub>4</sub>)<sub>2</sub> — 0.2; NH<sub>2</sub>OH — 2.0;  
 SiO<sub>2</sub> — 1.0;  
 4: ZnO — 10.0; H<sub>3</sub>PO<sub>4</sub> — 19.0; HNO<sub>3</sub> — 8.0;  
 FeCl<sub>3</sub>·6H<sub>2</sub>O — 0.3; Ce(SO<sub>4</sub>)<sub>2</sub> — 0.2; NH<sub>2</sub>OH — 2.0;  
 TiO<sub>2</sub> — 1.0

### Conclusion

The authors developed an energy and resource saving process of crystalline phosphatization that helps produce highly protective layers on steel surfaces. The authors found that the first layers that form consist of iron oxides and zinc phosphate crystals. Combining the generation of phosphate films and the adsorption of fine dispersed particles of SiO<sub>2</sub> or TiO<sub>2</sub> on the target surface makes it a simpler process in terms of equipment required and saves metals due to the exclusion of activation stage. The process consumes significantly less energy because the phosphatization solution temperature is reduced to 30 °C. The solution has the following composition: ZnO — 10 g/l, H<sub>3</sub>PO<sub>4</sub>—19 g/l, HNO<sub>3</sub> — 8 g/l, FeCl<sub>3</sub>·6H<sub>2</sub>O — 0.3 g/l, Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O — 0.2 g/l, NH<sub>2</sub>OH — 2.0 g/l, SiO<sub>2</sub> or TiO<sub>2</sub> — 1 g/l.

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