APPLICATION OF ORGANIC COATINGS ON AMORPHOUS PHOSPHATED ZINC SURFACES

Tsvetelina L. Liubenova, Dimka I. Fachikova

University of Chemical Technology and Metallurgy
8 Kliment Ohridski blvd., 1756 Sofia, Bulgaria
E-mail: dimkaivanova@uctm.edu

Received 05 June 2023
Accepted 19 July 2023

ABSTRACT

The phosphating of zinc surfaces, increasing their roughness and surface tension, provides high adhesion and a significant increase in the protective ability of subsequently applied organic coatings. This paper presents the results obtained in a study of combined coatings, including the formation of amorphous phosphate films on galvanized steel surfaces, followed by the application of layers of three type paints and varnishes.

By means of gravimetric and physical-analytical methods, the influence of various factors such as concentration and temperature on the formation, composition and properties of the coatings obtained on zinc surfaces in phosphating solutions have been investigated. Coatings obtained at pH 4.0 are distinguished with best homogeneity and color density. The thickness of the coatings grows with increasing of temperature, at other conditions being equal. The composition, structure, roughness and probable compounds of the obtained phosphate coatings have been determined by physical analytical methods. The phosphate coatings contain such elements as oxygen, phosphorus, zinc, molybdenum, nickel, which are probably combined as phosphate and oxide compounds.The phosphate films are X-ray amorphous, with indefinite habit and very well expressive relief. Using physico-mechanical methods, the adhesion, elasticity and impact strength of paint and varnish coatings on phosphated and non-phosphated zinc surfaces were measured.

Keywords: zinc coatings, conversion coatings, phosphating, organic coatings, protective coatings.

INTRODUCTION

Phosphating is known to be one of the most widely used surface treatments of articles made of ferrous and non-ferrous metals and alloys due to its simple and cost-effective realization, relatively good corrosion resistance and especially the provision of superior adhesion with subsequently applied organic coatings [1 - 4]. The earliest methods of phosphating Zn surfaces used the same recipes and technologies used to produce phosphate films on ferrous metals. The differences and peculiarities in the behavior of Zn and its alloys are explained by the higher dissolution rate of Zn in solutions of H_3PO_4 and its acid salts, compared to iron alloys. Compared to chromate, phosphate coatings are significantly more resistant to high temperature, sharply improve the adhesion properties of Zn and its additional resistance to cold deformation - deep drawing, stamping, etc. [5, 6].

In the recent decade, molybdate-based conversion coatings have been introduced as possible replacement for chromate coatings owing to their low toxicity and good corrosion resistance similar to those of chromate coatings. Most of the efforts have been directed towards molybdate-based conversion coatings for zinc, steel and magnesium alloys in order to increase their corrosion resistance [7 - 11, 14].

Duplex systems such as paints, varnishes or powder coatings on hot-dip or electrolytically galvanized steel are becoming more and more commonly used due to the combination of excellent corrosion protection and the achievement of a desirable aesthetic appearance. Correct the selected zinc surface preparation is a key to creating good adhesion between organic coatings and zinc surfaces [12, 13].

The presented work describes the topography and morphology of amorphous phosphating films on zinc surfaces, studied by SEM, EDX and AFM methods. Using physical and mechanical methods, the adhesion, elasticity and impact strength of the paint coatings on phosphated and non-phosphated zinc surfaces were measured.

EXPERIMENTAL

Samples - material, dimensions, treatments

Rectangular shaped specimens (thickness of 1 mm and working surface area $5x10^{-3}$ m^2) of mild steel (0.17 % C) were galvanized in a conventional KCl - electrolyte. Additionally, square-shaped samples (10x10 mm) are used for the physical analyses. The preliminary treatment of the galvanized specimens prior to phosphating include sequential brightening, activation in solutions based on organic acids, rinsing and drying.

The amorphous phosphating concentrate (APhC) is a liquid, containing zinc, nickel and molybdenum hydrogen orthophosphates, phosphoric acid, stabilizing agents and accelerators. The most important characteristics of APhC, used in the experiments: density, ρ, pH, conductivity, σ and a total acidity, $K_{ta,}$ are presented in Table 1.

The phosphating conditions are as follows:

Concentration, vol. %: 5.0; 10.0; 15.0 and 20.0;

Temperature, ^oC: 20.0; 40.0; 60.0 and 80.0;

Process duration, min: 0.5; 1.0; 3.0; 5.0 and 7.0.

Paints and varnishes

Three types of organic coatings were applied to the phosphated zinc surfaces by spraying with a spray gun. Drying of coatings was carried out at room temperature, only the combined urea varnish was baked at 180^oC for an hour.

Enamel varnish, gray. It is a suspension of pigments and fillers with epoxy, alkyd resins and nitrocellulose in a mixture with organic solvents, plasticizers and other components with specific action. They are designed for painting pre-primed metal surfaces, operated indoors.

Combined urea varnish, green. It is a well-homogenized suspension of finely ground pigments of urea-formaldehyde and alkyd resin in organic solvents.

Table 1. Characteristics of amorphous phosphating concentrate.

Concentrate	ρ, g cm^{-3}	pH	σ, mS sm^{-1}	K_{ta}
APhC	1.21	4.80	46.2	200

They are designed for painting pre-primed metal surfaces of machines, vehicles, etc., mainly for special production.

UV powder coating, anthracite-gray metallic. For architectural application - roofing material from an organic basis, thermally hardening, duroplastic, corresponding to the state of the art. Powder coating consists of polyester resin with suitable hardener, additives, suitable filler and weather resistant pigments.

Methods

The *Gravimetric method* was used for studying kinetics of forming and increasing of the coating's mass/thickness, depending on the influence of different factors. The method allows determining mass alteration of the samples after formation and removal of the phosphate coatings, defined as:

$$M = \frac{m_1 - m_2}{S}$$

where M, g m^{-2}, is *a mass* or as accepted to call *a thickness* of the obtained coating, m_1 and m_2 are the sample mass before and after removal a coating, g, and S is the sample surface area, m^2.

Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM/EDX). SEM/EDX provides a pictorial representation of the surface morphology and structure with the elemental composition of the selected area. The coatings were examined by a SEM/FIB LYRA I XMU, TESCAN electron microscope and an apparatus Quantax 200, BRUKER with spectroscopic resolution at Mn-Kα and 1 kcps 126 eV.

Atomic force microscopy (AFM). Imaging was performed on the NanoScopeV system and Caliber (Veeco Instruments Inc.) operating in tapping mode in air at RT. Silicon cantilevers (Tap300Al-G, Budget Sensors, Innovative Solutions Ltd, Bulgaria) with an aluminum reflective coating with a thickness of 30 nm were used. According to the producer's datasheet the cantilever spring constant was in the range of 1.5 to 15 N m^{-1} and the resonance frequency was 150 ±75 kHz.

The tip radius was less than 10 nm. The scan rate was set at 1 Hz and the images are captured in the height mode with 512x512 pixels in a JPEG format. Subsequently, all the images were flattened by means of the Nanoscope software. Images from three independent experiments were analyzed. The results quantification was performed by WSxM5.0 Develop 1.3 software.

Measuring of the adhesion - ISO 2409, Table 2 [15]. This test method cover procedures for assessing the adhesion by cuts made in the film and is used to establish whether adhesion of the coating to a substrate is at the required level. A lattice pattern with six sections in each direction at right angles is made in the film and with the help of descriptions and illustrations the adhesion is evaluated by comparison. The distance between the cuts in each direction must be the same and depends on the thickness of the coating, in our case, when the thick coating is 0 μm - 60 μm - 1 mm is the distance for hard substrates. The test specimens are 150 mm x 100 mm. Before the test, they shall be tempered for at least 16 hours at a temperature of 23 ± 2°C and a relative humidity of 50 ± 5 % .

Resistance of the paint and varnishes to cracking and/or stripping - impact test (ASTM D3359-09) [16]. The method consists in determining the maximum height from which, when a weight of a certain mass falls, no visible mechanical damage occurs on the surface of a metal plate with a combined coating applied. The determination is performed at a temperature of 20 ± 2°C and a relative humidity of 65 ± 5 %. The test is based on a falling mass of a certain weight (500 g) at a minimum drop height (1 m), which leads to cracking and/or removal of the film from the metal substrate.

RESULTS AND DISSCUTION

Gravimetric investigations

The change in the mass/thickness of the galvanized samples, phosphated in APhC solutions, was determined by means of gravimetric measurements (Fig. 1). From the course of the curves, it follows that the mass/thickness of the films formed on zinc surface grows with time (faster up to about 3rd min) when increasing the concentration and temperature, especially above 60°C, of the working solutions. The growth retardation after the 3rd minute can be explained by the shielding effect of the phosphate coating, formed on the zinc during this period. An increase in temperature leads to a rise in the mass/thickness of the coatings (5 - 10 times) in the entire studied concentration range - with the greatest and very close mass/thickness are the coatings obtained in 15 % and 20 % solutions.

Characterization of the amorphous phosphate coatings

The elemental quantitative composition of the amorphous phosphate coatings (O, P, Mo, Ni and Zn), determined by *EDX analysis*, is presented in Table 3. The

Table 2. Six-steps classification of ISO 2409 cross-cut adhesion test'

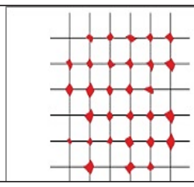
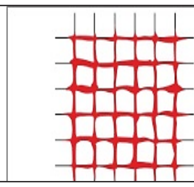
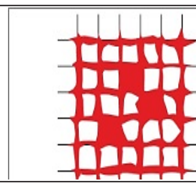
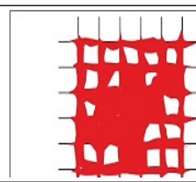
Classification	0	1	2	3	4	5
Detachment	*None*	*< 5 %*	*5 % ~ 15 %*	*15 % ~ 35 %*	*35 % ~ 65 %*	*> 65%*
Appearance of surface of cross-cut area	-					-

Table 3. EDX analysis of the elements in the phosphate coatings on zinc surfaces.

Elements	5 vol.%		10 vol.%		15 vol.%		20 vol.%	
	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %
O	11.25	33.95	17.65	46.42	15.05	41.72	13.65	38.98
P	2.24	3.49	4.53	6.15	2.58	3.69	2.38	3.52
Mo	5.69	2.86	13.11	5.75	6.16	2.85	5.53	2.63
Ni	0.53	0.44	0.70	0.50	0.49	0.37	0.54	0.42
Zn	80.28	59.26	64.01	41.18	75.73	51.38	77.91	54.45

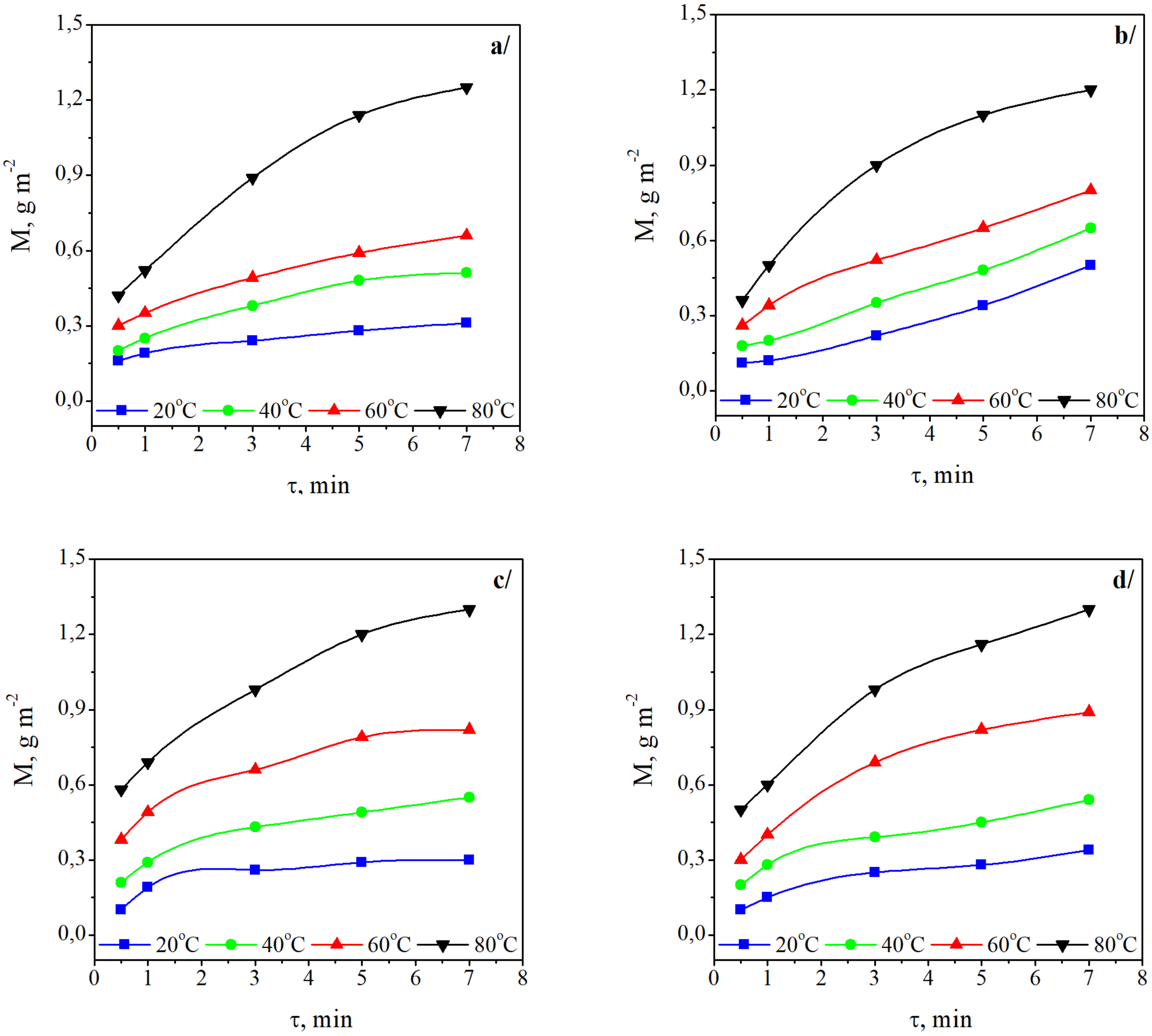


Fig. 1. Effect of phosphating duration (τ, min) on the thickness/mass (M, g m^{-2}) of the formed films: a) 5 vol. %; b) 10 vol. %; c) 15 vol. %; d) 20 vol. %.

results show that the content of all elements, except Zn, is the highest in the coating, obtained in 10 % solution. The amounts of elements in the coatings obtained at the other concentrations of the phosphating solutions do not differ significantly, but the amount of Zn is significantly higher in them, compared to the coating in a 10 % solution.

The *SEM micrographs* (Fig. 2) show the morphology of the amorphous phosphate coatings, obtained on zinc surfaces at 5.0, 10.0, 15.0 and 20.0 vol. % of the phosphate baths, duration 7 min and at 60°C. The morphology of the phosphate films is the same to all over the surface of samples. They are uniform, striated with an indeterminate geometry, and a deepening of the cracks is observed with increasing concentration of the working solutions. In the literature such type of surface structures are related to the conversion coatings (chromate or phosphate), is known as a „dry river bed". A grooved surface provides a good adhesion characteristic with the following organic coatings.

The topographic *AFM* view, shown in Fig. 3, corresponds to conditions of formation the phosphate films described above. Each coating was scanned three times by random selection onto the area 5x5 µm and 512 points per line. The results show a good reproducibility of the data for each sample, as well as the homogeneity of the obtained coatings, as was also confirmed by SEM observations. The records of these measurements are summarized in Fig. 4.

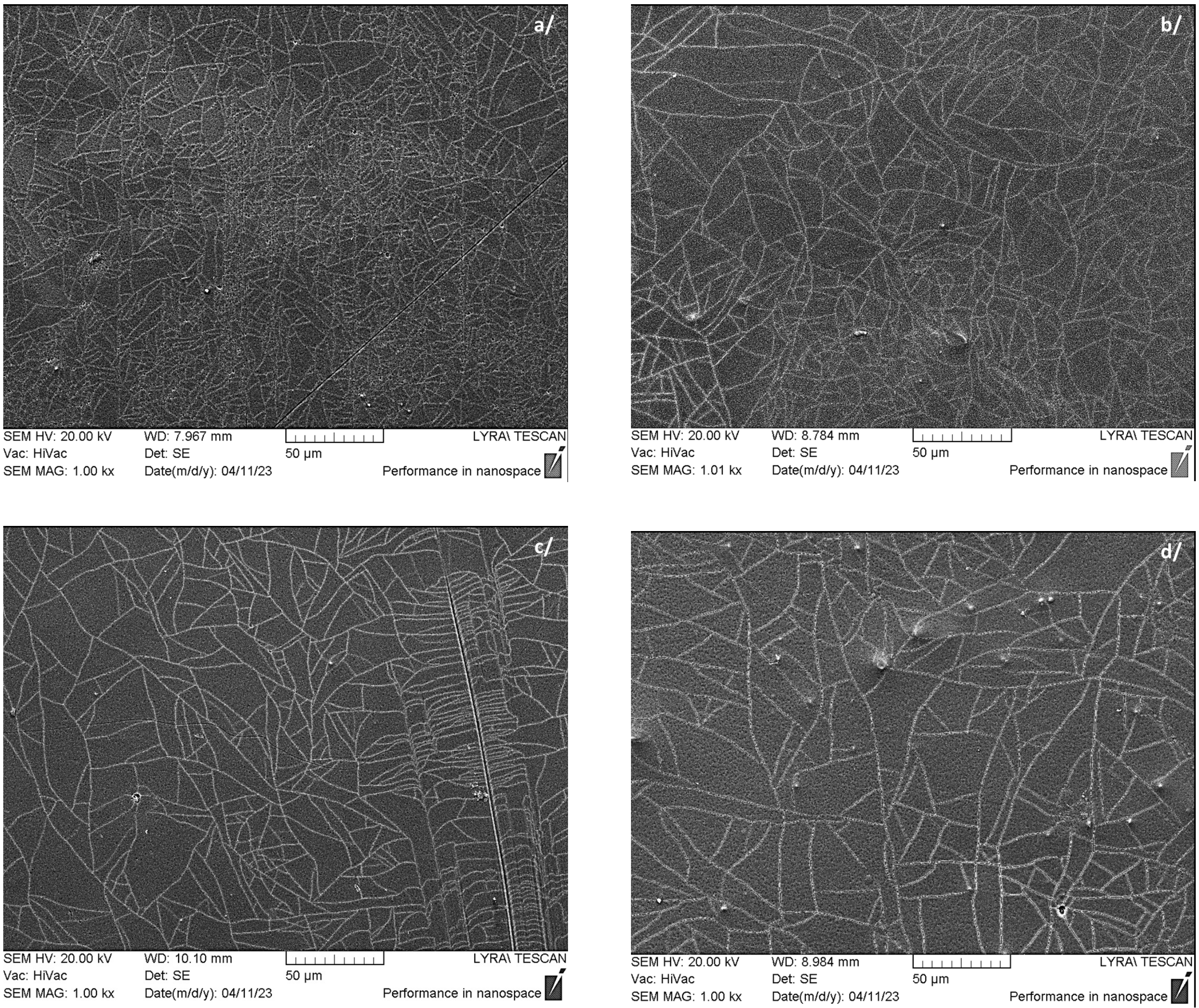


Fig. 2. SEM microphotographs of the phosphate coatings, obtained on zinc surfaces at 60°C, 7 min time of duration and concentration of the phosphating baths: a) 5 vol. %; b) 10 vol. %; c) 15 vol. %; d) 20 vol. %.

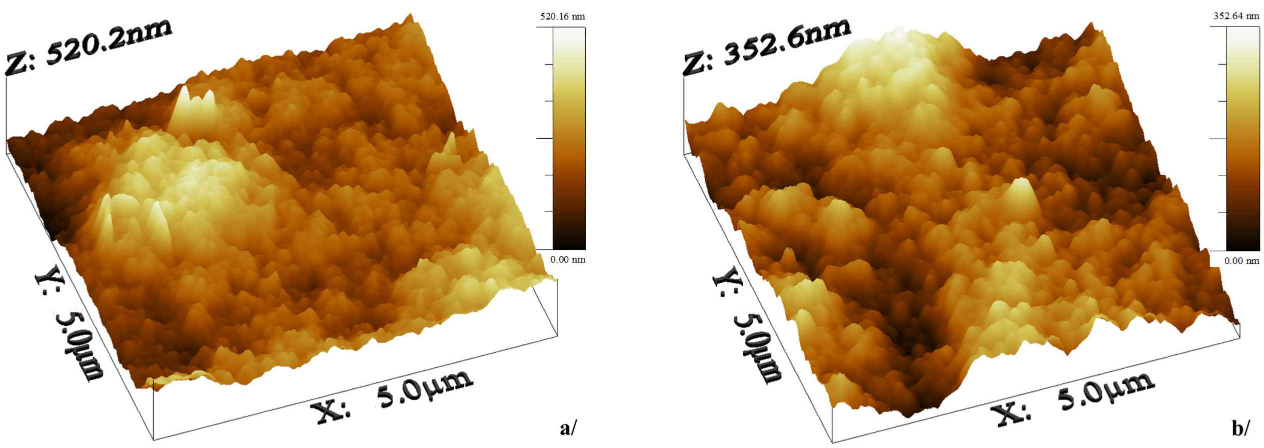


Fig. 3. AFM 3D images of amorphous phosphate films, formed in baths: a) 5 vol. %; b) 10 vol. % at 60°C, duration 7 min.

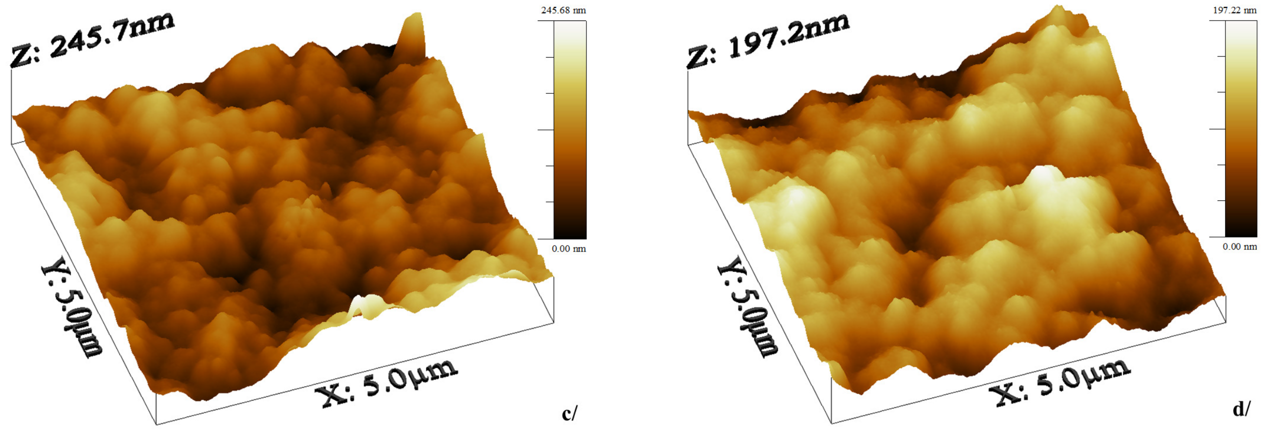


Fig. 3. AFM 3D images of amorphous phosphate films, formed in baths: c) 15 vol. %; d) 20 vol. % at 60^{o}C, duration 7 min .

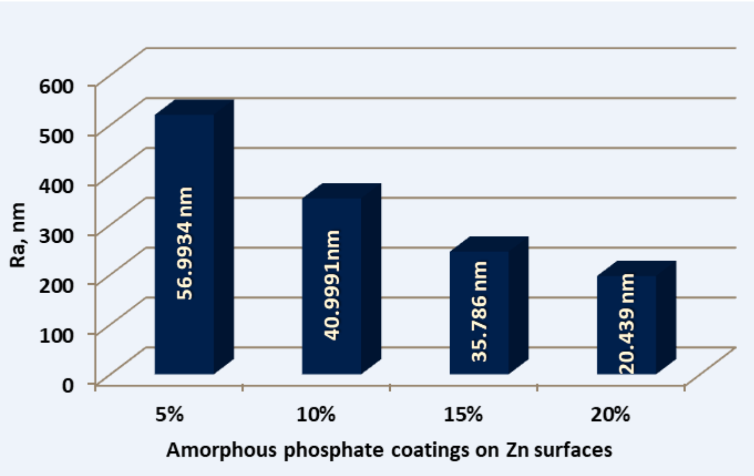


Fig. 4. Average roughnesses data of the amorphous phosphate films.

The amorphous phosphate coating formed in the 5 % solution has the highest roughness compared to that of the coatings obtained at the other concentrations of the solutions. This is probably related to the smaller number of nuclei around which the coating grows at this concentration, compared to the larger number at the higher concentrations, suggesting faster and more homogeneous coating formation.

The well-developed surface roughness of thin phosphate films, as well as their chemical composition, will improve adhesion to subsequent organic coatings. The test of three types of paint and varnish coatings by standard adhesion measurement methods was carried out according to the procedure described above. Fig. 5 shows the photographs of the test-samples after the cross-cuts and in Table 4 are presented results, indicating their classification unit.

The amorphous-phosphatized surfaces with *combined urea varnish (green)* and *UV powder coating (anthracite-gray metallic)*, applied to them correspond to qualification unit 0, according ISO 2409, Table 2 - the edges of the grooves are completely smooth and none of the grid squares are separated. The specified qualification unit 0 is a proof of excellent adhesion of these organic coatings to the substrate. The *enamel varnish (gray)* conforms to qualification unit 2 (coating is flaky at the edges and/or at the intersections - surface disturbed by scoring is significantly greater than 5 % but not greater than 15 %).

The test for resistance to cracking and/or stripping, through the so-called impact test, for the three tested organic coatings was performed according to the methodology described above. Fig. 6 shows the photographs of the samples after the impact test - ASTM D3359-09 .

Table 4. Results of cross-cut adhesion test.

Treatment steels	Enamel varnish /gray/	Urea varnish combined /green/	Powder UV coating /anthracite-gray metallic/
1. Zn	3 score	1 score	1 score
2. APhC	2 score	0 score	0 score

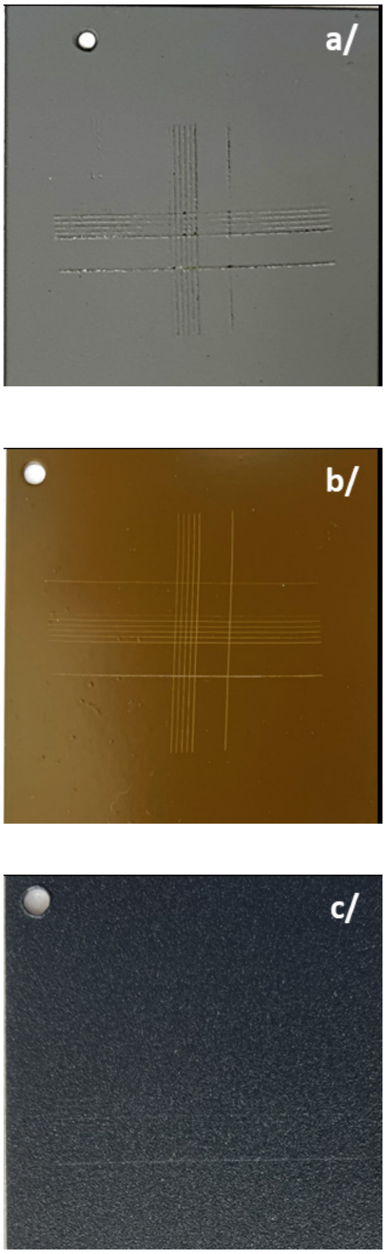


Fig. 5. Photographs of adhesion tapes after adhesion strength test: a) enamel varnish, gray; b) combined urea varnish, green; c) UV powder coating, anthracite-gray metallic.

Fig. 6. Results of the impact testing of organic coatings: a) enamel varnish, gray; b) combined urea varnish, green; c) UV powder coating, anthracite-gray metallic.

The study of the impact resistance of the coatings shows that no cracking and peeling of the organic coatings (grey, green and anthracite-gray metallic) is observed.

CONCLUSIONS

The phosphating processes of galvanized surfaces in the phosphate concentrate (*APhC*), followed by application of organic coatings have been studied by gravimetrical and physico-analytical methods. It was established that:

- The thickness of the phosphate coatings grows with the increase of concentration and temperature of the phosphating baths. The largest and smallest thickness of the phosphate coatings were obtained at 80°C and 20°C, respectively.
- The content of all elements (O, P, Zn, Ni and Mo), except Zn, is the highest in the coating, obtained in 10 % solution. The amounts of elements in the coatings obtained at the other concentrations do not differ significantly, but the amount of Zn is significantly higher in them, compared to the coating in a 10 % solution.
- The morphology of the phosphate films is uniform over the entire surface of the samples. They are uniform and grooved with an undefined geometry of the tracks.
- The adhesion and impact resistance of three types of organic coatings applied on phosphating and no phosphating Zn surfaces were measured and compared.

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