

D. FACHIKOVA^{1*}, T. LIUBENOVA¹, G. ILIEVA¹**COMBINED 3-COMPONENTS PHOSPHATE AND ORGANIC COATINGS ON ZINC SURFACES**

In recent years, the production of galvanized sheet steels with organic coatings applied to its surfaces has considerably expanded. Phosphating of the zinc surfaces raises its roughness and surface tension, providing high adhesion of subsequent organic coatings and respectively, significant increasing of their protective properties. The paper presents the results obtained in the investigation of combined anti-corrosion coatings, including formation of phosphate films on galvanized steel surfaces followed by the application of three types of paint and varnish coatings. The indicators characterizing the phosphating preparation (density, pH, conductivity, acid capacity) as well as the thickness of the coatings were measured. The chemical composition of the phosphate films, their morphology and topography were determined by means of EDX and SEM, respectively. The adhesion, elasticity and impact toughness of the organic coatings, with and without phosphating treatment of the zinc surfaces were measured. The corrosion resistance of the combined coatings in a model sodium chloride solution was also determined.

Keyword: Zinc surfaces; Phosphatizing; Zinc, Nickel and Calcium Phosphates; Organic coatings; Protective coatings

1. Introduction

Electrodeposited and hot-formed zinc coatings are widely used to protect carbon steels from corrosion, both alone and in combination with various organic coatings. To improve the adhesion of the latter, zinc coatings are pre-treated, and most often their phosphating is used. Phosphating is a widespread conversion process in many areas of industry and can be applied to surfaces of steels, galvanized steel, zinc, aluminum and their alloys [1-3].

Various approaches have been proposed to improve the quality of zinc phosphating, including: accelerating phosphating, reducing the temperature of the phosphating bath and reducing process time by using baths with low zinc content, organic compounds, metal salts – nobler than phosphating metal, the use of more than one heavy metal ion in an existing composition – in particular two- and three-cation phosphating, stabilizers, electric current, etc. [4-7,9-12].

The modification of zinc phosphating concentrates with manganese and nickel phosphates have led to the development of tri-cation phosphating baths consisting of zinc, manganese and nickel phosphates, which explored its potential utility mainly in the automotive industries to phosphate aluminium, steel and galvanized steel using the same formulations [3,6,10-14].

Incorporation of calcium phosphates in a zinc phosphating bath has resulted in a considerable decreased in grain size, more compact crystal structure, and better corrosion resistance and prevention ability of phosphate coatings [3,10,11]. Similarly, the addition of manganese and nickel ions in the zinc phosphating bath proves to be useful in refining the crystal size and improving the corrosion resistance of the resultant phosphate coating. The inclusions of manganese and nickel ions modify the hopeite deposits equivalent to phosphophyllite to have better thermal and chemical stabilities. This type of phosphating is classified as nickel and manganese modified zinc phosphating. Further, Ni²⁺-ions increased the alkaline stability of phosphate layers and they are suitable as substrate to alkaline type organic coatings [7,8,11].

Duplex systems consisting of paint or powder coatings on phosphated galvanized surfaces are widely used as a means of improving the corrosion protection of various products. Painting of zinc surfaces is a difficult task, the solution of which lies in their preliminary preparation. The application of organic coatings on phosphated galvanized surfaces is becoming more common and popular due to this combination of advantages – good adhesion, improved corrosion protection, desirable color and others [15,16].

The present work aims to investigate the phosphatizing of galvanized mild steel in tri-cations concentrates containing zinc,

¹ UNIVERSITY OF CHEMICAL TECHNOLOGY AND METALLURGY, FACULTY OF CHEMICAL TECHNOLOGY, 8 KLIMENT OHRIDSKI BLVD., 1756 SOFIA, BULGARIA

* Corresponding author: dimkaivanova@uctm.edu



nickel and calcium phosphates in correlation 7:2:1. The effects of bath concentration and temperature on the coating thicknesses, structures, phase and chemical composition were studied. The corrosion resistance of the phosphate coatings obtained was investigated, too. The adhesion and impact resistance of three types of organic coatings applied on phosphate films were measured and compared with those applied on bare zinc surfaces.

2. Experiment

2.1. Materials and samples

Disc shaped specimens (thickness of 1 mm and working surface area $1 \times 10^{-3} \text{ m}^2$) of mild steel (0.17% C) were coated by zinc in a conventional acidic potassium-chloride electrolyte. The electrochemical measurements are carried out with plate-shaped specimens and dimensions in accordance with ISO 17475:2005 and a fixed working surface area of $1 \times 10^{-4} \text{ m}^2$. In addition, samples of square plates (10×10 mm) are used for the physicochemical analyzes. The preliminary treatment of the zinc-plated specimens prior to phosphating include sequential brightening and activation in solutions based on organic acids, rinsing and drying.

2.2. Solutions and working conditions

The working media for the crystalline phosphating of zinc surfaces are aqueous solutions of a 3-component concentrate – ZnNiCaPh, containing zinc, nickel and calcium orthophosphates in proportions Zn:Ni:Ca = 7:2:1. Phosphating concentrate is a liquid, containing acidic orthophosphates of the respective metals, a free phosphoric acid, inorganic salts and others. The $\text{P}_2\text{O}_5:\text{NO}_3^-$ – ratio in the concentrate is 1:3.

The working conditions are as follows:

- Concentration of phosphating solutions: 5.0 vol. %, 10.0 vol.%, 15.0 vol % and 20 vol.%;
- Temperature of phosphating solutions: 20.0°C, 40.0°C, 60.0°C and 80.0°C;
- Duration of phosphating: 5.0 min, 10.0 min, 15.0 min and 20.0 min.

The model medium used to determine a corrosion resistance of the coatings at room temperature was 0.6 M NaCl.

2.3. Organic coatings

Three types of organic coatings were applied to the phosphated zinc surfaces by spraying with a spray gun. Only the combined urea varnish was baked at 180°C for an hour.

Varnish BT-58 /black/. It is a solution of asphalt resin in a mixture of organic solvents and is designed for painting the interior surfaces of products, to eliminate the contact of special substances with construction materials.

Enamel varnish EP-53 /gray/. It is a suspension of pigments and fillers with epoxy and alkyd resins and nitrocellulose in a mixture of organic solvents with the addition of plasticizers and other components with specific action. They are designed for painting pre-primed metal surfaces, operated indoors.

Urea varnish combined /green/. It is a well-homogenized suspension of finely ground pigments of urea-formaldehyde and alkyd resin in organic solvents. They are designed for painting pre-primed metal surfaces of machines, vehicles, etc., mainly for special production.

2.4. Methods of investigation

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 the 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 .

Potentiodynamic polarization method. The polarization relationships, recorded potentiostatically or potentiodynamically allow determination of various corrosion characteristics such as corrosion rate, corrosion potential, etc. The experiments were carried out with EG&G Princeton Applied Research, Potentiostat/Galvanostat, Model 263A, provided with the specialized software package PowerCORR®.

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 chosen areas. 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-K α and 1 keps 126 eV.

X-ray diffraction (XRD). The investigations to determine the phase composition of the coatings, were carried out by Automatic Powder X-ray Diffractometer Bruker D8 Advance Eco with high-resolution energy-dispersive detector LYNXEYE XE, using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) and Ni filter. X-ray spectra were recording in the interval $8^\circ < 2\theta < 80^\circ$ at a scan speed of $0.03^\circ 2\theta$ and time of counting 52.5 s/step. Quality phase analysis was achieved by using Powder Diffraction FileTM (PDF®) PDF-2 (2009) of International Centre for Diffraction Data (ICDD).

Atomic force microscopy (AFM). AFM imaging was performed on the NanoScopeV system and Caliber (Veeco Instruments Inc.) operating in "tapping mode" at RT. We used silicon cantilevers (Tap300-G, Budget Sensors) with 30 nm thick aluminum reflex coating. According to the producer's datasheet, the cantilever spring constant was in the range of 40 N/m and the resonance frequency was 300 kHz. The tip ra-

dus was less than 10 nm. The scan rate was set from 0.400 Hz to 0.500 Hz.

Thickness measurement without destruction. The thickness of the combined anti-corrosion coatings – will be measured with a caliper “MiniTEST 3100”, designed to measure the thickness of layers of different materials. The caliper works on the principle of magnetic-inductive or eddy current method depending on the type of probe with which it works. Operates at ambient temperature $0 \div 50^\circ\text{C}$. The initial sensitivity of the device is $0.1 \mu\text{m}$. Smallest measured surface – $5 \times 5 \text{ mm}$. Measurement range $0 \div 2000 \mu\text{m}$.

Standard test methods for measuring adhesion [17]. These test method covers procedures for assessing the adhesion of coating films to metallic substrates by applying cuts made in the film. Test method is not considered suitable for films thicker than $125 \mu\text{m}$. These test method is used to establish whether the adhesion of a coating to a substrate is at a generally adequate level. A lattice model with six sections in each direction, made at right angles, is made in the film to the substrate and the adhesion is evaluated by comparison with descriptions and illustrations. 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 coating is $0 \mu\text{m}$ thick $\div 60 \mu\text{m}$ – 1 mm distance for hard substrates. The test specimens are $150 \text{ mm} \times 100 \text{ mm}$. Before the test, they shall be tempered for at least 16 hours at a temperature of $23 \pm 2^\circ\text{C}$ and a relative humidity of $50 \pm 5\%$.

Resistance of paints and varnishes to cracking and/or stripping – impact test [18]. 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 $20 \pm 2^\circ\text{C}$ and a relative humidity of $65 \pm 5\%$. The test is based on a falling mass of a certain weight (500 g) at a certain minimum drop height (1 m), which leads to cracking and/or removal of the film from the metal substrate.

3. Results and discussion

3.1. Gravimetric method Results

The most important characteristics of the phosphating concentrate used in the experiments: density, ρ ; pH; conductivity, σ ; total, K_{ta} and free, K_{fa} acidity are presented in TABLE 1.

TABLE 1

Phosphating concentrate characteristics

Solution	ρ [g cm ⁻³]	pH	σ [mS cm ⁻¹]	K_{ta}	K_{fa}
ZnNiCaPh	1.325	1.85	174.6	356	60

Typical thickness kinetic plots (M vs. time) shown on Fig. 1 corresponds to coatings obtained on zinc coated steel surfaces

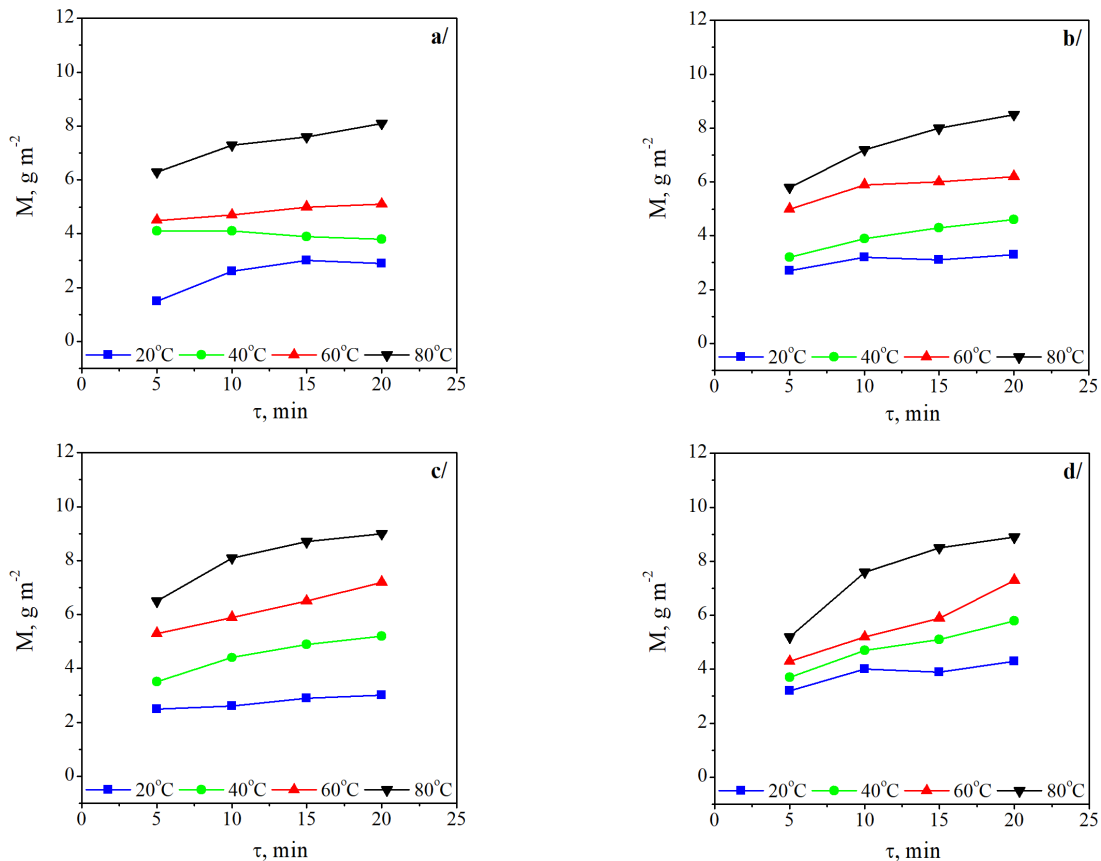


Fig. 1. “Thickness, M – process duration, τ ” relationships at different temperatures of the phosphating baths and concentrations on zinc surfaces (% vol.): a/ 5%; b/ 10%; c/ 15%; d/ 20%

in working solution of different concentrations (5.0-20.0 vol.%) and temperatures (20-80°C) of the phosphating baths. From the course of the curves, follows that the thickness of the coatings increases with the concentration and to a lesser extent by temperature of the solution. It attains highest values at 80°C and lowest at 20°C – more than twice.

3.2. Potentiodynamic polarization results

The aim of these experiments was to obtain information about behavior of the formed crystalline phosphate coatings under cathodic and anodic polarization in a model corrosion environment. The potentiodynamic polarization investigations of the phosphate coatings are carried out at room temperature (20°C) in a model aqueous solution of 0.6 M NaCl. The scanning rate 10 mV s⁻¹ was chosen, based on preliminary test runs.

The potentiodynamic polarization relationships of phosphate coatings on zinc surfaces (see Fig. 2) allow the determination of both the corrosion potentials and the corresponding corrosion current densities. The potential of the phosphate coating, obtained in solution of ZnNiCaPh on the zinc surface is more positive (about 150 mV) then the potential on unphosphating zinc surface. The more positive potentials and the lower corrosion current density of the phosphate coating indicate higher corrosion resistances and improved protective abilities when they are compared to referent pure zinc surfaces.

3.3. Characterization of the Coatings by SEM and EDX

Scanning electron microscopy (SEM) together with X-ray spectroscopy (EDX) and the SE detector (Secondary electron emission) represent ones of the most important material science and engineering analytical techniques. The micrographs in Fig. 3

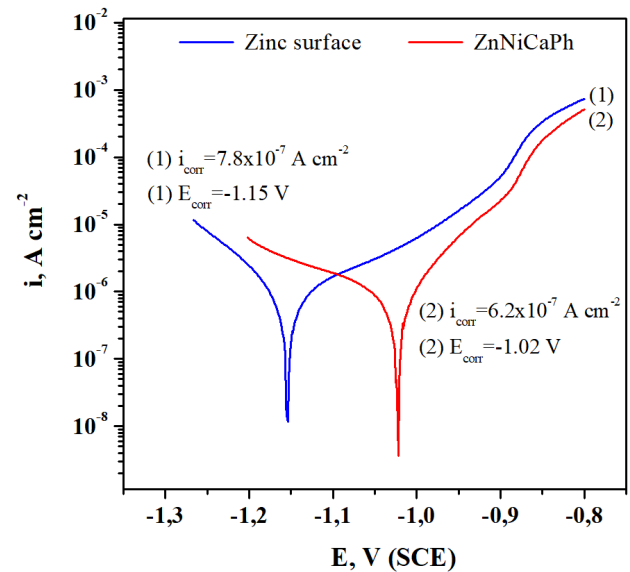
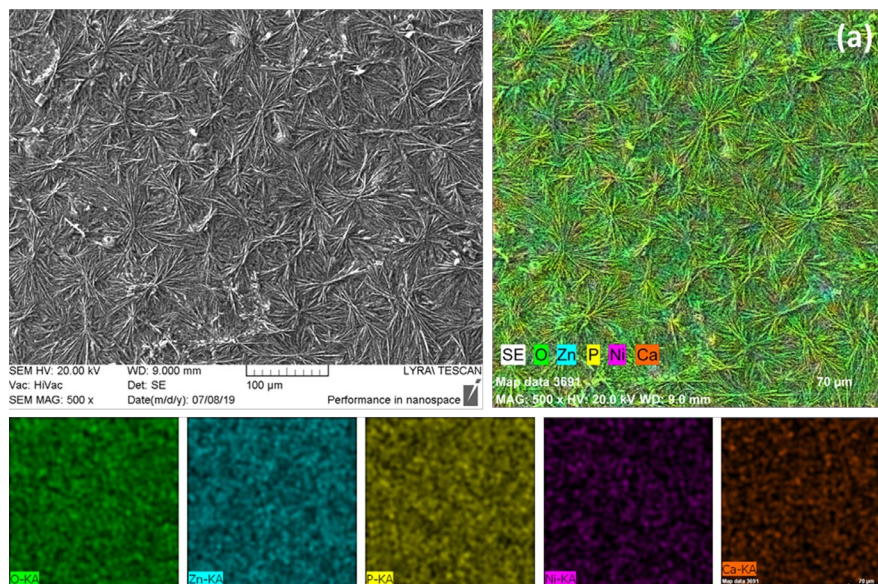


Fig. 2. Potentiodynamic polarization relationships of phosphate coating obtained in 15 vol.% at 60°C for 10 min and on an unphosphated zinc surface, in 0.6 M NaCl

show the morphology and distribution of the elements in the phosphate coatings, obtained on galvanized samples at 60°C and a duration of 10 minutes for different concentrations of the phosphate baths. The structure of the phosphate coatings is the same to all over the surface of the samples – i.e., the crystals initiate from one center and increase radially like spherulite. The crystals obtained in 5% concentration of the phosphating bath have dimensions of less than 100 µm, clearly defined and densely covering the surface. As should be expected with the increase of concentration of the phosphating solution, the crystals of the coatings grow and become denser.

TABLE 2 summarizes the element composition in atomic and weight percentages, obtained by the EDX-spectra of the coatings. The basic elements, which are registered in the coatings, are O, Zn, P, Ni and Ca – in relation with the composition of the main metal phosphates in solutions.



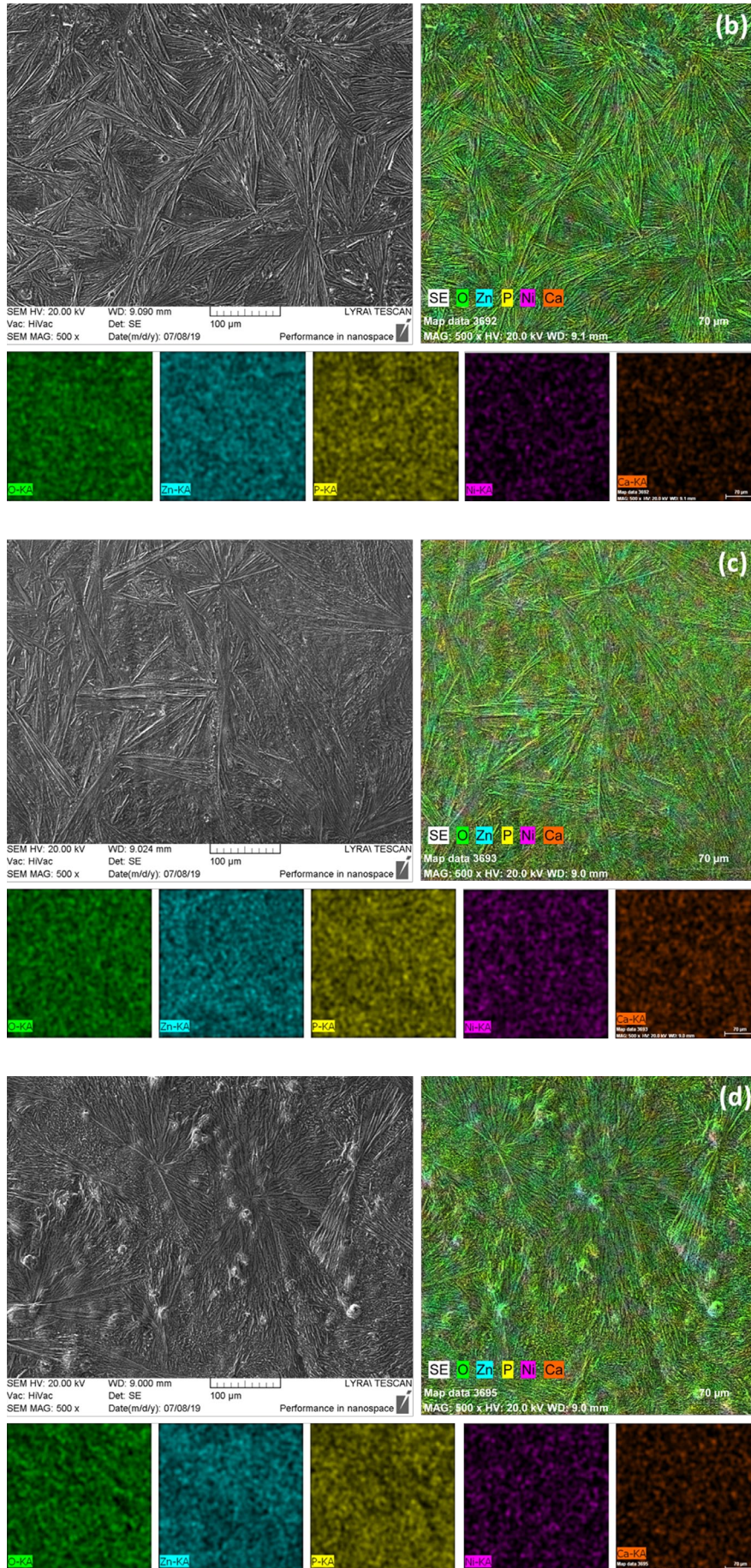


Fig. 3. SEM – microphotographs and the distribution of the elements in coatings, obtained on zinc-coated samples at 60°C and 10 minutes time of duration: (a) 5 vol.%; (b) 10 vol.%; (c) 15 vol.%; (d) 20 vol.%

TABLE 2

EDX analyses of the elements in the phosphate coatings on zinc coated surfaces

Elements	5 vol.%	10 vol.%	15 vol.%	20 vol.%
	Atomic %	Atomic %	Atomic %	Atomic %
O	59.42	60.07	59.52	58.03
Zn	28.67	26.45	28.26	29.80
P	11.65	13.11	11.78	11.59
Ni	0.15	0.20	0.23	0.30
Ca	0.11	0.17	0.21	0.28
Totals	100	100	100	100

3.4. Characterization of the Coatings by XRD

The X-Ray Diffraction-spectra (XRD) of the crystalline phosphate coatings on zinc surfaces grown in 5.0, 10.0, 15.0 and 20.0 vol.% concentration of the phosphating solutions at 60°C and 10 minutes time of duration on mild steel surface are shown on Fig. 4. The only phase clearly registered in the coatings is a *hopeite*. The amount of nickel and calcium phosphates, despite being registered in the coatings, are not sufficient for the formation of a new phase.

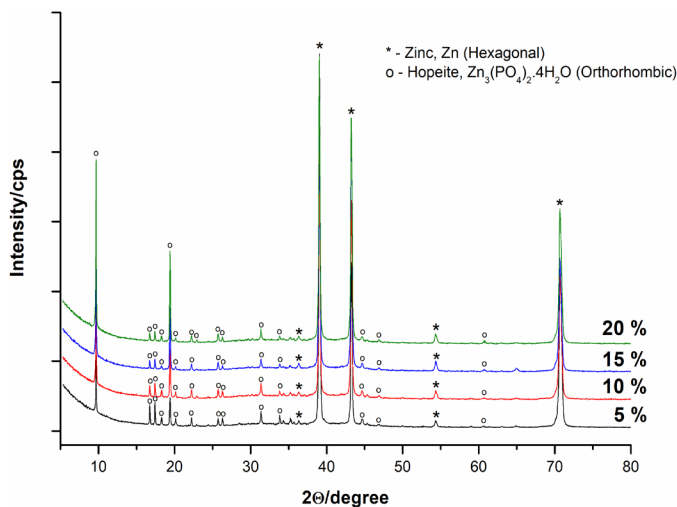


Fig. 4. XRD-spectra of the crystalline phosphate coating formed on the zinc surfaces

3.5. Characterization of the Coatings by AFM

The three-dimensional contour maps obtained by the Atomic Force Microscopy (AFM) on Fig. 5, illustrates the well-developed crystalline structures of the phosphate coatings obtained in solution with 15 vol.% concentration, at 60°C and 10 minutes time of duration. The areas of the scanned surfaces used for analyses are 50 μm × 50 μm. The AFM image indicates comparatively homogenous surfaces of the phosphate coatings. The average values of the coating roughnesses are listed in

TABLE 3. The well-developed surface roughness of the phosphate coatings, as well as their chemical contents will enhance the adhesion to subsequent paint or polymer coatings.

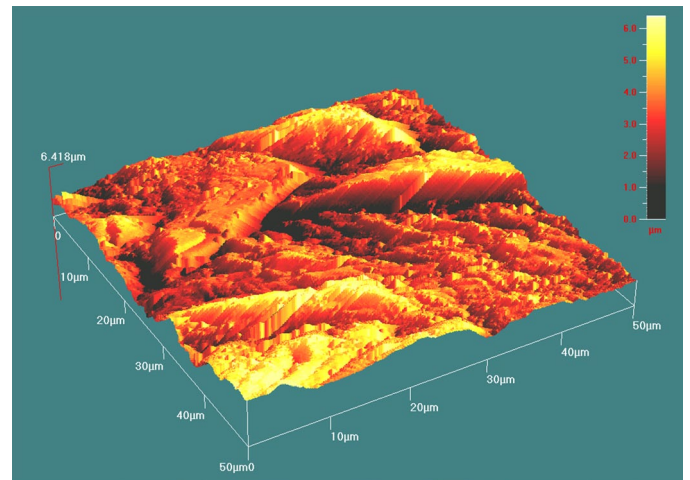


Fig. 5. AFM three-dimensional image of crystalline phosphate coating on zinc surface

TABLE 3

Roughness data of the phosphate coatings

Sample	Ra , μm	Rq , μm	Rp , μm	Rv , μm	Rt , μm
zinc surface	0.767	0.972	2.955	3.463	6.418

3.6. Thickness measurement without destruction

The measurement of thicknesses of the combined coatings was performed according to the methodology described above. The combined caliper works by the method of eddy currents for non-ferrous metal substrates. The measured thicknesses of the organic coatings are 22 μm for a black lacquer, 34 μm for a gray enamel lacquer and 41 μm for the green combined urea varnish. The measured thicknesses correspond to the recommendations for their practical applications.

3.7. Standard test methods for measuring adhesion

The test of the three organic coatings for adhesion by the standard test methods for measuring adhesion, was performed according to the procedure described above. Fig. 6 shows the photographs of the samples after the cuts. TABLE 4 presents the test results, indicating their classification unit.

Coatings with the applied black and green paint correspond to qualification unit 0 (the edges of the cuts are completely smooth; none of the squares of the lattice is detached). Qualification unit 0 is proof of excellent adhesion to the substrate. The grey coating corresponds to qualification unit 2, according ISO 2409 (the coating has flaked along the edges and/or at the

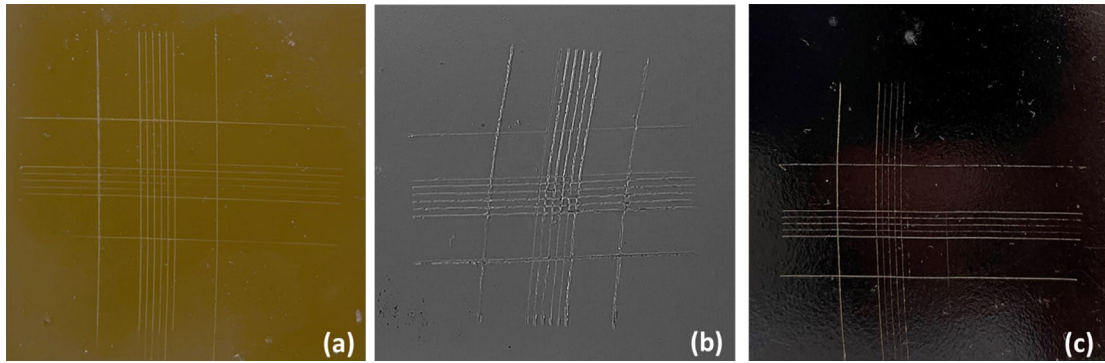


Fig. 6. Photographs of adhesion tapes after adhesion strength test

TABLE 4

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	—					—

intersections of the cuts; a cross-cut area significantly greater than 5%, but not significantly greater than 15%, is affected).

3.8. Resistance of paints and varnishes to cracking and/or stripping – impact test

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 in section Methods of investigation. Fig. 7 shows the photographs of the samples after the impact test.

The study of the impact resistance of the coatings shows that no cracking and peeling of the organic coatings (green and gray) is observed, while with the black organic coating, damage is observed, albeit small.

4. Conclusions

The phosphating processes of electrogalvanized surfaces in three-cation concentrate (ZnNiCaPh), followed by application of organic coatings have been studied by gravimetric, potentiodynamic polarization, SEM/EDX, XRD, AFM and standard methods for measuring the adhesion. It was established that:

- The thickness of the phosphate coatings increases with the rise of concentration and temperature of the bath solution. The highest and the lowest thicknesses of coatings were received at 80°C and 20°C, more than twice respectively.
- All coatings formed in the studied phosphate baths have good resistance in a model 0.6 M NaCl corrosion medium. The more positive potentials (about 150 mV) and the lower corrosion current density also show higher protective abilities, compared to the bare zinc surface.

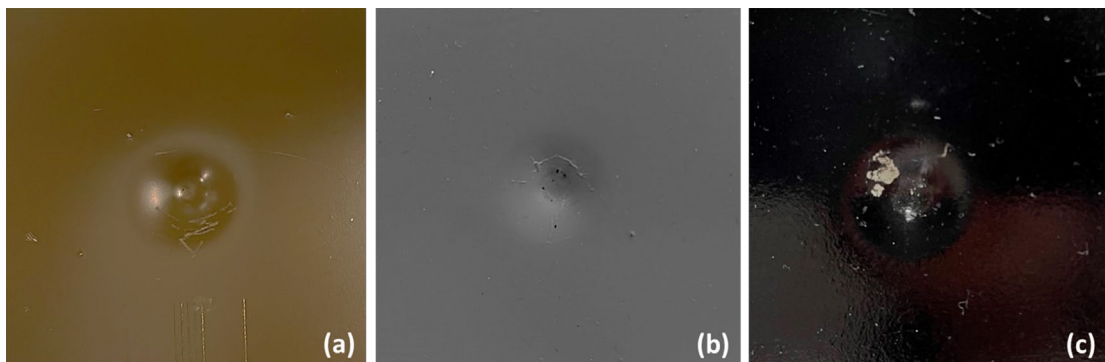


Fig. 7. Results of the impact testing of organic coatings

- The *hopeite* is the main phase registered in phosphate coatings on the zinc surfaces.
- The chemical elements in the phosphate coatings are O, P, Zn, Ni and Ca. The amounts of O, P and Zn in all tested coatings are almost the same. The content of Ni and Ca in the coatings increasing with reasing concentration from 5 to 20 vol.% of the phosphating baths.
- The habitus of the obtained phosphate coatings on galvanized surfaces remains almost the same – the crystals start from one center and increase radially like a spherulite.
- The adhesion of the combined coatings were measured by the cut test and impact resistance test. Coatings with the applied black and green paint correspond to qualification unit 0 according to the adhesion test-the edges of the cuts are completely smooth; none of the squares of the lattice is detached. The grey coating corresponds to qualification unit 2-the coating has flaked along the edges and/or at the intersections of the cuts; a cross-cut area significantly greater than 5%, but not significantly greater than 15%. From the impact resistance test of the coatings shows that no cracking and peeling of the organic coatings (green and gray) is observed, while with the black organic coating, damage is small.

The results obtained in the presented work show that the phosphate coatings guarantee a good contact for paints and varnishes, as well as an excellent corrosion protection.

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