Corrosion inhibition of galvanized steel by thin superhydrophobic phosphonate-siloxane films¹

A.S. Sergienko,¹ G.V. Redkina,¹¹⁰* A.S. Rozhkov^{1,2} and Yu.I. Kuznetsov¹¹⁰

 ¹A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation
²Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, 125047 Moscow, Russian Federation
*E-mail: GVRedkina@mail.ru

Abstract

The work suggests an environmentally friendly and efficient method of galvanized steel passivation for protection from atmospheric corrosion, which can serve as an excellent alternative to toxic chromate treatment. In particular, an important advantage of such passivation is the use of aqueous solutions of corrosion inhibitors (or those containing no more than 10% ethanol) to obtain superhydrophobic nanoscale anticorrosion films, which makes it a fire safe method. The method is based on laser and heat treatment of galvanized steel surface followed by layer-by-layer chemisorption of sodium dodecylphosphonate (SDDP) and vinyltrimethoxysilane (VTMS) or *n*-octyltriethoxysilane (OTES). A comparative assessment of the thickness, protective, hydrophobic properties and stability of thin coatings formed by layer-by-layer adsorption of the alkylphosphonate and trialkoxysilanes on the surface of galvanized steel with different morphology was carried out. It was shown that preliminary modification of the galvanized steel surface using laser exposure and heating enhances the protective and hydrophobic properties of the nanoscale phosphonate-siloxane films formed and increases its corrosion resistance in corrosive atmospheres. The polymodal morphology of the galvanized steel surface obtained using a laser promotes strong adsorption of the lower phosphonate layer, which in combination with the barrier properties of the siloxane network in the top layer, provides high protective and hydrophobic properties of phosphonate-siloxane films and their stability in corrosive atmospheres. The most effective method involves the layer-by-layer passivation of laser textured surfaces of galvanized steel with SDDP and OTES, which allows one to obtain stable superhydrophobic coatings with high anticorrosive properties in corrosive atmospheres of high humidity and salt spray.

Received: February 8, 2022. Published: February 24, 2022 do

doi: <u>10.17675/2305-6894-2022-11-1-19</u>

Keywords: galvanized steel, passivation, corrosion inhibitor, alkylphosphonates, trialkoxysilanes, laser treatment, superhydrophobicity.

¹ This work was supported by the Russian Foundation for Basic Research (Grant no. 20-33-90012 "Formation of hydrophobic coatings by alkylphosphonates and trialkoxysilanes on zinc and galvanized steel for their corrosion protection").

1. Introduction

Zinc coatings are an efficient means for anti-corrosion protection of steel. Thereby, galvanized steel is widely used in various areas of industry for the manufacture of machine parts, fasteners, supports, etc. The efficiency of protection of such products against corrosion is determined by the corrosion resistance of zinc coatings themselves, which mainly depends on their thickness, porosity, adhesion to the steel substrate, as well as the conditions of exposure to corrosive media. Although zinc coatings are highly resistant to corrosion, especially under atmospheric conditions, additional corrosion protection is required in some cases [1, 2]. For example, it is necessary to preserve their decorative properties, to prepare for soldering or painting, to prevent the formation of corrosion products ("white rust") during storage and transportation, and to extend the service life of galvanized steel products. The latter is especially relevant for thin zinc coatings (less than 12 µm) that break down relatively quickly in service. The problem of protection of zinc coatings is particularly acute under the conditions of high air humidity, marine atmosphere, and with temperature fluctuations with abundant dewfall when their corrosion rate increases significantly. In these cases, in order to enhance the corrosion resistance of galvanized steel, it is advisable to use corrosion inhibitors, which are capable of forming thin protective films on the metal surface, instead of increasing the thickness of the zinc layer. For many years, galvanized steel was passivated in solutions based on compounds Cr(VI) [2, 3]. This method is efficient and cheap, but due to the high toxicity of chromates their use was restricted in 2006 [4]. Therefore, the search for environmentally friendly corrosion inhibitors for the passivation of galvanized steel, which is as effective as chromate treatment, is particularly relevant today.

Corrosion inhibitors for zinc and zinc coatings such as vanadates, molybdates, Cr(III) compounds, rare earth metal salts, azoles, carboxylate, silane, phosphate and organophosphate [5-20] have been described in the literature as an alternative to Cr(VI) compounds. They all have advantages and disadvantages. A special place among them is occupied by corrosion inhibitors capable of forming self-assembling monolayers (SAMs) on the surfaces of metals and alloys with polyfunctional properties (anticorrosive, hydrophobic, adhesive, anti-fouling, self-cleaning and anti-icing). These compounds include higher phosphonic and carboxylic acids, thiols and trialkoxysilanes (TAS) [21-26]. Alkylphosphonic acids (C_nPAs) are particularly promising among them, since the SAMs they form are more strongly bonded to the oxidized surface of a metal and are more ordered, dense and stable under the exposure of corrosive media [27–29]. Despite numerous studies on the formation mechanism, structure and properties of SAMs formed by C_n PAs, there are few studies of corrosion inhibition of zinc or galvanized steel and these are mainly concern the modification of a ZnO surface [29-31]. However, successful modification of a ZnO surface with C_n PAs to give it a number of valuable properties suggests that they can be used for the same purpose for zinc or its alloys. For example, C.F. Glover et al. [32] investigated inhibiting properties of phenylphosphonic acid (PhPA) toward hot dip galvanized steel in 5.0% NaCl solution in a wide pH range (2.0-11.5). The results of *in situ* studies by scanning

vibrating electrode technique was shown that PhPA efficiently suppresses the local dissolution of metal at concentration of 50.0 M in a neutral solution (pH 7.0). The inhibiting effect of phosphonic acid is due to the formation of a protective film of zinc phosphonate as a result of the additional deprotonation of HPhP⁻ anions to give PhP²⁻ upon alkalization of the near-electrode layer on the cathodic surface areas. P. Thissen *et al.* [33] demonstrated that the treatment of ZnAl alloy (containing 0.5, 5.0 and 55.0% Al) with 1.0 mM ethanol solution of octadecylphosphonic acid can be used for temporary corrosion protection as well as for promoting of adhesion of coatings.

The modification of the metal surface with C_nAPs provides not only anticorrosive and hydrophobic properties, but also increases the wear resistance of a metal, which may have an additional practical value. D. Hill *et al.* [34] investigated the tribological properties of the phosphonate self-assembling films as potential lubricants used in deep drawing of galvanized steel sheets to produce parts for vehicle bodies. Such SAMs were obtained on the surface of galvanized steel coated with titanium oxide by immersion into 100.0 mM solutions of octyl-, dodecyl- or octadecyl-phosphonic acids in isopropyl alcohol. The phosphonate films enhanced the hydrophobicity of the surface of galvanized steel, reduced the coefficient of friction (by 65.0%) and significantly reduced its wear. Unfortunately, we failed to find information about the results of direct corrosion test of zinc or zinc coatings with passivating films formed by C_nAPs in the literature.

The possibility of zinc passivation in solutions of alkylphosphonates, including together with TASes of various structures, in order to prevent corrosion in chloride-containing aqueous solution and in atmosphere of high humidity was shown in [35, 36]. In particular, we have found that layer-by-layer passivation in solutions of sodium dodecylphosphonate (SDDP) and vinyltrimethoxysilane (VTMS) or *n*-octyltriethoxysilane (OTES) not only increases the corrosion resistance of zinc under investigated conditions, but also hydrophobicizes its surface. However, the contact angle of wetting the surface with water did not exceed $106\pm4^{\circ}$. It is known that, as a rule, the creation of microstructural (polymodal) surface roughness is required to obtain superhydrophobic coatings on metals.

Among the methods of modification of metal surfaces, laser treatment has recently attracted the attention of researchers. Varying the parameters of laser exposure allows changing the structure and properties of the surface layer in a wide range not only for texturing metal surfaces, but also to increase their corrosion resistance, hydrophobicity and wear resistance [37–40]. In this connection, laser modification of surfaces of metals and alloys is widely used for the treatment of parts of machines, responsible assemblies of constructions and equipment in enterprises of various branches of industry. The possibility of its use for nanostructuring the surface of zinc or galvanized steel was demonstrated in several works [41–44]. For example, in [41–43] the galvanized steel surface was prepared via laser ablation for subsequent applying paint coatings or removal of various surface steel by means of femtosecond and picosecond lasers followed by vacuum ageing that accelerates the transition from hydrophilic to superhydrophobic state of the surface. Recently, we have

shown the possibility of obtaining superhydrophobic coatings on zinc by laser texturing of its surface with subsequent layer-by-layer chemosorption of SDDP and VTMS or OTES [45, 46]. The polymodal roughness of the zinc surface has made it possible to produce stable phosphonate-siloxane coatings with high protective and hydrophobic properties in an atmosphere of 100% humidity. In the present paper, this corrosion protection method has been investigated for galvanized steel.

In this regard, the purpose of this work was to comparative evaluation of the thickness, protective and hydrophobic properties and stability of thin coatings formed in the presence of SDDP and TAS on the surface of galvanized steel with different morphologies.

2. Experimental

A zinc coating was applied galvanically to samples of St3 low-carbon steel (ISO 1052:1982). Steel plates 50×30 mm in size were preliminarily polished with emery paper, degreased with acetone and Vienna lime powder, and then washed with distilled water. Steel samples were etched in 2.8 M HCl solution for 30 s before galvanizing, then thoroughly washed in distilled water and immersed in a working solution. Galvanic deposition of zinc was carried out from a slightly acidic ammonium-free electrolyte containing (g/l): 80–90 ZnCl₂, 80–90 KCl, 25–30 H₃BO₃; as well as gloss-forming additives (35–50 ml/L "ECOMET-C32A" and 2–3 ml/L "ECOMET-C32B"). The deposition process was carried out at room temperature and a current density of 1.5 A/dm² for 1 h. After the completion of electrodeposition, the electrode was removed from the cell, washed with distilled water and dried at 60°C for 1 hour. The thickness of the resulting zinc coating calculated from the change in the mass of the sample before and after galvanizing according to ISO 1463-82 was 24 µm.

 $(CH_3 - (CH_2)_{11} - PO(ONa)_2)$ We used SDDP and TAS such as VTMS (H₂C=CH-Si(OCH₃)₃) or OTES (CH₃-(CH₂)₇-Si(OC₂H₅)₃) as corrosion inhibitors of galvanized steel. The structures of these compounds are shown in Figure 1. To obtain a concentrated solution of SDDP, a dodecylphosphonic acid powder (Alfa Aesar, 95%) was dissolved in distilled water by heating to 60°C with stirring, then neutralized with NaOH in a molar ratio of 1:2. VTMS and OTES were dissolved in ethyl alcohol. Alcoholic solutions of silanes were diluted with distilled water to prepare working solutions with the required concentration and with an alcohol content of 10.0%.

The properties of protective layers were studied on smooth and laser textured surfaces of galvanized steel. To obtain microstructural roughness of the surface, the polished and degreased samples were subjected to laser treatment under ambient conditions using an XM-30 ytterbium short pulse optical fiber laser (China) with the following parameters: P=4.5 W; v=20 kHz; d=0.01 mm; l=0.01 mm; V=100 mm/s, where P is the radiation power, v is the radiation frequency, V is the scanning speed, d is the laser beam diameter, and l is the distance between two adjacent linear trajectories. Laser scanning was performed by a grid. After laser treatment, the samples were cleaned by ultrasound in acetone for 60 s to remove the particles formed that were weakly bound to the metal surface, and then kept in an oven

at 150°C for 1 h. A similar surface preparation was previously tested by us on zinc to obtain phosphonate-siloxane coatings with high protective and hydrophobic properties [45].



Figure 1. Structures of SDDP and TAS (VTMS and OTES).

Previously [36, 45], we have identified the optimal conditions for the treatment of zinc in with SDDP and TAS solutions for it anticorrosive protection. In this regard, in this work, samples of galvanized steel were successively kept in stirred solutions of 2.5 mM SDDP and/or 10.0 mM TAS at 40°C. After treatment with SDDP, the samples were dried for 1 h at 60°C and for 1 h at 150°C after treatment in TAS solutions. The exposure duration in the case of passivation with individual corrosion inhibitors was 2 h, and it was 1 h in a solution of each of them upon layer-by-layer treatment.

The roughness of the surface of galvanized steel was estimated by the probe method using a Model-130 profilometer (PROTON, Russia). The study of the irregularities of the metal surface was carried out in several steps: the surface was "probed" with a diamond needle, then the averaged value of the parameters was calculated based on a series of measurements. As a result, the roughness parameters were obtained: R_z is the average height of irregularities at 10 points in μ m; R_a is arithmetic mean deviation in μ m; S is the average pitch of local protrusions in μ m; and the roughness class according to ISO 1302-2002.

The thickness of formed films was studied on a manual ellipsometer (Gartner) with light-beam modulation and modernized registration of light radiation. The radiation source was a solid-state laser with diode pumping LSM-S-111-10-NNP25 with the wavelength λ =540 nm. The incidence angle was 68.5°. The accuracy of polarizer and analyzer in determination of angles was ±0.05°. The ellipsometric angles Δ (the phase angle) and Ψ (the angle of recovered polarization) were measured according to the zero scheme by turning alternately the polarizer and the analyzer, at the minimum intensity (in the damping position). Thus, we determined experimentally the changes in angles: $\delta\Delta = \Delta - \Delta_0$ and $\delta\Psi = \Psi - \Psi_0$, where Δ_0 and Ψ_0 refer to the initial surface of galvanized steel samples, Δ and Ψ are the angles after treatment of the metal substrate (N_{St}) and the film (N_{film}) on its surface, as well as on the film thickness and are related by the fundamental equation of ellipsometry. The fundamental equation of ellipsometry was solved using the McCrackin software and the coating thickness (d) was thus determined.

The corrosion tests of galvanized steel samples treated in solutions of SDDP and TAS were carried out in the heat and moisture chamber (KTV-0.1-002, Russia) providing conditions of 100% humidity with daily moisture condensation, as well as in a salt spray chamber (Weiss SC/KWT 450, Germany) according to ISO 4536 and ISO 9227 standards. Inspection of the samples was carried out at regular intervals from the beginning of the tests to determine the time of appearance of the first corrosion damage (τ_{cor}).

Based on the data obtained, the coefficients of corrosion retardation by inhibitors (γ) and the degree of protection (*Z*) were calculated using the following formulas:

$$\gamma = \frac{\tau_{\rm cor}^{\rm pas}}{\tau_{\rm cor}^0} \tag{1}$$

where τ_{cor}^0 – time of appearance of the first corrosion damage before passivation and τ_{cor}^{pas} – after passivation of the galvanized steel surface with corrosion inhibitors;

$$Z,\% = \left(1 - \frac{1}{\gamma}\right) \cdot 100 \tag{2}$$

The hydrophobic properties of the protective layers on galvanized steel formed in the presence of corrosion inhibitors were evaluated by the value of the static contact angle (Θ_c) of a drop of distilled water. The Θ_c values were determined in the graphic editor Corel R.A.V.E. 2.0 from photographs of a water drop on the investigated surface obtained using a laboratory unit with an integrated DCM300 camera. The drop volume was 5 µl in each measurement. The standard deviation of Θ_c was 2.0°. The stability of the hydrophobic properties of the films obtained was estimated by the change in the Θ_c value with time during corrosion tests of samples in a heat and moisture chamber. Over time, the standard deviation increased to $3.0-5.0^\circ$ in some cases due to uneven degradation of the coatings.

3. Results and Discussion

The results of *ex situ* ellipsometric studies showed that the treatment of galvanized steel in solutions of SDDP and VTMS or OTES leads to the formation of nanoscale protective films with thicknesses of 61.5 and 70.0 ± 2.5 nm, respectively. In this case, the thickness of the first chemisorbed phosphonate layer is 9.4 ± 0.6 nm.

The hydrophobic properties of SDDP and TAS, characterized by the values of $\log P$ and $\lg D$ [47] (Table 1), as well as the formation of SAMs in their presence contribute to the hydrophobization of the galvanized steel surface. So, the smooth galvanized steel surface after drying at 60°C is hydrophilic and is characterized by the Θ_c value of $80\pm 2^\circ$. Treatment in solutions of the investigated corrosion inhibitors gives it hydrophobic properties (Table 2).

ol-water) for neutral molecules $(\log P)$ of SDDP and TAS and their anions $(\log D)$.				
Corrosion inhibitors	logP	$\log D^2$ at pH 7.4		
SDDP	3.83±0.58	0.22		

Table 1. Calculated logarithms of the distribution coefficients in the system of two immiscible liquids (octanol–water) for neutral molecules ($\log P$) of SDDP and TAS and their anions ($\log D$).

Table 2. The value Θ_c and images of water droplets on smooth and textured surfaces of galvanized steel samples passivated in solutions of SDDP and TAS.

 3.12 ± 0.66

 5.45 ± 0.42

VTMS

OTES

Composition of the inhibiting solution, mM	Θc,°			
	smooth su	rface	textured surface	
Without treatment with corrosion inhibitors	6	80±2		105±1
2.5 SDDP		120±2	0	151±3
10.0 VTMS		92±3	0	132±3
10.0 OTES	0	133±2	0	160±2
2.5 SDDP / 10.0 VTMS		131±3	0	150±3
2.5 SDDP / 10.0 OTES	0	135±2	0	166±3

² The log *D* value is used for dissociated forms of organic compounds. It depends on the solution pH and is related to log *P* and the acidity constant (p*K*_a) by the following relationship [48]: log $D_{(pH)}$ =log *P*-log[1+10^(pH-pKa)]. The log *D* value of the SDDP anion was calculated by the ACD-Lab software (https://ilab.acdlabs.com).

At the same time, layer-by-layer passivation by SDDP with VTMS or OTES allows one to obtain a Θ_c value slightly higher than in the case of treatment by these compounds separately. However, even upon layer-by-layer treatment of a smooth galvanized steel surface by SDDP with the most hydrophobic of the silanes studied (OTES), it is not possible to achieve its superhydrophobization (Θ_c does not exceed 135±2°).

The hydrophobization of galvanized steel surface in solutions of SDDP with TAS along with strong chemisorption of the alkylphosphonate [35] favors an increase in its corrosion resistance under corrosive atmospheres (Figure 2). The efficiency of joint passivation of galvanized steel with SDDP and TAS was found to be higher than that by the individual corrosion inhibitors. This is apparently due to the formation of more perfect protective film consisting of a phosphonate layer strongly bound to the metal surface and a siloxane network in the upper layer. The latter is formed as a result of interaction of reactive silanol groups with each other, which were formed during the hydrolysis of silane alkoxy groups in wateralcohol solutions, and is capable of blocking existing defects in the film formed by alkylphosphonate. At the same time, the use of OTES together with SDDP in layer-by-layer passivation allows one to obtain coatings with better protective properties than in the case of using VTMS. Such phosphonate-siloxane films increased the corrosion resistance of galvanized steel 22.8 and 33.8 fold in atmospheres of 100% humidity and salt spray, respectively (Table 3). This can be explained not only by the higher hydrophobic properties formed in the presence of SDDP and OTES films, but also by their greater thickness. The proposed passivation treatment of galvanized steel is superior in efficiency to chromate passivation, because according to the recommendations of ISO 9227 [49] for rainbow chromate conversion coatings, the τ_{cor} value of at least 72 h in the salt spray chamber is considered satisfactory.



Figure 2. The τ_{cor} value in a heat and moisture chamber (a) and in a salt spray chamber (b) on smooth samples of galvanized steel with subsequent treatment in SDDP and TAS solutions. The concentrations of corrosion inhibitor solutions are given in mM.

Composition of	γ					
inhibiting solution,	Heat and mo	ister chamber	Salt spray chamber			
mw	Smooth surface Textured surface		Smooth surface Textured surface			
Without treatment with corrosion inhibitors	_	1.6	_	1.8		
2.5 SDDP	5.3	10.0	6.0	8.8		
10.0 VTMS	6.0	11.2	8.0	11.5		
10.0 OTES	7.9	12.8	20.5	24.8		
2.5 SDDP / 10.0 VTMS	20.2	20.8	30.0	38.3		
2.5 SDDP / 10.0 OTES	22.8	30.4	33.8	48.0		

Table 3. The coefficients of corrosion retardation by inhibitors calculated based on the results of corrosion tests in aggressive atmospheres for galvanized steel samples treated in solutions of SDDP and TAS.

To obtain a superhydrophobic coating on galvanized steel and hence to increase its corrosion resistance, laser surface treatment with subsequent adsorption of SDDP and TAS was carried out, similar to the method we demonstrated for zinc in [45]. Laser texturing of the galvanized steel surface has its own features, in particular, it is necessary to control the depth of penetration of the laser beam in order to avoid violating the integrity of the zinc coating. In this regard, the optimal mode of laser surface treatment described in Section 2 was experimentally selected, after which the decrease in the thickness of the zinc coating, determined by the weight loss of the sample, was no more than 6 µm. The obtained profilometry results demonstrate an increase in galvanized steel surface roughness after laser exposure (Table 4). The roughness class increases from 2 (for a smooth surface) to 7. Subsequent heat treatment of the samples at 150°C leads to a slight decrease in the roughness parameters. Such preparation of metal surfaces gives it polymodal morphology and enriches the surface layer with metal oxide, in this case ZnO [39, 40, 50]. This is due to ablation and subsequent deposition of nanoparticles formed in plasma onto the treated surface during laser treatment. It can be assumed that the fraction of Zn(OH)₂ decreases in the surface layer upon heating due to the transformation into ZnO. As a result, smaller and more compact surface structures are formed consisting mainly of ZnO. As we showed earlier [35], a decrease in the fraction of $Zn(OH)_2$ on the zinc surface enhances the protective properties of alkylphosphonate films.

The surface of galvanized steel after laser and thermal treatments acquires hydrophobic properties (Table 2). Despite this, it corrodes quickly in chambers of heat and moisture or salt spray. Treatment of galvanized steel surface with polymodal roughness in solutions of SDDP or TAS enhances its hydrophobicity in comparison with the smooth surface modified with inhibitors. The greatest value of Θ_c (166±3°) is observed in the case layer-by-layer passivation of textured surface with SDDP and OTES. This is due not only to the polymodal

morphology of the galvanized steel surface, but also to the high hydrophobicity of OTES molecules. OTES has a long alkyl radical in the molecule in contrast to VTMS and is capable of forming more ordered and dense SAMs on metal surfaces.

Table 4. Surface roughness parameters of galvanized steel samples before and after laser and heat treatments.

Surfac	ce types	Rz, µm	Ra, µm	S, µm	Roughness class	Profilograms
smooth with heat	n surface treatment	0.71	0.03	12.74	2	
laser	without heat treatment	6.62	21.74	21.74	7	henny for the property of the property of the property of the second second second second second second second
surface	with heat treatment	6.27	19.38	19.38	6	the post of the property of the second state of the second state of the second state of the second state of the

Theoretically, the superhydrophobic state of the galvanized steel surface with a phosphonate-siloxane film can be explained using the Cassie–Baxter model. A superhydrophobic metal surface is characterized by a heterogeneous wetting regime in which a layer of air trapped in the micro/nanostructures of the surface limits the contact between liquid droplets and the surface. In this case, the following equation is valid [51]:

$$\cos\Theta_{\rm c} = f_1 \cos\Theta_{\rm c,1} + f_2 \cos\Theta_{\rm c,2} \tag{3}$$

where f_1 and f_2 are surface area fractions of polymodal structures and trapped air in the voids between them that are in contact with the liquid, respectively; $\Theta_{c,1}$ – contact angle on a smooth surface; $\Theta_{c,2}$ – contact angle on the surface of pores with air. Given that $f_1+f_2=1$, $\Theta_c=166^\circ$, $\Theta_{c,1}=80^\circ$ and $\Theta_{c,2}=180^\circ$, f_1 and f_2 are 0.026 and 0.974, respectively. These results show that when a liquid hits a superhydrophobic surface of galvanized steel, on average, only 2.6% of the surface is in contact with the liquid drop, and the remaining 97.4% correspond to the liquid drop contact area with air. The small area of contact between the liquid and the solid surface can increase the resistance of such surface with a phosphonatesiloxane film in a corrosive media.

The results of corrosion tests in atmospheres of high humidity and salt spray have shown that, despite the superhydrophobic properties, films obtained by treating the textured surface of galvanized steel with individual corrosion inhibitors have weaker protective properties than those obtained layer-by-layer passivation by SDDP with TAS (Figure 3). Two-stage treatment of galvanized steel by SDDP and TAS with preliminary laser preparation of the surface allows significantly increase its corrosion resistance in corrosive atmospheres. At the same time, phosphonate-siloxane films are significantly superior in protective efficiency to similar films formed on a smooth surface. As well as on a smooth surface, the coating formed with SDDP and OTES by layer-by-layer method had the best protective properties. The coefficients of corrosion retardation by inhibitors calculated by the τ_{cor} values show that the corrosion resistance of galvanized steel with this superhydrophobic coating increased 30.4-fold in an atmosphere of 100% relative humidity with daily condensation of moisture on the samples, and 48.0-fold under more corrosive conditions of a salt spray (Table 3). This corresponds to a high degree of protection of galvanized steel under the conditions studied, 96.7 and 97.9%, respectively. An increase in the efficiency of anticorrosion protection in the case of using OTES, in comparison with VTMS, is associated with the different structure of their molecules. It is known that the stability of the siloxane layer formed by silane rises with an increase in the length of the alkyl in its molecule as a result of the formation of high-molecular cross-linked structures in it due to lateral interactions between neighboring molecules (horizontal siloxane bonds, van der Waals interactions between alkyl chains) [21, 52]. In addition, superhydrophobic surfaces are negatively charged, which hinders the adsorption of chloride ions and oxygen [52], and leads to corrosion inhibition of metal. Thus, a negatively charged superhydrophobic coating is formed on the galvanized steel surface, which consists of chemisorbed SDDP and a strong siloxane network that blocks possible defects in the lower phosphonate layer.



Figure 3. The τ_{cor} value in a heat and moisture chamber (a) and in a salt spray chamber (b) on textured samples of galvanized steel with subsequent treatment in SDDP and TAS solutions. The concentrations of corrosion inhibitor solutions are given in mM.

An important indicator for the practical application of superhydrophobic protective coatings is their ability to maintain their properties under the influence of corrosive media during operation. The degradation rate of coatings formed on the textured surface of galvanized steel was carried out simultaneously with corrosion tests in the heat and moisture chamber. The results of the change in the Θ_c value with time are shown in Figure 4. It can be seen that the film obtained in an aqueous solution of SDDP loses its superhydrophobic properties the fastest: the Θ_c value less than 150° already after 40 h of testing. A similar character of the change in the Θ_c value can be noted on samples with films formed in water-alcohol solutions of VTMS and OTES, when the film begins to rapidly degrade after the

appearance of the first corrosion damage. Thin coatings obtained by layer-by-layer passivation of galvanized steel in SDDP and TAS solutions turned out to be more stable. At the same time, the use of OTES together with SDDP makes it possible to obtain superhydrophobic protective films capable of maintaining their properties ($\Theta_c \ge 150^\circ$) for 500 h of test in an atmosphere of 100% humidity with daily condensation of moisture on the surface. It is important to note that the degradation of such films is nonuniform. In this connection, the surface of galvanized steel still remains superhydrophobic even with the appearance of the first small pitting.



Figure 4. Change in Θ_c value with time (τ) in the heat and moisture chamber on textured surfaces of galvanized steel samples treated in solutions of corrosion inhibitors (mM): 1 - 2.5 SDDP; 2 - 10.0 VTMS; 3 - 10.0 OTES; 4 - 2.5 SDDP / 10.0 VTMS (layer-by-layer); 5 - 2.5 SDDP / 10.0 OTES (layer-by-layer).

Thus, the proposed environmentally friendly method of galvanized steel passivation to protect it from atmospheric corrosion by laser treatment followed by layer-by-layer chemisorption of alkyl phosphonate and TAS can serve as an excellent alternative to the toxic chromate treatment. In particular, an important advantage of such passivation that aqueous solutions of corrosion inhibitors (or those containing no more than 10% ethanol) are used to obtain superhydrophobic nanoscale anticorrosion films, which makes it a fire safe method.

Conclusions

- 1. Layer-by-layer passivation of galvanized steel in SDDP and TAS solutions increases its corrosion resistance in atmospheres of high humidity and salt spray due to the formation of nanoscale hydrophobic films.
- 2. Preliminary modification of the galvanized steel surface using laser exposure and heating enhances the protective and hydrophobic properties of thin films formed in the presence of SDDP and TAS.

- 3. The polymodal morphology of the galvanized steel surface obtained using a laser promotes strong adsorption of the lower phosphonate layer, which in combination with the barrier properties of the siloxane network in the top layer, provides high protective and hydrophobic properties of phosphonate-siloxane films and their stability in corrosive atmospheres.
- 4. The most efficient method involves layer-by-layer passivation of galvanized steel in SDDP and OTES solutions with preliminary laser and heat treatment of the surface, which allows one to obtain stable superhydrophobic coatings with high protective properties in corrosive atmospheres of high humidity and salt spray.

References

- 1. A.A. Mikhailov, Yu.M. Panchenko and Yu.I. Kuznetsov, *Atmospheric corrosion and protection of metals*, Tambov, Pershin R.V. Publishing House, 2016, 555 (in Russian).
- 2. X.G. Zhang, Corrosion and electrochemistry of zinc, Springer-Verlag US, 1996, 474.
- 3. B.R.W. Hinton, Corrosion Prevention and Chromates, the End of an Era?, *Met. Finish.*, 1991, **89**, 15–20.
- 4. Restriction of Hazardous Substances Directive, 2002/95/EC.
- Z. Zhongli, L. Ning, L. Deyu, L. Haiping and M. Songlin, A vanadium-based conversion coating as chromate replacement for electrogalvanized steel substrates, *J. Alloys Compd.*, 2011, **509**, no. 2, 503–507. doi: <u>10.1016/j.jallcom.2010.09.080</u>
- A.A.O. Magalhaes, I.C.P. Margarit and O.R. Mattos, Molybdate conversion coatings on zinc surfaces, *J. Electroanal. Chem.*, 2004, 572, no. 2, 433–440. doi: 10.1016/j.jelechem.2004.07.016
- 7. E. Almeida, L. Fedrizzi and T.C. Diamantino, Oxidizing alternative species to chromium VI in zinc-galvanized steel surface treatment. Part 2. An electrochemical study, *Surf. Coat. Technol.*, 1998, **105**, 97–101.
- 8. T. Bellezze, G. Roventi and R. Fratesi, Electrochemical study on the corrosion resistance of Cr III-based conversion layers on zinc coatings, *Surf. Coat. Technol.*, 2002, **155**, no. 2–3, 221–230. doi: <u>10.1016/s0257-8972(02)00047-6</u>
- 9. E. Almeida, T.C. Diammantino, M.O. Figueiredo and C. Sa, Oxidising alternative species to chromium VI in zinc galvanized steel surface treatment. Part 1. A morphological and chemical study, *Surf. Coat. Technol.*, 1998, **106**, no. 1, 8–17. doi: <u>10.1016/S0257-8972(98)00464-2</u>
- K. Ogle, A. Tomandl, N. Meddahi and M. Wolpers, The alkaline stability of phosphate coatings I: ICP atomic emission spectroelectrochemistry, *Corros. Sci.*, 2004, 46, no. 4, 979–995. doi: <u>10.1016/S0010-938X(03)00182-3</u>
- 11. A. Tomandl, M. Wolpers and K. Ogle, The alkaline stability of phosphate coatings. II: In situ Raman spectroscopy, *Corros. Sci.*, 2004, 46, no. 4, 997–1011. doi: <u>10.1016/S0010-938X(03)00183-5</u>

- L. Lin, J.T. Lu and G. Kong, Effect of molybdate post-sealing on the corrosion resistance of zinc phosphate coatings on hot-dip galvanized steel, *Corros. Sci.*, 2008, **50**, no. 4, 962–967. doi: <u>10.1016/j.corsci.2007.12.002</u>
- A.I. Kartsonakis, S.G. Stanciu, A.A. Matei, R. Hristu, A. Karantonis and C.A. Charitidis, A comparative study of corrosion inhibitors on hot-dip galvanized steel, *Corros. Sci.*, 2016, **112**, 289–307. doi: 10.1016/j.corsci.2016.07.030
- S. Liu, Y. Zhong, R. Jiang, Z. Zeng, Z. Feng and R. Xiao, Corrosion inhibition of zinc in tetra-*n*-butylammonium bromide aerated aqueous solution by benzotriazole and Na₃PO₄, *Corros. Sci.*, 2011, **53**, no. 2, 746–759. doi: <u>10.1016/j.corsci.2010.11.007</u>
- 15. C. Georges, E. Rocca and P. Steinmetz, Synergistic effect of tolutriazol and sodium carboxylates on zinc corrosion in atmospheric conditions, *Electrochim. Acta*, 2008, **53**, no. 14, 4839–4845. doi: <u>10.1016/j.electacta.2008.01.073</u>
- 16. K. Aramaki, Protection of zinc from corrosion by coverage with a hydrated cerium(III) oxide layer and ultrathin polymer films of a carboxylate self-assembled monolayer modified with alkyltriethoxysilanes, *Corros. Sci.*, 2007, **49**, no. 4, 1963–1980. doi: 10.1016/j.corsci.2006.07.008;
- K. Aramaki. Prevention of zinc corrosion in oxygenated 0.5 M NaCl by treatment in a cerium (III) nitrate solution and modification with sodium hexadecanoate, *Corros. Sci.*, 2006, **48**, no. 10, 3298–3308. doi: <u>10.1016/j.corsci.2005.10.020</u>
- K. Aramaki, Preparation of chromate-free, self-healing polymer films containing sodium silicate on zinc pretreated in a cerium (III) nitrate solution for preventing zinc corrosion at scratches in 0.5 M NaCl, *Corros. Sci.*, 2002, 44, no. 6, 1375–1389. doi: 10.1016/S0010-938X(01)00138-X
- 19. K. Aramaki, Treatment of zinc surface with cerium(III) nitrate to prevent zinc corrosion in aerated 0.5 M NaCl, *Corros. Sci.*, 2001, **43**, no. 11, 2201–2215. doi: <u>10.1016/S0010-938X(00)00189-X</u>
- A.A. Abrashov, N.S. Grigoryan, T.A. Vagramyan, E.A. Zheludkova and V.P. Meshalkin, Passivation of zinc coatings in cerium-containing solutions, *Russ. J. Appl. Chem.*, 2015, 88, 1594–1598. doi: 10.1134/S1070427215100067
- 21. G.V. Lisichkin, A.Yu. Fadeev, A.A. Serdan, P.N. Nesterenko, P.G. Mingalev and D.B. Furman, *Chemistry of surface grafted compounds*, Moscow, Fizmatlit, 2003, 592 (in Russian).
- K. Aramaki and T. Shimura, Self-assembled monolayers of carboxylate ions on passivated iron for preventing passive film breakdown, *Corros. Sci.*, 2004, 46, 313–328. doi: 10.1016/S0010-938X(03)00156-2
- 23. M.G.S. Ferreira, R.G. Duarte, M.F. Montemor and A.M.P. Simoes, Silanes and rare earth salts as chromate replacers for pre-treatments on galvanized steel, *Electrochim. Acta*, 2004, **49**, no. 17–18, 2927–2935. doi: 10.1016/j.electacta.2004.01.051
- 24. W.E.G. Hansal, S. Hansal, M. Polzler, A. Kornherr, G. Zifferer and G.E. Nauer, Investigation of polysiloxane coatings as corrosion inhibitors of zinc surfaces, *Surf. Coat. Technol.*, 2006, **200**, no. 9, 3056–3063. doi: <u>10.1016/j.surfcoat.2005.01.049</u>

- 25. N.A. Polyakov, I.G. Botryakova, V.G. Glukhov, G.V. Red'kina and Yu.I. Kuznetsov, Formation and anticorrosion properties of superhydrophobic zinc coatings on steel, *Chem. Eng. J.*, 2021, **421**, 127775. doi: <u>10.1016/j.cej.2020.127775</u>
- 26. Yu.I. Kuznetsov, Organic corrosion inhibitors: where are we now? A review. Part IV. Passivation and the role of mono- and diphosphonates, *J. Corros. Scale Inhib.*, 2017, **6**, no. 4, 384–427. doi: 10.17675/2305-6894-2017-6-4-3
- 27. E. Hoque, J.A. DeRose, P. Hoffmann, B. Bhushan and H.J. Mathieu, Alkylperfluorosilane self-assembled monolayers on aluminum: A comparison with alkylphosphonate self-assembled monolayers, J. Phys. Chem. C, 2007, 111, no. 10, 3956–3962. doi: 10.1021/jp066101m
- 28. P.G. Mingalyov and G.V. Lisichkin, Chemical modification of oxide surfaces with organophosphorus(V) acids and their esters, *Russ. Chem. Rev.*, 2006, **75**, no. 6, 541–557. doi: <u>10.1002/CHIN.200645245</u>
- P.J. Hotchkiss, M. Malicki, A.J. Giordano, N.R. Armstrong and S.R. Marder, Characterization of phosphonic acid binding to zinc oxide, *J. Mater. Chem.*, 2011, 21, no. 9, 3107–3112. doi: <u>10.1039/c0jm02829k</u>
- R. Quiñones, K. Rodriguez and R.J. Luliucci, Investigation of phosphonic acid surface modifications on zinc oxide nanoparticles under ambient conditions, *Thin Solid Films*, 2014, 565, 155–164. doi: <u>10.1016/j.tsf.2014.06.057</u>
- C.L. Perkins, Molecular anchors for self-assembled monolayers on ZnO: a direct comparison of the thiol and phosphonic acid moieties, *J. Phys. Chem.*, 2009, **113**, 18276–18286. doi: <u>10.1021/jp906013r</u>
- 32. C.F. Glover and G. Williams, Inhibition of localized corrosion of hot dip galvanized steel by phenylphosphonic acid, *J. Electrochem. Soc.*, 2017, **164**, no. 7, 407–417. doi: 10.1149/2.1551707jes
- P. Thissen, J. Wielant, M. Köyer, S. Toews and G. Grundmeier, Formation and stability of organophosphonic acid monolayers on ZnAl alloy coatings, *Surf. Coat. Technol.*, 2010, 204, 3578–3584. doi: <u>10.1016/J.SURFCOAT.2010.04.027</u>
- 34. D. Hill, P.J. Holliman, J. McGettrick, M. Appelman, P. Chatterjee, T.M. Watson and D. Worsley, Study of the tribological properties and ageing of alkyphosphonic acid films on galvanized steel, *Tribol. Int.*, 2018, **119**, 337–344. doi: <u>10.1016/j.triboint.2017.11.015</u>
- 35. G.V. Redkina, Yu.I. Kuznetsov, N.P. Andreeva, I.A. Arkhipushkin and L.P. Kazansky, Features of zinc passivation by sodium dodecylphosphontate in a neutral aqueous solution, *Corros. Sci.*, 2020, **168**, 108554. doi: <u>10.1016/j.corsci.2020.108554</u>
- 36. G.V. Red'kina, A.S. Sergienko and Yu.I. Kuznetsov, Two-Stage passivation of zinc by solutions of sodium dodecylphosphonate and trialkoxysilanes, *Prot. Met. Phys. Chem. Surf.*, 2021, 57, no. 7, 1370–1378. doi: <u>10.1134/S2070205121070157</u>
- 37. I.N. Zavestovskay, Laser nanostructuring of materials surface, *Quantum Electronics.*, 2010, **40**, no. 11, 942–954.

- 38. L. Ma, L. Wang, C. Li, J. Guo, P. Shrotriya, C. Deng and J. Zhao, Hybrid nanosecond laser processing and heat treatment for rapid preparation of super-hydrophobic copper surface, *Metals*, 2019, **9**, no. 6, 668. doi: <u>10.3390/met9060668</u>
- D. Wei, J. Wang, H. Wang, Y. Liu, S. Li and D. Li, Anti-corrosion behavior of superwetting structured surfaces on Mg-9Al-1Zn magnesium alloy, *Appl. Surf. Sci.*, 2019, 483, 1017–1026. doi: <u>10.1016/j.apsusc.2019.03.286</u>
- 40. L.B. Boinovich, A.M. Emelyanenko, A.D. Modestov, A.G. Domantovsky and K.A. Emelyanenko, Synergistic effect of superhydrophobicity and oxidized layers on corrosion resistance of aluminum alloy surface textured by nanosecond laser treatment, *ACS Appl. Mater. Interfaces*, 2015, 7, no. 34, 19500–19508. doi: <u>10.1021/acsami.5b06217</u>
- 41. H. Mustafa, D.T.A. Matthews and G.R.B.E. Römer, Investigation of the ultrashort pulsed laser processing of zinc at 515 nm: morphology, crystallography and ablation threshold, *Mater. Des.*, 2019, **169**, 107675. doi: <u>10.1016/j.matdes.2019.107675</u>
- 42. H. Mustafa, M. Mezera, D.T.A. Matthews and G.R.B.E. Römer, Effect of surface roughness on the ultrashort pulsed laser ablation fluence threshold of zinc and steel, *Appl. Surf. Sci.*, 2019, **488**, 10–21. doi: <u>10.1016/j.apsusc.2019.05.066</u>
- 43. X. Zhou, K. Imasaki, H. Furukawa, H. Umino, K. Sakagishi, S. Nakai and C. Yamanaka, A study of the surface products on zinc-coated steel during laser ablation cleaning, *Surf. Coat. Technol.*, 2001, **137**, no. 2–3, 170–174. doi: <u>10.1016/S0257-</u> <u>8972(00)01118-X</u>
- 44. S.A. Khan, G.S. Boltaev, M. Iqbal, V. Kim, R.A. Ganeev and A.S. Alnaser, Ultrafast fiber laser-induced fabrication of superhydrophobic and self-cleaning metal surfaces, *Appl. Surf. Sci.*, 2021, **542**, 148560. doi: <u>10.1016/j.apsusc.2020.148560</u>
- 45. G.V. Redkina, A.S. Sergienko and Yu.I. Kuznetsov. Hydrophobic and anticorrosion properties of thin phosphonate–siloxane films formed on a laser textured zinc surface. *Int. J. Corros. Scale Inhib.*, 2020, 9, no. 4, 1550–1563. doi: 10.17675/2305-6894-2020-9-4-23
- 46. Yu.I. Kuznetsov and G.V. Redkina, Thin protective coatings on metals formed by organic corrosion inhibitors in neutral media, *Coatings*, 2022, **12**, no. 2, 149. doi: <u>10.3390/coatings12020149</u>
- 47. C. Hanch and A. Leo, Substituent constants for correlation analysis in chemistry and biology, New York: Wiley, 1979, 339.
- 48. R.A. Scherrer and S.M. Howard, Use of distribution coefficients in quantitative structure-activity relationships, *J. Med. Chem.*, 1977, **20**, no. 1, 53–58. doi: 10.1021/JM00211A010
- 49. ISO 9227:2017, Corrosion tests in artificial atmospheres Salt spray tests.
- 50. B. Zhang, S. Lu., W. Xu and Yu. Cheng, Controllable wettability and morphology of electrodeposited surfaces on zinc substrates, *Appl. Surf. Sci.*, 2016, **360**, 904–914. doi: 10.1016/j.apsusc.2015.11.083

- 51. D. Zhang, L. Wang, H. Qian and X. Li, Superhydrophobic surfaces for corrosion protection: a review of recent progresses and future directions, *J. Coat. Technol. Res.*, 2016, **13**, 11–29. doi: <u>10.1007/s11998-015-9744-6</u>
- M.A. Petrunin, N.A. Gladkikh, M.A. Maleeva, L.B. Maksaeva and T.A. Yurasova, The use of organosilanes to inhibit metal corrosion. A review, *Int. J. Corros. Scale Inhib.*, 2019, 8, no. 4, 882–907. doi: 10.17675/2305-6894-2019-8-4-6

*** * ***