ELECTROCHEMICAL BEHAVIOR OF ZINC LAYERS PASSIVATED IN PHOSPHATE SOLUTIONS

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ABSTRACT

Phosphate conversion coatings are used on the galvanized steel. By forming a thin protective film on the surface of the steels this treatment enhances corrosion resistance. This paper presents studies on phosphate passivation solutions. The results of treatments for different treatment times and more compositions were analyzed in terms of layer thickness, structural aspects, adherence, and continuity of films. Corrosion resistance was assessed by the linear voltammetry test. Active-passive curves were analysed and compared with unpassivated galvanised samples. For each passivation solution experimented Tafel curves were drawn and corrosion rates were determined. The optimal passivation conditions were settled as function on obtained results.

KEYWORDS: galvanized steel, phosphate conversion coatings, corrosion behaviour

1. Introduction

The phosphate-based conversion is a method used to protect the metal against corrosive environments. This is one of the chemical conversion methods and involves a surface modification that increases the passivation tendency of zinc coated steel. By forming a physical barrier on the surface of galvanizing steels the appearance of the "storage stain" or "white rust" is inhibited.

These are more attractive alternatives to chromate conversion treatments that involve the use of chromic acid containing Cr6+ species. The chromate conversion coating based on Cr6+ presents environmental and health risks and was banned by the EC today. There are numerous restrictions of hexavalent chromium bearing chromate conversion coatings as top-coat of zinc coated steel [1, 2]. As a result, environmentally friendly chromate free passivation treatments were developed. As potential alternatives to hexavalent chromium, molybdates, tungstates, permanganates, vanadates, rare earth elements (especially cerium) and organic compounds were studied [3-7].

The phosphating is a common chemical conversion treatment that is applied to enhance corrosion resistance [8-10]. It is preferred because it is economical, demonstrates speed of operation and ability to afford excellent corrosion resistance, wear resistance, adhesion and lubricative properties. For the first reliable record of phosphate coatings applied to prevent rusting of iron and steel (a British patent of 1869 [11]), numerous developments have taken place. Certain factors influenced the processes and, as a consequence, the formation of a stable and uniform coating for corrosion protection remains a challenge. To improve the quality of conversion coatings the works have been concentrated on the study of process parameters and their optimization. [12]. The structure and composition of the phosphate deposition is influenced by numerous factors. Working temperatures, the degree of agitation of the bath and the concentrations of the constituents in the phosphating bath are the most important parameters that affecting the process. On point of economical view to achieve the coating formation in a practicable time a wide variety of acceleration methods (chemical, mechanical, electrochemical) for the immersion processes must be applied as an alternative to Cr(VI) post treatment. The addition of specific compounds to the phosphating baths has also its own influence on phosphating. A wide variety of phosphating compositions are available and new types of phosphate coatings were developed in respect to the regulations imposed by the environmental pollution control. For example, the molybdate–phosphate system was introduced by Tang et al. for corrosion protection of galvanized steel [13,

14]. In this paper a passivation treatment based on phosphate stabilization was analysed. The quality of the phosphating deposition was analysed by some characteristics. Coating thickness and coating porosity were observed. The stability of the phosphate coating as an important property was characterized in terms of the electrochemical behaviour of the zinc layer in phosphate passivation solutions.

2. Experimental results and discussion

The hot dip galvanized steel sheet has been passivated by total immersion of samples into zinc phosphating solution.

Its chemical composition is given in Table 1. The phosphating was carried out at variable times: 10, 15, 20, 30 and 60 seconds respectively.

Table 1. *Chemical composition of the pasivation coating*

Code	Zinc dihydrogen phosphate	Fluotitanic acid	Molybdate diamonium
	[g/L]		
P1	1.0	0.25	0.25
P2	2.0	0.5	0.5
P3	4.0	1.0	1.0
P4	6.0	1.5	1.5

For fastening of the conversion coating the samples were heated at 120^0C. The thickness of the deposition has been quantified in terms of weight per unit area (as g/m^2). This has been determined by weighing of the samples before and after immersion into solution and drying of the passivating layer. The thickness of the layer depends on the chemical composition of the solution and the immersion time as show the results in Figure 1. The thickest layers are obtained for samples treated in the passivating solution code P4 and the thinnest for those immersed in the solution code P1. The thickness of the zinc passivating layers varies between 1 and $3g/m^2$. From this point of view the zinc passivating solutions P_2 and P_3 are optimal. The phosphating coatings were examined by optical microscopy (Figure 2). For the sample immersed in solution code P_2 and 10 seconds for treatment time, uniform layers were obtained.
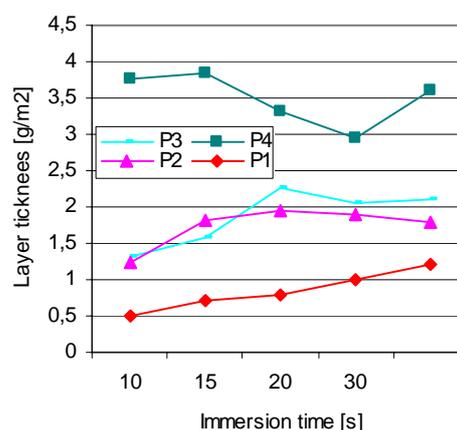
Fig. 1. *Thickness of layer depending on the immersion time and composition of the passivating solution*

| 5%, 10 s | 5%, 20 s | 10%, 10 s | 10%, 20 s |
| 20%, 10 s | 20%, 10 s | 30%, 10 s | 30%, 20 s |
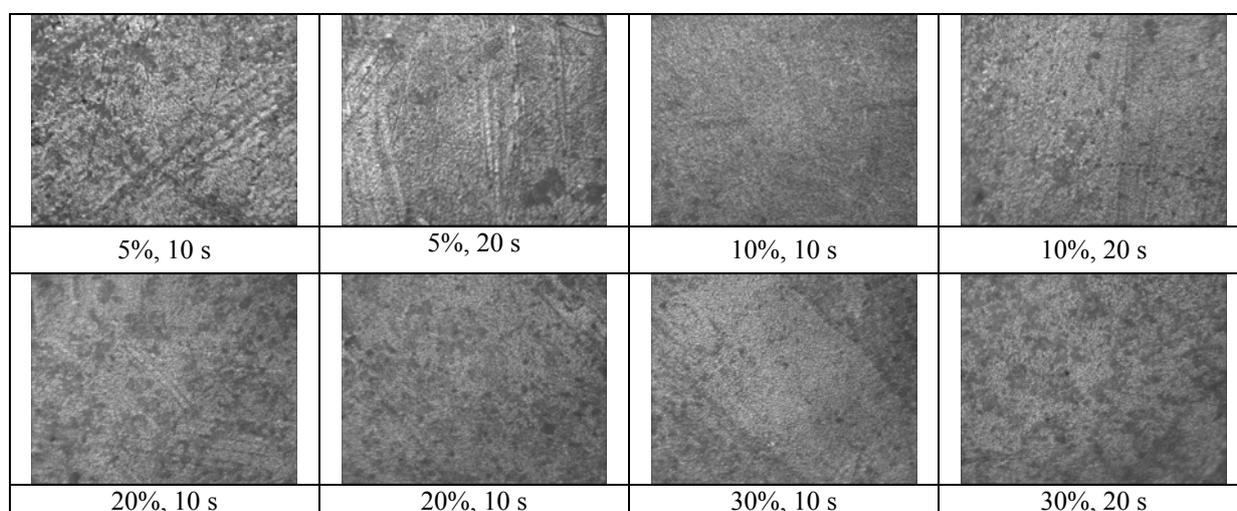
Fig. 2. *Appearance of the surface of samples depending on passivating conditions (X500)*

The corrosion behaviour was carried out with a potentiostat. The linear voltametry i=f(E) method was applied from -2000mV toward the anodic direction of 1000mV with a scan rate of 100 mV/min

The corrosion behaviour of the layers has been observed by introducing them in corrosive environments, 3%NaCl solution. A three electrode system with an electrochemical cell volume of 100mL was used to perform the experiments. The auxiliary electrode was a platinum sheet and the reference electrode was calomel. The working electrode was the experimental samples which has an electroactive area of $1cm^2$.

Before the experiments, samples was degreased in acetone and alcohol, rinsed with distilled water and then, dried in air.
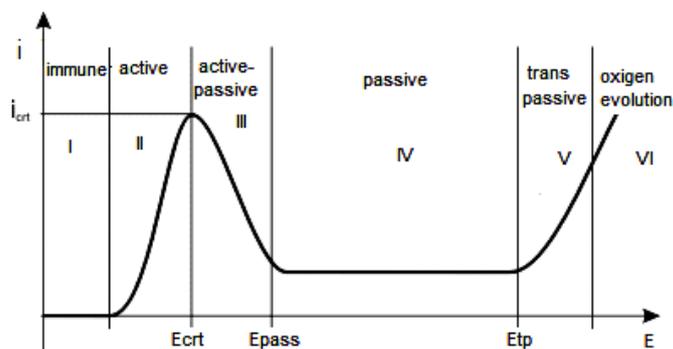
Fig. 3. *Schematic representation of cyclic voltammogram*

The electrochemical evaluation of corrosion resistance of phosphate coatings can be done by analysing the curve of polarization of the metal in question. This allows potential electrochemical separation in the areas of: immune, active, active-passive, passive, transpassive and oxygen evolution as shown schematically in Figure 3. The corrosion process takes place in the active zone were the metal passes into corrosive media as ions by the reaction $M{\rightarrow}M^{n+}$. In this interval the current density is increased up to a critical value (i_{crt}) and then start to decline until the passivating potential (E_{pass}). The passivation is the result of formation of corrosion products film in accordance with the corrosion reaction $M{\rightarrow}M_xO_y$. In the transpassive region, the oxide film starts to dissolve oxidatively [15].
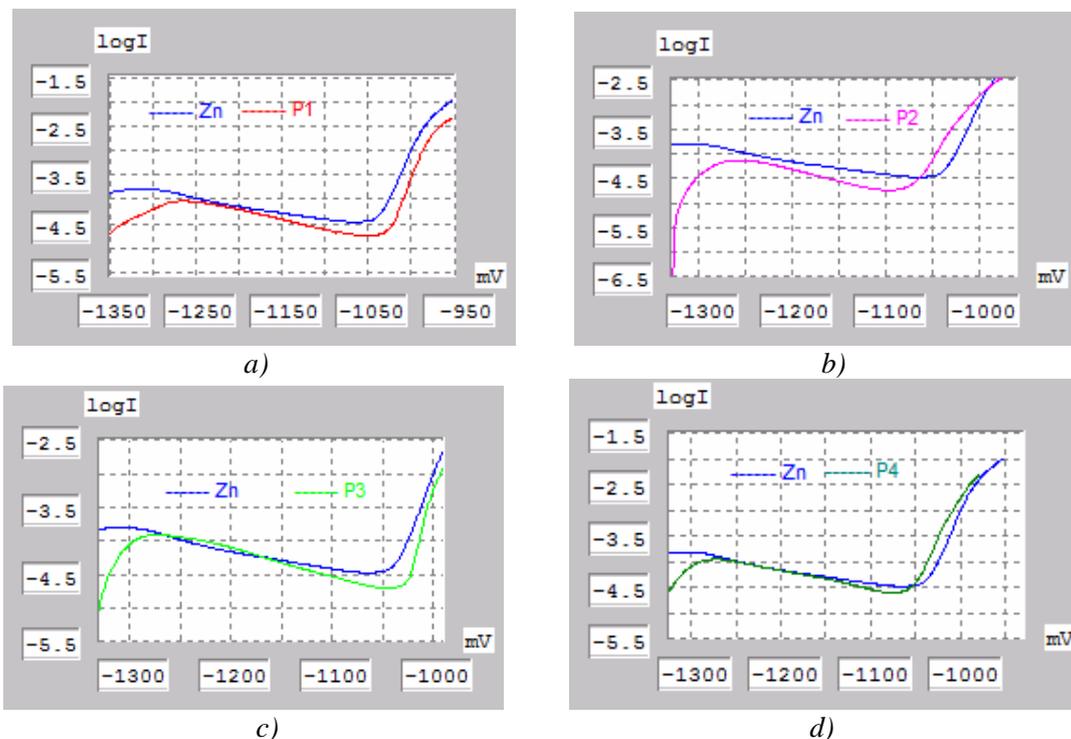
Fig. 4. *Anodic polarization curves obtained for zinc phosphate coated steel compared with galvanized sample*

Figure 4 presents the anodic polarization curves obtained for zinc phosphate coated samples compared with an untreated hot dip galvanized steel sample. It should be noted that all of the four solutions ensure for material a lower active zone than for zinc. Also this is valid for the critical potential ($E_{crt.}$), respectively: $E_{crt.P2} < E_{crt.P3} < E_{crt.P1} < E_{crt.P4} < E_{crt.Zn}$.

Sample 2 (Figure 4b) is the most rapidly passived ($E_{pass} \approx -1100mV$) compared with the galvanized sample ($E_{pass} \approx -1050mV$).

From the experimental data obtained from measurements we chose the Tafel method to study the corrosion behaviour.

The analysis of the graphical representations made it possible to determine the electrochemical parameters of the corrosion process: corrosion potential E_{corr}, corrosion current density i_{corr}, polarization resistance R_p and corrosion rate V_{corr}, (Table 2).

Table 2. Electrochemical parameters of the corrosion process

Code	I_{cor}	E (i=0)	R_p	V_{cor}
	[mA]	[mV]	[$k\Omega.cm^2$]	[mm/y]
Zn	31.300	-1392.1	0.30166	0.366
P1	16.2355	-1374.4	1.15	0.190
P2	8.2595	-1328.0	1.01	0.097
P3	12.9615	-1335.0	0.53508	0.152
P4	15.7984	-1344.0	0.64429	0.185

Figure 5 shows the Tafel curves in case for each sample studied. The E_{corr} potential was shifted to most negative values. The passivated sample into solution code P_2 has the most negative E_{corr} value potential, thus confirming the highest corrosion rate value.
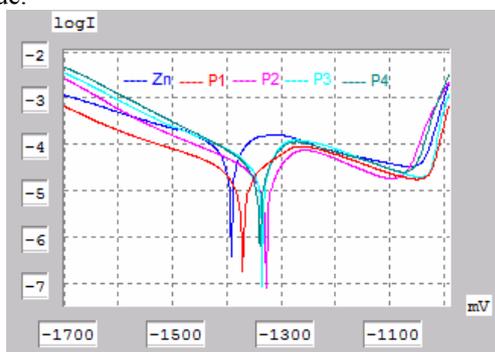
Fig. 5. *Tafel curves for galvanized sample and respectively for passivated samples*

3. Conclusion

Surface quality of the passivated galvanized steel is important for the corrosion behavior of the coating. The passivated surfaces show a yellow-green appearance for solutions code P_1, and green for code P_4.

Microscopic appearance for high immersion times has shown a continuous and thin layer.

Layer thickness is high for solution code P_4, minimum for the solution code P_1, medium for solution code P_2 and P_3. For each solution the layer thickness increases at the immersion time.

In all solutions tested, result coatings more resistant to corrosion in seawater compared with galvanized steel.

The highest rate of corrosion corresponds to passivating solutions P_2, P_3 and P_4; the best being the solution P_2.

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