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PHOSPHATE PASSIVATION SOLUTIONS ENHANCED BY CHEMICAL ADDITIVES FOR TREATMENT OF THE HOT DIP GALVANIZED STEEL

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ABSTRACT

To stabilize the surface of the galvanized steel it is important to apply a passivation treatment during its manufacturing. The general aim of the passivation treatment is to prevent the formation “storage stain” or “white rust”. For many decades, the chromium conversion treatments involving the use of chromic acid containing Cr6+ species have been used for their corrosion protection and adhesion promotion performances. Today all hexavalent chromates have been banned by the EC. Toxicological studies have evidenced the hazardous character of hexavalent chromium. Therefore more economical and environmentally friendly passivation solutions have been studied and used to replace the chrome passivations on galvanized steel.

Phosphate conversion coatings are commonly used on the galvanized steel. They form a thin protective film on steels surface. However, the formation of a stable and uniform coating for corrosion protection remains a challenge. More complexes passivating solutions with chemical activators added are the potential alternatives.

In this paper are presented the studies about such molybdate–phosphate passivation solutions as environmentally friendly alternative for chromium passivates. The results of treatments realized for different treatment times and more compositions were analyzed. Also the corrosion resistance of the passivated samples has been studied.

KEYWORDS: hot dip galvanized steel, molybdate–phosphate passivation film, corrosion resistance

1. Introduction

The protection of steel sheets is often obtained using a zinc coating by hot dip galvanizing technology. For inhibition of the formation “storage stain” or “white rust” on the surface of galvanizing steels must applied the passivating treatments.

The reducing the corrosion rate of the zinc layer, in the past, a very common and popular way was chromate conversion coating based on Cr^{6+}. This could increase the passivation tendency of zinc layer. However, hexavalent chromium is regarded as toxic and cancer-producing, there are environmental and health risks associated with the use of chromate ions [1, 2]. Therefore, all hexavalent chromates have been banned by the EC and have been generally replaced by other chromium-free passivates [3 - 6].

As potential alternatives to hexavalent chromium was studied several passivating inhibitors like molybdates, tungstates, permanganates, vanadates, and organic compounds [7, 8].

The phosphating is one of the most important chemical conversion processes used for corrosion protection or painting primer for the galvanized layers [9 - 11]. Zinc phosphate is used as main component for the passivating solutions. Molybdate can be added for the deposition of a superior zinc phosphate coating. This is an environmentally acceptable and effective corrosion inhibitor for galvanized steel [12, 13].

The molybdate additives into phosphate solution lead to accelerate the phosphating processes or to improve the corrosion resistance of phosphate coatings [14 - 16].

Molybdate films are amorphous, but they have cracks during a longer immersion [17]. As result were proposed molybdate–phosphate solutions. The molybdate–phosphate system was introduced by Tang et al. for corrosion protection of galvanized steel [18].

Other studies have been suggested that molybdate-phosphate based conversion coatings are an attractive alternative to chromate conversion coatings [19, 20]. For building films of significant thickness the presence of fluoride ions is also important [21].

In this paper are presented the results of study about the utilization of three molybdate–phosphate passivation solutions with different compositions to enhance the properties of coatings on the surface of galvanized steel sheets.

The treatments realized at different concentrations and dipped times were analyzed.

Also the corrosion resistance in sea water solution of the passivating samples has been studied and discussed. Was make a comparative analyzes of corrosion rates for different passivation solutions and different times of exposure in corrosion medium.

2. Experimental method and materials

More series of rectangular galvanized steel sheet samples were used. Zinc protective coating was obtained by hot dip galvanized process.

Before passivation the specimens were cleaned sequentially. The galvanized steel samples were degreased with acetone. The surface that has been subjected to phosphating was rinsed with deionized water to remove any residue and non-adherent particles present on it. After rinsing the samples were dried. The zinc phosphate coating is applied by immersion of samples in a zinc phosphate solution. After the passivating film is deposited, the steel samples are removed from solution and then thoroughly rinsed and dried.

The solution used for coatings obtaining was prepared with zinc dihydrogen phosphate ($Zn(H_2PO_4)_2$). Also molybdate diamonium ($(NH_4)_2MoO_4$) as source of molybdenum ions was added. Fluotitanic acid ($H_2TiF_6$0) for pH correction and source of active ion Ti for activation passivating process was added in solution.

***Table 1**. Composition of the phosphating solutions used in this work*

Code of treatment solution	**Zinc dihydrogen phosphate**	**Fluotitanic acid**	**Molybdate diamonium**
	[g/L]		
I	30	10	10
II	45	15	15
III	90	30	30

Three compositional variants for the passivation solution that has been applied on the surface of galvanized steel sheet samples are given in Table 1. The specimens were dipped in each passivating solution (open to air) at room temperature for 10, 15, 20, 30 and 60 seconds.

The corrosion properties of passivated samples have been tested by their exposing in the sea water solution as corrosion medium for different exposure times. The solution for corrosion tests have 27g/L NaCl, 6g/L $MgCl_2$, 1g/L $CaCl_2$, 1g/L KCl at pH = 6.5-7.2. The protective properties of the molybdate–phosphate conversion coatings obtained for those three passivating solutions and different exposure times (168, 336, 504, 672 and, 840 h) have been evaluated by corrosion rates measurements.

3. Results and discussions

To evaluate the quality of molybdate–phosphate conversion coatings the physical characteristics as well as the performance in corrosive environment were determined.

Firstly was analyzed the physical characteristics of passivating films. To determine the passivated coating thickness the determination of coating weight was adopted.

***Table 2.** Passivated coating thickness as coating weight in g/m^2 at increasing immersion time*

Immersion time in s	**Coating thickness as coating weight** in g/m^2 for:		
	Solution I	**Solution II**	**Solution III**
10	1.314	3.775	12.375
15	1.579	3.85	8.204
20	3.256	2.318	9.414
30	2.06	2.95	8.979
60	2.11	3.595	7.97

This method involves the determination of change in weight of a coated specimen after immersion in the treatment medium.

The difference in weight after coating and before is divided by the surface area of sample in m^2 to obtain unit coating weight in g/m^2. The time evolution of the layer thickness corresponding to the samples dipped into the three solutions is presented in Table 2, respectively Figure 1.

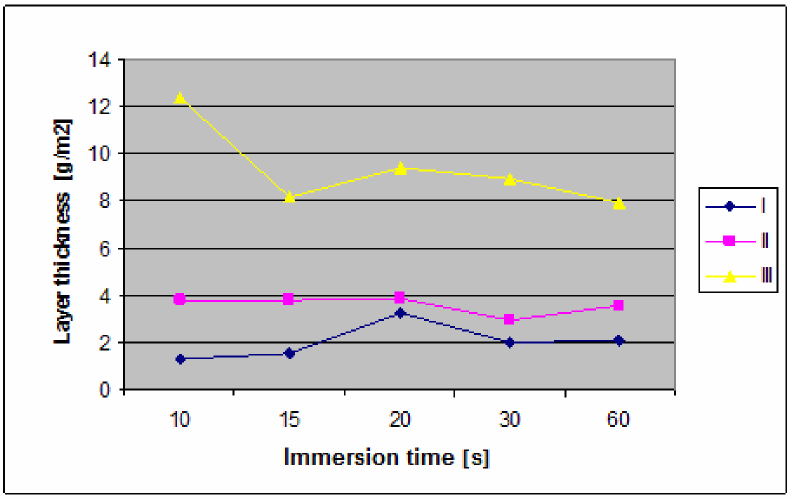


Fig. 1. *Layer thickness of molybdate–phosphate conversion coatings as a function of duration of immersion for different passivating solutions.*

The thicknesses of conversion films obtained at different immersion times and the composition of the passivating solutions have been different. The thicker film was obtained for the solution III with higher phosphate and molybdate addition. At prolongation of the immersion time a slowly reducing of the thicknesses of the layers was observed for all solutions. For the treatments developed into all solutions the films were developed rapidly. In simple passivating solutions, phosphating reaction tends to be slow owing to the polarization caused by the hydrogen evolved in the cathodic reaction. To achieve coating formation in a practicable time for classical phosphating solution, some mode of acceleration must be employed. For this study the chemical additives were added into zinc phosphate solution and their action was evidently. Molybdenum and titanium compounds were added into phosphating bath as chemical accelerators. For all solutions after short immersion times (~15-20s) were obtained stable thicknesses for layers.

The length of period for developing of a stable film corresponds with the first stage in coating formation (namely, the induction stage) into classical phosphating process. For developing a stable layer is observed that the classical phosphating process involves more time.

The process for the coating formation care divided into four distinct stages: the induction stage, the commencement of film growth, the main exponential growth stage and the stage of linear increase in film growth [22].

The quality of passivating process for different solutions and immersion times was analyzed by examination of physical appearance of coated surfaces of samples. The surface morphologies of the molybdate-phosphate films are presented in the Figure 2-4.

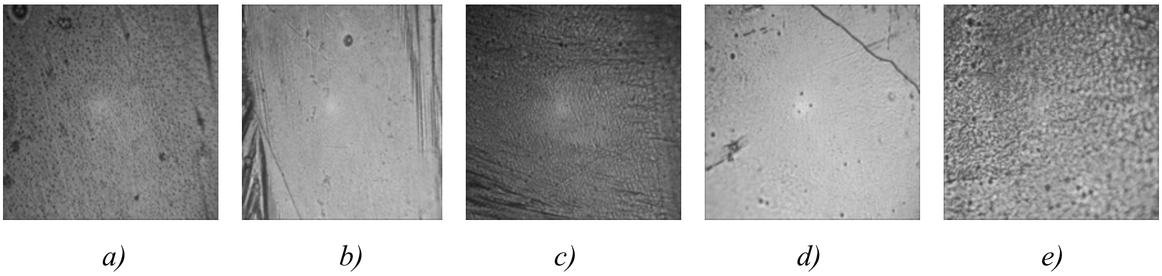
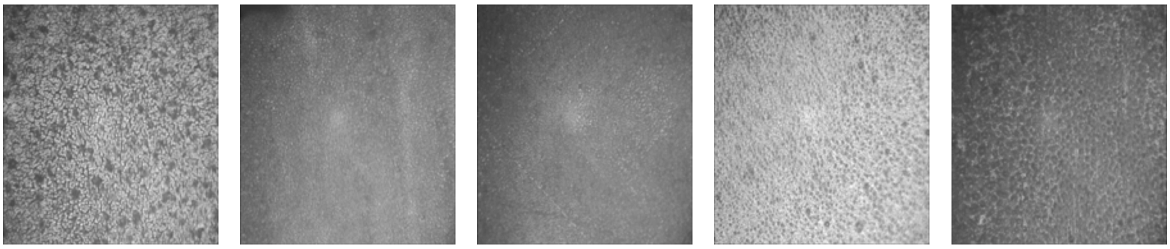
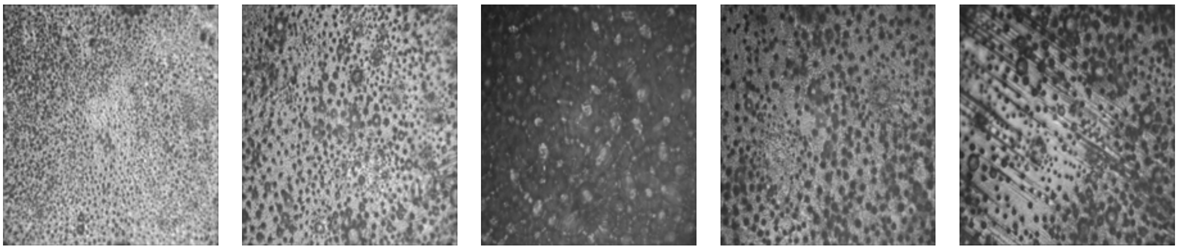

a) *b)* *c)* *d)* *e)*

Fig. 2. *Surface appearance of passivating layer for solution I at different immersion times: 10 (a), 15 (b), 20 (c), 30 (d) and, 60s (e).*



a) b) c) d) e)

Fig.3. *Surface appearance of passivating layer for solution II at different immersion times: 10 (a), 15 (b), 20 (c), 30 (d) and, 60s (e).*



a) b) c) d) e)

Fig.4. *Surface appearance of passivating layer for solution III at different immersion times: 10 (a), 15 (b), 20 (c), 30 (d) and, 60s (e).*

During the treatment the surface is in contact with the phosphate solution that dissolves a small amount of the coating. At the surface of the zinc, the attack of the zinc phosphate produces a localized increase in the pH, resulting in the precipitation and deposition of insoluble zinc phosphate crystals on the surface of the zinc coating.

After some time of reaction developing, this crystallizing action leaves behind a continuous, relatively thick solid film of zinc phosphate.

The phosphate films on surface of hot dip galvanizing steel may range in colors from light gray to dark gray, depending on the type of bath and the grade of steel substrate used. The chemical additives can generated the depositions with other colors. The layers obtained in the experimental are have yellowish green color for solution I and green for solution III.

For solution I at all immersion times tested the passivating film obtained is uniform and adherent.

For obtaining an optimum surface appearance at dipping into solution II was necessary an immersion time in range of 15-20s. This is lower than the corresponding immersion in solution I.

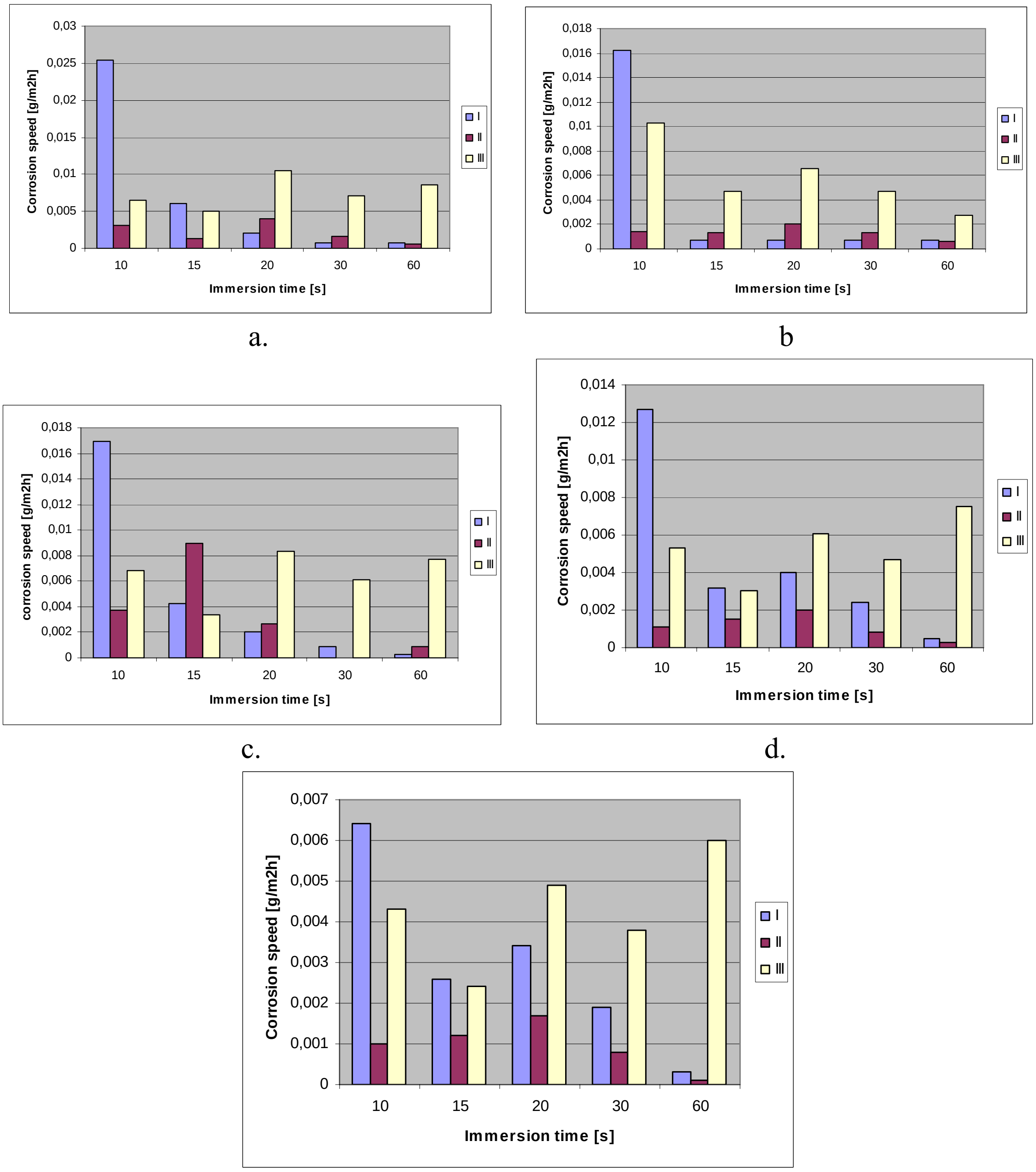
The solution III has a higher content of dihydrogen phosphate and as result the passivating reaction is more intensive.

As result a thicker layer was developed. Because over 20s the layer becomes less uniform and adherent must be established the optimum immersion time. In respect to these parameters of the passivating treatments (the composition of the solutions and immersion times) can concluded that a bigger thickness was obtained for a solution enriched in phosphate and for controllable immersion time. More phosphate addition negatively affects the coating. Sometimes for solution III was obtained non uniform and rough layers. Also uncovered areas were observed.

It is generally accepted that the composition of the phosphate layer has a strong influence on its chemical stability. For this reason in this study this was analyzed by corrosion tests at which were subjected the samples after the passivating treatments.

Is knows that the passivity (or reactivity) of the molybdate–phosphate layer at interaction with a corrosive medium is an important property of conversion layer. In order to determine the corrosion speeds in sea water medium the samples (obtained at different passivating treatments and different immersion times) were maintained at room temperature in sea water solution with 27g/L NaCl, 6g/L MgCl2, 1g/L CaCl2, 1g/L KCl, pH = 7.1.

The corrosion speeds were measured for different exposure times in corrosion medium: 168, 336, 504, 672 and 840 h. The results of experiment are given in comparison charts, Figure 5.



a. b

c. d.

e.

***Fig.5.** Comparison chart of corrosion speeds for different passivation solutions and different immersion times at variation of exposure time in corrosion medium: 168 (a), 336 (b), 504 (c), 672 (d) and, 840 hours (e).*

By selecting the results for corrosion tests obtained for the three passivating solutions and variable immersion times in these solutions was possible to choose the better treatment, Figure 6.

For solution III was obtained passivation layer the thickest but it did not show the best resistance to corrosion. This explication is done by the quality of the layer developed at higher phosphate content into passivating solution.

Can be observed that for passivation solution with more molybdate–phosphate content the corrosion rate slowly decreases with exposure time into corrosion medium.

For the other solutions the corrosion speeds are lower and appreciatively remain at these lower values at prolongation of exposure time.

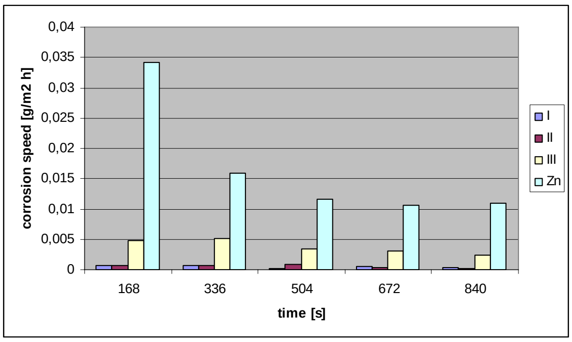


Fig.6. *Variation of the corrosion speed as a function of the exposure time to the corrosive environment.*

4. Conclusions

The surface quality of the passivating hot dip galvanized steel sheet is important for its corrosion behavior.

The thickness of passivating coating obtained on galvanized steel surface varies with immersion times and phosphating compounds added. The addition of chemical additives influences the process. Comparatively with the classic process the times required for forming of continuous and solid molybdate-phosphate films were lower and their color was yellowish green or green. The passivating process was developed rapidly.

The thickness of molybdate–phosphate conversion coatings depends by chemical composition of the passivating solutions and by times of immersion.

The thickness of layer is higher for solution III, minimum for the solution I and, medium for solution II. The solution with the following chemical composition zinc dihydrogen phosphate 45g/L fluotitanic acid 15g/L, molybdate diamonium 15g/L and immersion time of 60 second gives the best corrosion resistance. The appearance of the corroded surfaces for all the samples shows a general and uniform corrosion.

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