INNOVATIVE PASSIVATION FILM ON GALVANIC ZINC COATINGS BASED ON TANNIN AND GELATIN

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Abstract

Steels are widely applied traditional materials in the transport industry as well as for buildings, bridges, railway facilities etc. However, their application often leads to significant financial expenses due to the need for increased protection against corrosion destruction. This protection can be realized by usage of additional passive films on the metal surface. Tannin and gelatin are well known environmentally friendly natural products, they are easily accessible and profitable from a financial point of view. The chemical interaction of tannin and gelatin with each other, as well as with metal ions ensure the possibility for bonding the layers with both the zinc base as well as the individual layers for each other to form a sandwich structure. Galvanized low-carbon steel with such a film has been placed in a 5% NaCl solution and its corrosion behavior was compared with that of the ordinary zinc coating. The results demonstrate the positive influence of the passive film on the protective characteristics of the zinc layer in chloride containing medium.

Keywords: *passivation film, zinc coating, corrosion, gelatin*

1. INTRODUCTION

In recent years, corrosion protection has been focused predominantly on “green chemistry”, especially after limiting the use of chromium and other hazardous compounds, which are being intensively replaced by environmentally friendly materials.

In antiquity, natural products (such as bitumen) were used in the practice as anticorrosion coatings. In Europe in the Middle Ages, these coatings were based on wood tar or molten pitch [1]. Essential oils were some of the first corrosion inhibitors described in the scientific journal in the 19-th century [2]. In the early 20-th century there were already patented corrosion inhibitors.

Plant extracts containing tannins were used as anticorrosive agents long time before their chemical composition was known. Depending on the species of plants from which the tannin is extracted, tannins contain different compounds and can be defined as water-soluble phenolic compounds with molecular weights between 500 and 3000 $g.mol^{-1}$ [3-6]. Tannic acid is an ester of glucose with digalic acid, containing 10 galloil units, but in commercial products the number of galloil units varies – Figure 1.

The use of tannins as rust converters and corrosion inhibitors is based on the ability of polyphenols to form complexes with iron ions. Tannins also form stable complexes with ions of other metals, including zinc. This property allows tannins to be used in toxic metal extraction processes [7] and in ultra-trace level detection of metallic ions [8]. In addition, tannic acid is used as a major component in various anti-corrosion coatings [9-11].

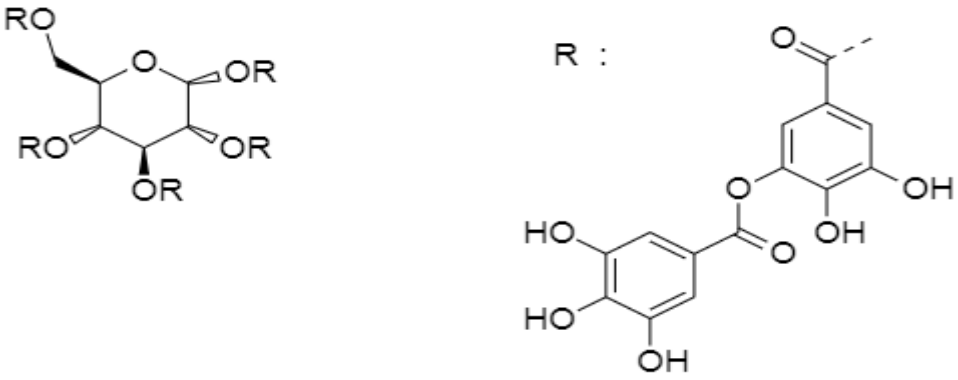


Figure 1. Tannic acid

Gelatin films, coatings, capsules, etc. are used in analog photography, pharmacy, food industry. Recently, biodegradable gelatin-based materials are expected to be able to replace traditional plastic packaging. Hardening of gelatin is an industrial process by which amino-acids are crosslinked with a suitable reagent. Most often, the hardening of gelatin is carried out with formaldehyde, as formaldehyde or its hydrates and dimers react with the amino-groups of the amino-acids of gelatin, forming methylene and oxymethylene bridges [12-13]. This process significantly improves the physical and mechanical properties of gelatin coatings, reduces solubility and increases temperature resistance.

The interaction between polyfunctional tannic acids and gelatin leads to crosslinking of the protein matrix of gelatin which significantly improves the mechanical properties and temperature resistance [14, 15]. Formaldehyde forms methylene bridges between phenolic tannin nuclei [3].

This work presents the initial stage of our research on organic anticorrosion coatings based on affordable and inexpensive products from processing of animal and plant raw materials – tannic acid and gelatin. The main idea is to combine the advantages of gelatin coatings - harmless, elastic and with good resistance to various conditions, with the properties of gelatin as a corrosion inhibitor [16, 17]. For the crosslinking of gelatin both classic agents like formalin and tannic acid were used. Tannic acid is an important component of the coating due to its anti-corrosion properties and a propensity to form stable complexes with metal ions.

2. MATERIALS AND METHODS

2.1. Sample types

A selection of organic compounds for preparation and obtaining of passive surface films on galvanized low-carbon steel was made in order to meet the following requirements:

- to demonstrate good adsorbtion on the zinc surface;
- to have good adhesion with the substrate;
- to form a dense layer.

Tannin and gelatin have been selected since they are natural products and do not pose an environmental hazard. In addition, they are easily accessible and their ability to interact both with each other and with zinc ions is a good prerequisite for connecting the layers both with the substrate as well as the individual layers for each other forming in such a way a “sandwich-like” structure.

Ordinary zinc coatings were electrodeposited on low-carbon steel plates with sizes 30 x 10 x 1 mm from slightly acidic electrolyte containing 150 g/l $ZnSO_4.7H_2O$, 30 g/l NH_4Cl and 30 g/l H_3BO_3.

The low-carbon steel substrates have following composition (wt.%): C - 0.05–0.12; S ≤ 0.04; P ≤ 0.35; Mn - 0.25–0.5; Cr ≤ 0.1; Si ≤ 0.03; Ni ≤ 0.3; Cu ≤ 0.3; As ≤ 0.08; Fe – balance.

The electrodeposition of zinc coatings was carried out at cathodic current density 2A/dm^2 and pH value between 4.5-5.0. Soluble metallurgical zinc anodes and 2 additives - wetting agent (AZ1) and brightener (AZ2) – have been also applied.

The gelatin-based passivation surface films were obtained on the galvanized samples in three steps as described below:

- The pre-calculated and weighed amount of gelatin is poured with the calculated amount of water and waited until it swells completely. Thereafter the samples are immersed for 10 minutes in the gelatin solution the latter being heated up;
- The galvanized samples are immersed in 35% HCHO solution for 10 minutes at ambient temperature;
- The samples stay for 10 minutes in tannin solution.

2.2. SEM investigations

The surface morphology of the so prepared samples was studied by applying of Scanning electron microscope INCA Energy 350 device.

2.3. Potentiodynamic investigations

Potentiodynamic polarization curves (PDP) have been realized in a three-electrode glass cell with a volume of 300 mL. Reference electrode was saturated calomel electrode (SCE) and the counter was a platinum wire. This investigation was carried out with a VersaStat 4 PAR device.

2.4. Polarization resistance

Polarization resistance method (Rp) was applied for evaluation of the protective ability of the surface passivation films toward the substrate. The principle of this method is based on the fact that the Rp value is inversely proportional to the corrosion current density according to Stern-Geary equation. The investigations were carried out with “Corrovit” device the latter being specially designed for this type of measurements.

2.5. Open-circuit potential measurements

Open circuit potential (OCP) investigations were carried out simultaneously with the polarization resistance test in order to estimate the potential displacement value during the immersion period of the test samples in the model medium.

2.6. Corrosive medium

All electrochemical and corrosion investigations were performed in a test solution of 5% NaCl with pH value about 6.7 and ambient temperature.

2.7. Reproducibility

The results from the investigations were in average of 5 samples per type, i.e. for each experiment 5 replicates/samples were conditioned for the measurements.

3. RESULTS

3.1. SEM studies

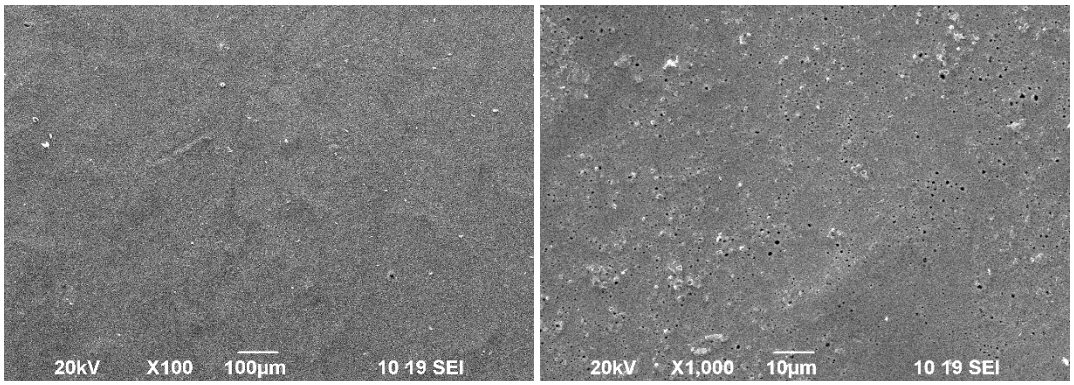


Figure 2. SEM images of the investigated samples at different magnifications

The surface morphology of the passive gelatin-based films on the galvanized low-carbon steel samples is demonstrated in Figure 2. It is well visible that at the lower magnification (x100) the surface of the protective film looks smooth and even.

However, at the greater magnification (x1000) some holes with a mean diameter of maximal 1 µm can be observed. The latter are spread unevenly which seems to be most probably a result of hydrogen evolution process occurring during the stay of the sample in the respective solution according to the operation procedures.

3.2. Potentiodynamic investigations

PDP curves of the galvanized steel samples with and without additional surface gelatin-based film are presented in Figure 3. According to the figure it is obvious that the ordinary zinc coating without additional surface film shows shorter curve in the anodic zone (up to about -0.6V) which means that it lasts shorter time at external anodic polarization compared to the other sample.

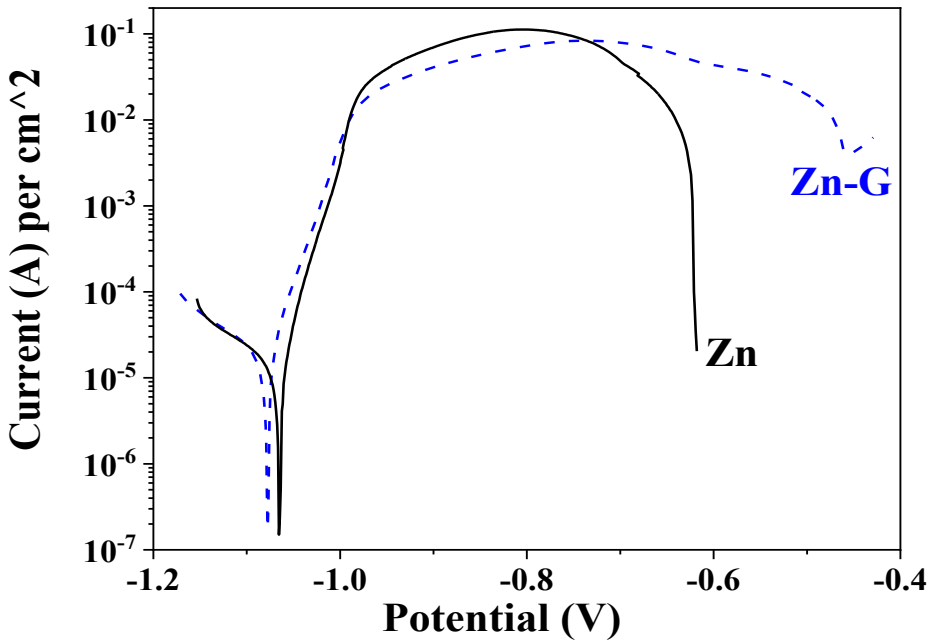


Figure 3. Potentiodynamic curves of ordinary zinc and sample with gelatin layer

The polarization curve of the sample with additional surface film (Zn-G) demonstrates longer anodic curve (up to about -0.45 V), i.e. this coating is more corrosive resistance at external anodic polarization compared to the case with the ordinary zinc. In addition, its anodic current density in the potential interval between -0.98V ÷ -0.74V is lower compared to the other investigated sample which means that its anodic dissolution rate is lower.

The maximal anodic current density can be registered at about 0,8 V and that of Zn-G – at -0.72V. It is also well visible that this arrangement is a result of the elongated anodic curve of the sample with surface protective film of gelatin.

Somewhat surprising is the fact that the corrosion current density of the sample Zn-G is particularly higher compared to that of the ordinary zinc. The reason for this could be for example the presence of some holes on the surface which act as corrosion accelerators in the initial stages of the dissolution before the appearance of corrosion products which will fill in their volume.

Some of the most important electrochemical parameters obtained from the application of this electrochemical method are summarized in Table 1.

Table 1. Some electrochemical parameters of the PDP curves from Figure 3

Sample	E_{corr}, mV	I_{corr}, A.cm^{-2}	I_{max}, A.cm^{-2}	Length of the anodic curve
Zn	-1,065	1,5.10^{-5}	0,114	up to - 0,60 V
Zn-G	-1,080	1,6.10^{-6}	0,083	up to - 0,45 V

3.3. Polarization resistance measurements

The experimental results from the polarization resistance measured for a time period of 20 days immersion in the model test corrosive medium are demonstrated in Figure 4. It can be summarized that the Rp values of the ordinary zinc without additional gelatin-based film remain very close during the whole period. An increasing trend can be observed during the first 10 days up to about 750 Ω.cm^2. Thereafter the Rp values slowly decrease until 650 Ω.cm^2 being about two times lower compared to the sample with additional protective surface film.

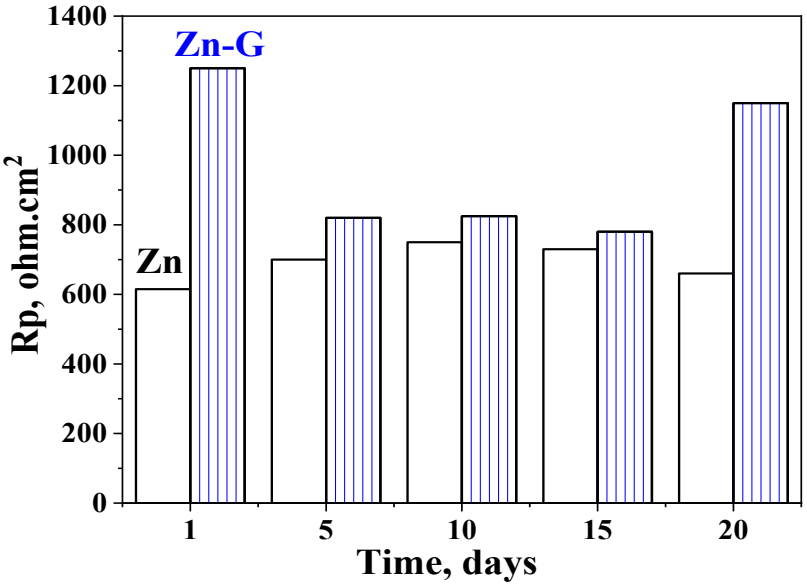


Figure 4. Polarization resistance measurements

Contrary to this the other investigated sample with surface gelatin-based layer shows at the beginning of the investigation very high polarization resistance up to 1200 Ω.cm^2 followed by gradually decreasing in the middle of the period demonstrating values between 780 – 820 Ω.cm^2 after 2 weeks.

However, at the end of the test the Rp values of the passivated galvanized sample increase again up to about 1150 Ω.cm^2 at the 20-th day. Most probably, these results follow from the partial dissolution of the protective layer in that medium and from the consecutive appearance of newly formed corrosion products or organic-Zn^{2+} complexes, which seem to "seal up" the surface and impede the penetration of the chloride ions deeply inside.

3.4. OCP measurements

The open circuit potential data obtained during the polarization resistance measurements of the test samples are presented in Figure 5. Generally, the observed trends of changing the OCP values qualitatively correspond to the polarization resistance changes the latter well visible in Fig. 4. It could be summarized that OCP values of the sample Zn-G are more positive than that of the ordinary zinc during the whole period of investigation.

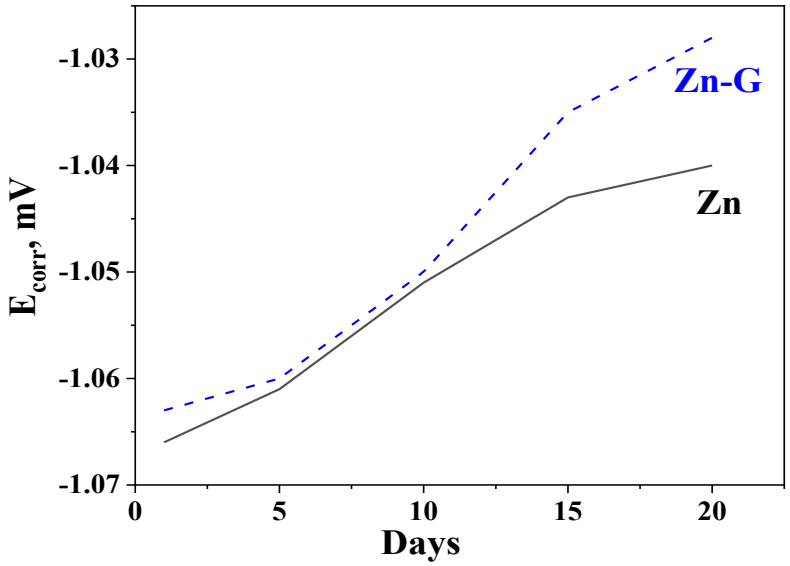


Figure 5. Open circuit potential measurements

This observation can be explained with the peculiarities and the nature of the passive surface film based on gelatin and tannin. This means that the film becomes more noble – it is a cathodic film toward the protected substrate.

These results together with the Rp data demonstrate the effectiveness of the protective film in aggressive medium containing chlorine ions.

4. CONCLUSIONS

The presented experimental data demonstrate that the presence of a gelatin- and tannin-based surface film on galvanized steel samples influence positively the protective characteristics of the low-carbon steel in a model test medium of 5% NaCl. This environmentally friendly film leads to potential displacement in positive direction (i.e. the sample becomes more noble compared to the ordinary zinc) as well as to higher corrosion resistance at open-circuit potential and at conditions of external polarization. The main reason for these effects seems to be the simultaneous application of two natural products with clearly expressed inhibitor properties.

The obtained results give us reason to continue research in two directions - on the one hand - to add other suitable corrosion inhibitors to the coating, and on the other hand - to investigate the structure of the coating and how the two main components - gelatin and tannic acid - interact with each other and with formaldehyde under different coating deposition conditions.

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