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# EIS study of organic coating on zinc surface pretreated with environmentally friendly products

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**Abstract**

The life time of many steel structure can be remarkably improved by protecting the steel with zinc layers. However, also the zinc coating can be involved by corrosion phenomena with the consequence that some steel surface is unprotected.

The reduction of the corrosion rate of zinc is therefore an important topic. These results can be obtained by introducing zinc alloys with lower corrosion rate (ZnNi, ZnFe, etc.) or by protecting the zinc surface with organic or inorganic layers able to reduce the corrosion rate.

In the past a very popular way to reduce the corrosion rate of zinc was the use of chemical conversion layers based on $Cr^{6+}$, able to increase the passivation tendency of the zinc (chromating). This procedure is quite effective also for improving the adhesion of organic coatings deposited on the zinc surface, but there is the important problem that the use of chromium salts is now restricted because of environmental protection legislation.

It is therefore very important to develop new zinc surface treatments environmentally friendly to improve the corrosion resistance of zinc and the adhesion with the final organic protective layer.

In this paper a characterisation of environmentally friendly conversion treatments based on $Cr^{3+}$ for zinc surface will be reported in comparison with traditional based $Cr^{6+}$ pretreatments on different zinc layers protected by organic coatings.

The samples were studied using EIS measurements, and the data analysis was mainly based on the discussion of the mathematical combination (ratio, product, etc.) of different parameters of the equivalent electrical circuit model.

This approach was found more useful, in order to compare the performance of different materials, in comparison to the simple discussion of the numerical values of the parameters, being these values generally influenced by random defects present in the samples, affecting the measured impedance.

The results showed that the performance (adhesion and corrosion protection) of good formulated $Cr^{3+}$ based pretreatments are not far from the results, which it is possible to obtain with industrial $Cr^{6+}$ pretreatments and therefore $Cr^{3+}$ conversion layers can be considered an interesting alternative to the traditional ones.


*Keywords:* Duplex system; Chromates; Adhesion; Impedance

## 1. Introduction

The corrosion protection of steel structure is often obtained, in particular for outdoor applications, by using a duplex system: the combination of a zinc coating with an organic coatings [1]. In order to reduce the corrosion rate of the zinc layer and increase the adhesion between the two coatings, a pretreatment of the metal layer is necessary and this pretreatment generally consists in a chemical conversion layer [2].

A very common zinc surface pretreatment is the passivation in chromates bath, very efficient both in reducing the zinc corrosion rate and increasing adhesion [3].

Unfortunately the cancer-producing and toxic activity of $Cr^{6+}$, important component of the pretreatment bath and

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chemical conversion layer, is well known [4]. For this reason it is probable that in the next future this pretreatment will be abandoned, also under the pressure of legislative actions.

Many different pretreatments have been studied in the last decade in order to avoid the use of $Cr^{6+}$, in addition to the typical phosphating treatment: chromium free, including molybdates, permanganates, vanadates, and tungstates (pretreatments with protecting mechanism similar to $Cr^{6+}$ acting as passivating agents) [5,6], or adhesion promoters like fluozirconates, fluo-titanates, organosilanes, etc. [7,8].

A further possibility is to use pretreatments based on $Cr^{3+}$, which is not considered carcinogenic [9].

Many papers are available in the literature dealing with new pretreatments of zinc and their corrosion protection characterisation [10,11]; some works are also focused on studying the influence of the pretreatment in the complete duplex system (zinc coating, pretreatment and organic coating) [12].

The aim of this work is the comparison of traditional and new industrial pretreatments based on $Cr^{6+}$ and $Cr^{3+}$ on different zinc coatings and further covered by an organic waterborne primer. The comparison is obtained mainly by electrochemical impedance spectroscopy measurements and a new approach to the EIS data analysis is proposed, based on the combination of different parameters, able to give information on the duplex system performance.

## 2. Materials and experimental procedure

Materials with different metallic coatings were studied: hot-dip galvanised coatings and electrodeposited coatings.

The hot-dip galvanised coatings were deposited on steel sheets with the following chemical composition: C 0.04–0.11%, Si 0.02%, P 0.07%, Fe balance (low-silicon substrate). It is very important to maintain low the Si and P content because these elements can remarkably affect the microstructure and the thickness of the metal layer, producing metallic coatings with low performance [13].

The coating deposition (symbol H) was carried out at 450 °C in a bath of molten zinc containing Ni (∼0.5%), Pb (∼1%) and Bi (∼1%), immersion time about 2 min and extraction rate about 70 cm/min. The coating thickness is about 70 μm.

The electrodeposited coatings were produced on Q panel of mild steel after degreasing. Two different coatings were produced: the first one is pure zinc (symbol Z), the second one is a Zn–Fe alloy (Fe about 0.7%, symbol ZF), using the two cyanides free baths reported in Table 1. For both materials the coating thickness is about 17 μm.

All the materials were further pre-treated and passivated in two industrial baths. The first bath is a traditional chromate treatment based on $Cr^{6+}$, working at room temperature, with 0.5% of nitric acid, 0.1–0.2 g/l of $Cr^{6+}$ and additives; the time of permanence in the bath is 15 min (pretreatment symbol CrVI).

The second passivation treatment is based on $Cr^{3+}$, working temperature 50–55 °C, bath composition: 0.5% nitric acid, 0.1% $Cr^{3+}$ and additives; the time of permanence in the bath is also 15 min (pretreatment symbol CrIII).

The samples were organic coated using an environmentally friendly product: Epoxyphenolyc unpigmented waterborne resin (Polifix®) by dipping of samples for 90 s, curing temperature 250 °C, curing time 15 min, final dry thickness $7 \pm 2$ μm.

This coating should be considered as an example of a primer and it is a model system useful to evaluate the pretreatment influence on the adhesion and corrosion protection properties of the organic coating. Actually a thicker coating with higher barrier properties could hide the electrochemical behaviour of the interface for a long time [14].

The samples produced in this way were characterised microstructurally and morphologically by optical and electronic microscopy and they were analysed chemically by EDXS measurements.

The protective properties of the system were studied by electrochemical impedance spectroscopy measurements (EIS) obtained in a 0.3% $Na_2SO_4$ solution, which is a not aggressive environment. The EIS measurements were obtained at the free corrosion potential using a potentiostat and FRA equipment, signal amplitude 10 mV, frequency range 100 KHz–0.001 Hz and testing area about 15 $cm^2$. The electrochemical data were modelled using equivalent electrical circuits with the software Equivcrt [15].

The adhesion measurements in dry and wet conditions were obtained by pull-off technique (Sebastian IV instrument) and they are the average value of five measurements with the same failure mode (failure at the metal-coating interface) and neglecting all the measurements with coating de-cohesive failure. The wet adhesion measurements are obtained after immersion of the samples in distilled water for 24 h at room temperature.

## 3. Results and discussion

### 3.1. Pretreatments characterisation

After the pretreatment deposition, the samples have been observed by electron microscopy; two observed examples of

Table 1
Composition of the baths for the electrodeposition of zinc layers

| Bath | Composition (g/l) | Temperature (°C) | Current density (A/$dm^2$) | Symbol |
|---|---|---|---|---|
| Zn alkaline | Zn 10–20 NaOH 110–190 additives | 20–35 | 1.5–3 | Z |
| ZnFe alkaline | Zn 15 Fe 0,03 NaOH 130 additives | 22 | 2 | ZF |