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Ph. D THESIS

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**Effect of different galvanised coatings
on the materials structure of conversion layers**

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Introduction

The galvanised steel surface has been protected against corrosion by applying of chromate containing conversion layers for many decades [Wilhelm, 1936.]. The metal sheet is immersed into solution of chromic-acid or Cr(VI)-salt [Nevison, 1987][Zhang, 1996.][Williams, 1972.]. During immersion chemical reaction occurs on the metal surface developing a thin coating of 10-1000 nm. This layer is composed of zinc-oxides, -hydroxides, -chromates, Cr(III)- and Cr(VI)-oxides at last Cr(III)- and Cr(VI)-hydroxides. This layer acts as a physical barrier and hinders the moisture, humidity and air pollutants to get to the zinc surface however supports the dissolution of Cr(VI) to inhibit the corrosion [Almeida 1, 1998][Almeida 2, 1998.]. The Cr(VI) has a “self healing” property what means that by leaching into the water in mechanical surface damages the cracks will be sealed.

Concerning the excellent solubility and reactivity of the Cr(VI)-ion, it can react easily with the organic and inorganic components causing damages in the natural environment and serious carcinogenic risk. The European Parliament recognised these detrimental properties and, in 2003, developed the RoHS directive [RoHS, 2001.] concerning the restriction of amount of hazardous materials in electronic, electrical equipments. In pursuance of the directive the regulation came into force in July of 2006. Besides this directive the European Parliament framed the REACH regulation about the registration, evaluation, authorisation and restriction of chemicals in December of 2006. [REACH, 2006.]. Thenceforward the chemicals imported to the EU must have precise and adequate documentation. Concerning the regulations the allowable amount of hazardous material especially for Cr(VI) is up to 1000 ppm. The „End of Life Vehicle” directive determined the quantity of Cr(VI) in motor car in 2.0 g from July of 2003. According to the regulation, the USA and Japan eliminated the Cr(VI) from the car manufacturing process. Having recognised the toxicity and carcinogenic effect of Cr(VI) researchers are encouraging to replace this inhibitor by environmental friendly conversion layers. These regulations restrict the chemicals for the purpose of

temporary corrosion protective materials for zinc coatings. Molybdates, tungstates, permanganates, and vanadates including chromium-like elements, were the first chemical elements tried as hexavalent chromium substitutes [Wilcox, 1987.][Wilcox, 1988.][Korobov, 1998.][Hosseini, 2007.][Deck, 1992.]. Lately, many alternative coatings have been developed based on zirconium and titanium salts, cobalt salts [Hinton, 1991.][Barbucci, 1998.], organic conductive polymers [Gonzalez, 2001.][Hosseini 1, 2006.][Hosseini 2, 2006.] and in my Ph.D. work accentuated rare earth salts [Baoshan, 2006.][Lu, 2006.]. However, preparation and corrosion behaviour of these coatings are not clear. To find an alternative treatment to Cr(VI) conversion coating, several treatments, which present a good anti-corrosive behaviour, a high cost/benefit ratio, and mainly, low environmental impacts are still to be developed.

The aim of the Ph.D. work

Several publications deal with in laboratory electro galvanised steel samples to characterise the corrosion protective abilities of rare earth containing conversion layers [Arenas, 2004.][Rosalbino, 2007.][Arenas, 2006][Arenas, 2004][Akiyama, 2003.] Based on earlier results I have studied the temporary corrosion protection of continuously hot dip galvanised, hot dip galvanised and electro galvanised, low alloyed steel plates treated by Cr(VI)-free, cerium-, yttrium- and lanthanum-containing inhibitors. Based on the hypothesis in the references on the galvanised steel surface developed rare earth inhibitor containing conversion layer composed of oxides, oxy-hydroxides and hydroxides. The morphological information of this coating has not been well defined in publications yet therefore I will focus on the morphological investigation of the developed layers. From the view of corrosion protection the nature of cation and the immersion time are determined parameters. [Montemor, 2002.], hence I treated the surfaces with three different rare earth cations in four salt solutions for two immersion time intervals.

The aim of my work was

- to determine the chemical composition and the reaction mechanism of the conversion layers produced on the different galvanised coatings.
- to establish the correlation between the physical parameters of the galvanised coatings and the homogeneity of the conversion layers.
- to select the most promising rare earth salt for corrosion protection of galvanised steel surface.
- to rank by a numerical factor the protective ability of the conversion layers against the corrosion.
- to give the relation between the immersion time and the physical, chemical and preventive properties of the conversion coatings.
- to explain the electrochemical processes on the zinc/conversion layer surface and set an equivalent circuit for modelling the physical properties of the developed coating systems and define the electrochemical parameters that characterise the corrosion mechanism besides establish the time-dependence of the corrosion protective behaviour of the film coatings.

To attain the aims of my work the microstructure of the developed conversion layers was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM), the composition of the coatings was controlled by electron probe microanalysis (SEM), glow discharge optical emission spectroscopy (GD-OES) and X-ray photoelectron spectroscopy (XPS). The corrosion inhibition behaviour of the conversion layers was characterised by DC polarisation as well as impedance spectroscopy (EIS). Modelling the real ambient atmosphere and storage effect a special pressing corrosion test was applied to prove the corrosion protection ability of the coating systems.

New scientific results, thesis

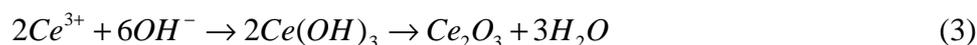
My Ph.D. work focused on temporary corrosion protection of continuously hot dip galvanised, hot dip galvanised and electro galvanised, low alloyed steel plates applying new generation of Cr(VI)-free, environmental friendly rare earth containing chemicals. The treatment of the galvanised steel surface was carried out by immersion of the plates into $2 \cdot 10^{-4}$ M CeCl_3 , $\text{Ce}(\text{NO}_3)_3$, LaCl_3 and YCl_3 solutions for 20 and 40 minutes. The investigation of the physical and chemical properties of the developed layers were characterised by SEM-EDS, AFM, XPS methods. The corrosion protective ability was controlled by a special pressing corrosion test as well as electrochemical technique. After the pressing corrosion test the corroded surface was examined by GD-OES method. The novel scientific results as thesis are summarised in the next paragraphs:

1. I have proved by EDS and XPS examination that the conversion layers developed on all type of galvanised steel surfaces. In case of treatment of the continuously hot dip galvanised steel by immersion into $2 \cdot 10^{-4}$ M CeCl_3 solution the developed conversion layer consists of CeO_2 , Ce_2O_3 , $\text{CeO}(\text{OH})$, $\text{Ce}(\text{OH})_3$, $\text{Ce}_2(\text{CO}_3)_3$ while in case of LaCl_3 treatment the layer composed by La_2O_3 , $\text{LaO}(\text{OH})$, $\text{La}(\text{OH})_3$ and $\text{La}_2(\text{CO}_3)_3$ [2]. The cerium-containing reaction products generate according to the 1-5 chemical reactions.

Cathodic oxygen reduction:



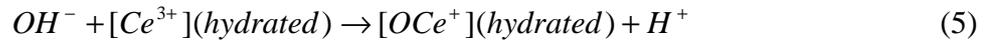
Film development reaction:



Oxidation of the cerium(III):



Reaction between the hydrated cerium(III) and the hydroxide ion of the zinc-hydroxide:



The reactions of the lanthanum-containing solution and the zinc surface follow the reactions above except for reaction (4).

2. I have proved by SEM and AFM studies, that on the galvanised surface with 0,8 μm average surface roughness and 0,18 % aluminium component produced by Sendzimir process developed a homogenous, compact and defect-free conversion layer [2,3,6].
3. I have assigned by pressing corrosion test in Na_2SO_4 electrolyte for 48 hours that in case of CeCl_3 and LaCl_3 treatment the best protective effect can be achieved by applying CeCl_3 on the Sendzimir process hot dip galvanised steel sheet. The prepared conversion layer can be characterised by a homogenous, micro cracks-free and uniform structure that explains both of mechanical and corrosion protective stability [1,5].
4. I have shown by protective coefficient calculated from the current densities (6) obtained by electrochemical polarisation measurements that in case of the continuously hot dip galvanised steel immersed into $\text{Ce}(\text{NO})_3$ solution, the increase of rate was 42%. After treatment by CeCl_3 this value achieved however 86%, because after immersion the plates for 20 min the thickness and homogeneity of the conversion layer gets into steady-state condition [1,2].

$$V (\%) = \frac{j_0 - j_k}{j_0} \cdot 100 (\%) \quad (6)$$

V(%): inhibition efficient

j_0 : current density for untreated galvanised steel sample (A/cm^2)

j_k : current density for treated galvanised steel sample (A/cm^2)

5. The effect of the LaCl_3 treatment on the continuously hot dip galvanised steel surface depends on the immersion time. Based on the polarisation measurements after 20 min operating develops a cathodic barrier on the surface, then in case of 40 min immersion increase both of cathodic and anodic corrosion rates, because the long immersion time results in micro cracks in the thicker layer. In this regions anodic zinc solution can be occurred [2,4].
6. The corrosion mechanism of the cerium-, lanthanum-containing conversion layers of the three types of galvanised steel plates can be described by a simplified equivalent circuit model consisting of two time constants (Fig 1). The first time constant the parallel connection of the elements R_p and $\text{CPE}_{\text{coating}}$ represents the resistance and capacitance of the conversion layer. The second time constant also parallel connection of the element $R_{\text{charge transfer}}-\text{CPE}_{\text{double layer}}$ characterises the electrochemical charge transfer reactions, occurred [1,2,3].

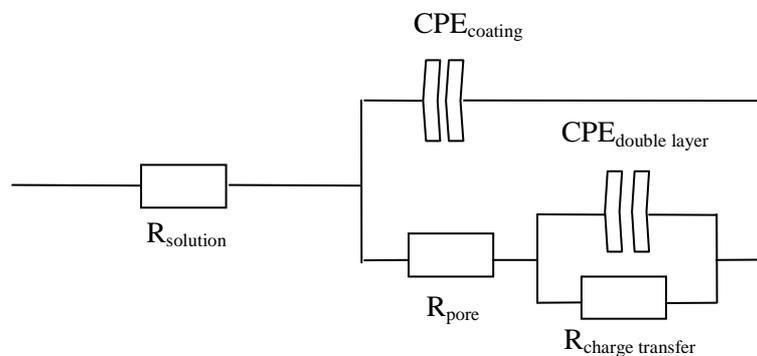


Fig 1

R_{solution} : resistance of the electrolyte; $\text{CPE}_{\text{coating}}$: frequency depending capacitance of the coating; R_{pore} : Resistance of the electrolyte in the pore of coating; $\text{CPE}_{\text{double layer}}$: frequency depending capacitance of the double layer; $R_{\text{charge transfer}}$: charge transfer resistance

The accuracy of the physical circuit model was proved; because the results of impedance measurements and the pressing corrosion test in Na_2SO_4 solution were

correspond. It means that the CeCl_3 treatment for 40 min of Sendzimir-process fabricated galvanised steel plates represent the best corrosion protection of galvanised coating [1].

Industrial adaptability

The experimental results indicate that the studied Cr(VI)-free, environmental friendly conversion layers on the galvanised surfaces produced by different methods prove promising procedures for the industry. Essentially the treatment by CeCl_3 represents in case of continuously hot dip galvanised steel the best temporary corrosion protection among the applied rare-earth solutions. The homogenous conversion coatings were developed on the surface by dipping procedure and the corrosion protection has remained for long time proved by electrochemical method, and modelled by corrosive medium and pressing applying corrosion tests. The experiments to be settled in the near future must optimise and approach the industrial producing parameters considering the immersion time. The needful requirements for the process optimisation are the systematic planning of experiments and applying the methodical of the corrosion- and morphological studies of this thesis.

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