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The influence of zinc surface pretreatment on the adhesion of epoxy coating electrodeposited on hot-dip galvanized steel

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Abstract

The adhesion and electrochemical properties of epoxy coatings electrodeposited on hot-dip galvanized steel with and without passive films were investigated during exposure to 3% NaCl. The passive films were formed in hot air, in boiling water and by chromating. Adhesion was measured both by a standardized pull-off method and by swelling in *N*-methyl pyrrolidone. Pretreatment of hot-dip galvanized steel with passive film formed in hot air increases both dry and wet adhesion strength of the epoxy coating compared to pretreatment with passive film formed in boiling water and chromate coating. The overall increase of wet adhesion for this sample was maintained throughout the whole investigated time period. It was shown that the change in adhesion of epoxy coating on a chromate coating is smallest of all investigated samples, although the initial value of adhesion on this surface had the lowest value. The corrosion stability of coated Zn samples pretreated by different methods, was investigated by electrochemical impedance spectroscopy and in the initial time of exposure to NaCl the highest values of pore resistance were also obtained for the epoxy coating on Zn pretreated in hot air, whereas the epoxy coating on a HDG steel with a chromate coating showed the smallest change in electrochemical properties (pore resistance, coating capacitance, charge-transfer resistance) during prolonged exposure time.

Keywords: Hot-dip galvanized steel; Passive films; Epoxy coatings; Adhesion; Corrosion; EIS

1. Introduction

Zinc coatings are widely used for sacrificial cathodic protection of steel parts. Galvanized steel sheets are usually protected from corrosive environments by conversion coatings (phosphate, chromate, etc.) and then top-coated with some organic coatings, particularly in outdoor applications [1–3]. The role of a conversion coating is providing more efficient corrosion protection, as well as increasing adhesion of organic coating.

One of the most important factors in corrosion prevention by protective coatings is the coating adhesion loss under environmental influence [4–7]. There are many factors influencing the adhesion of organic coatings and in this work an attempt was made to determine the influence of zinc surface pretreatments on the adhesion and corrosion stability of epoxy cataphoretic coating on hot-dip galvanized (HDG) steel. Two different thermal methods were tested in order to improve adhesion performance of an epoxy coating on HDG steel. The first method studied was by drying a substrate in a hot air at 200 °C, thus having predominately an oxide layer at the surface. The second method was by immersion of HDG steel in boiling water, so metal surface was hydrated and consisted mainly of hydroxides. Chromate conversion coatings are widely used in metal finishing industry because chromate films are known to supply a good corrosion resistance, improve the adhesion for paints and are easy to operate [8]. However, since hexavalent chromium involved in these treatments is known to be toxic this treatment will not be used in the coming years, and it is shown here just for comparison, because of its good corrosion properties and good adhesion. Thin, non-pigmented epoxy coatings (primers) were electrodeposited on pretreated hot-dip galvanized steel, as well as on bare HDG surface, as a reference.

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2. Experimental

2.1. Substrate pretreatment

The hot-dip galvanized steel panels (40 mm × 40 mm × 0.25 mm for adhesion pull-off measurements, 14 mm × 14 mm × 0.25 mm for NMP test and 20 mm × 20 mm × 0.25 mm for EIS measurements) were pretreated by degreasing in acetone and pickling in 3%H_2SO_4 solution for 30 s. Passive films were formed: in hot air at 200 °C during 60 min; in boiling water during 60 min and chromate coating was formed chemically by immersion in a solution containing 1.3 g dm^{-3} CrO_3 and 1.3 g dm^{-3} H_3PO_4 at 40 °C during 90 s (thickness of ∼1.5 μm).

2.2. Surface roughness

The surface roughness of bare HDG steel and HDG steel modified by passive films and chromate coating, as substrates for epoxy coating deposition, was determined by TR-200 HAND-HELD ROUGHNESS TESTER.

2.3. Surface morphology

The surface morphology of bare HDG steel and HDG steel modified by passive films and chromate coating was studied using scanning electron microscopy (SEM).

2.4. Electrodeposition of epoxy coatings

The epoxy coatings were electrodeposited from an epoxy resin emulsion modified by amine and isocyanate, on bare HDG steel and HDG steel with passive films and chromate coating, using a constant voltage method (CATOLAC emulsion 543.052, produced by PPG). The resin concentration in the electrodeposition bath was 10 wt.% solid dispersion in water at pH 5.7; the temperature was 26 °C and the applied voltage was 250 V [9]. After coating for 2 min, coatings were rinsed with distilled water and cured for 30 min and measured thickness was 17 ± 1 μm. This low thickness primer was chosen in order to be able to evaluate the influence of the metal pretreatment on the adhesion and corrosion stability of protective systems more accurately.

2.5. Adhesion measurements

The adhesion strength of epoxy coatings on different substrates was determined by two methods: by a direct pull-off standardized procedure and by determining the *N*-methyl pyrrolidone retention time (NMPRT).

2.5.1. Pull-off test

The adhesion strength of epoxy coatings on bare HDG steel and HDG steel modified by passive films and chromate coating was determined by Erichsen Adhesionmaster 513 MC/525 MC. The adhesion measurements were performed prior to exposure to 3% NaCl solution ("dry" adhesion), as well as in certain time intervals during exposure to 3% NaCl solution at room temperature, for the period of 14 days ("wet" adhesion).

According to ISO 4624, prior to bonding the dollies to epoxy primer the circular dollies (20 mm diameter) were degreased by acetone. After that, epoxy primer was firmly polished by fine emery paper (No. 1000) and also degreased by acetone. The cyanoacrylate adhesive, Loctite "Super bond" (Henkel) was used. After curing of the adhesive for 24 h the epoxy coating was cut around the dolly and the dolly was pulled-off vertically while measuring the necessary force *i.e*. adhesion strength.

The prepared panels were also immersed in 3% NaCl at room temperature for 14 days. In order to determine the influence of corrosive agent on the adhesion strength of different protective systems the samples were removed from the solution, rinsed with distilled water, and dried in air at room temperature for 1 h, and after that the dollies were adhered to the panels. The adhesion strengths of these samples were determined 24 h afterwards.

For each type of protective system five samples were tested and the average value of these measurements was taken. For all measuremets only the ones with adhesive failure were taken into account.

2.5.2. NMP test

The *N*-methyl pyrrolidone (NMP) used was a p.a. chemical. In the NMP delamination test [10] panels of 2 cm^2 area were immersed in NMP at 60 °C. The paint always delaminated from the edges inwards. The time when the paint had completely come off was recorded. The experiment was done five times per panel and the average value was calculated as the NMPRT (NMP retention time, or the time for the paint film to delaminate completely from the substrate) for a particular protective system. Each panel was always treated in a fresh solvent.

2.6. Electrochemical impedance spectroscopy (EIS)

For ac impedance measurements the epoxy-coated samples were exposed to 3% NaCl in distilled water for 14 days. A three-electrode cell arrangement was used in the experiments. The working electrode was a coated sample situated in a special Teflon holder. The counter electrode was a platinum mesh with a surface area considerably greater than that of the working electrode. The reference electrode was a saturated calomel electrode (SCE). The ac impedance data were obtained at the open-circuit potential using a PAR 273 potentiostat and PAR 5301 lock-in amplifier. The impedance measurements were carried out over a frequency range of 100 kHz to 10 mHz using a 5 mV amplitude of sinusoidal voltage.

2.7. Gravimetric liquid sorption measurements

Gravimetric liquid sorption measurements were performed by weighing samples on an analytic balance following immersion in 3% NaCl at 25 °C. The samples were periodically removed from electrolyte and weighed. Sorption curves were used to evaluate the diffusion coefficient of water across an epoxy coatings electrodeposited on bare HDG steel and HDG steel modified by passive films and chromate coating.