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Corrosion of painted galvanneal steel

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Abstract

The annealing galvanized steel (Galvanneal) is produced from hot-dip galvanized steel thermally treated. The result is a coating formed by Fe-Zn phases. Its main advantage over the conventional galvanized steel is the absence of the characteristic spangles affecting these coatings and the presence of iron providing better weldability than the pure zinc coating. In this work, the corrosion behavior of pre-treated and painted with environmentally friendly schemes, conventionally hot-dip galvanized, and annealing galvanized (Galvanneal) steel were studied. A γ-mercaptopropyltrimethoxysilane (MTMO) pre-treatment was applied. A waterborne polyurethane paint developed at CIDEPINT was used. Assays were performed in the salt spray and controlled humidity chambers. The metal-paint adhesion was determined by Tape Test. The systems deterioration was evaluated by means of periodical visual inspections, optic and electron microscopes, EDXS, and electrochemical impedance measurements. The MTMO showed to be a good adhesion promoter for the systems exposed to the present testing conditions.

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1. Introduction

In the automotive industry, the increasingly demanding market requirements have made in recent years significantly increase the percentage of coated steel sheet use for manufacturing both bodywork and structural parts of automobiles. In this sense, the electro-galvanized and Galvanneal are the two most commonly used materials [Goodwin et al. (2011), Suzuki (2011)]. The latter is gaining more and more markets due to its low cost and

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excellent weldability conditions. The Galvanneal process involves applying a heat treatment after hot-dip galvanizing in order to eliminate the typical spangles of these coatings, increase the roughness to improve paint adhesion and improve the weldability. During this annealing are formed by diffusion different phases of Fe-Zn, resulting in a coating consisting of inter-metallic layers with decreasing Fe content from the interface coating/substrate to the surface, reaching here values between 9 and 12%.

When galvanized steel is painted, either for being exposed to a very aggressive medium or for aesthetic reasons, is built up the so-called duplex system, which acts synergistically, since the protection provided by the paint plus the zinc coating is greater than the sum of both separate effects. [van Eijnsbergen (1994), Cabanelas et al. (2007), Pérez et al. (2002), del Amo et al. (2004)]. Among the failures that significantly affect the service life of these systems, the most important are related to adhesion problems at the organic coating-zinc interface. In this sense, the surface pre-treatments have been a crucial step to mitigate this type of failure. Nowadays, in Argentina most pre-treatments are based on Cr(VI), however, since these products are harmful to the environment and health, in recent years several studies are being made for it replacement and, in this sense, silane pre-treatments have proven to be one of the most interesting alternatives [van Ooij et al. (2005), Gang et al. (2009), Gang et al. (2010)]. Silanes form a protective film on the zinc substrate by adhering to it by covalent bondings of the type Si-O-Metal formed by the hydrolysis products of R'O groups and the film of oxy-hydroxides present on the metal, greatly improving the paint-substrate adhesion [Chico et al. (2012)].

On the other hand, solvent-based polyurethane paints have excellent weather resistance under various atmospheric conditions like marine environments with high humidity and solar radiation, without damaging its gloss and color [Elsner et al. (2012)]. Nevertheless, volatile organic solvents are polluting and this has led to study alternatives to diminish their concentration or replace them by changing painting formulations, being one alternative the use of water as solvent. Compared with solvent-based paints, the waterborne ones have less resistance to weathering but in recent years were reached formulations whose performance is highly satisfactory.

In this paper, the corrosion behavior of conventional hot-dip galvanized steel and annealing galvanized steel (Galvanneal), both pre-treated and painted with environmentally friendly schemes was studied. γ-mercaptopropyltrimethoxysilane (MTMO) was used as adhesion promoter and a water-based polyurethane paint developed at the CIDEPINT as organic coating. To evaluate the corrosion behavior, samples were exposed in salt spray chamber (SSC) or humidity chamber (HC). Dry and wet paint adhesion were evaluated by the tape and impact tests while the systems degradation was quantified by visual inspection, optical and electron microscopes, EDXS and electrochemical impedance spectroscopy (EIS).

2. Experimental procedure / methodology

Samples (15 x 7.5 x 0.70 cm) of galvanized steel (ZN) and Galvanneal (GAL) were built up from continuous hot-dip galvanized sheets of commercial origin. All the samples were subjected to an electrochemical cleaning by dipping for 20 s in a 10% w/v NaOH solution and applying a current of 9 A. The substrates roughness was measured with a Hommel Tester T1000 profilometer and the results are shown in Table 1, where Ra is the average roughness and Rt the full or maximum roughness. To evaluate the effect of MTMO as adhesion promoter, some samples were pre-treated with silane in the conditions listed in Table 2. With this aim, 3.6 mL of MTMO were mixed with 5.4 mL of a solution 60% v/v methanol and 40% v/v distilled water. The pH of this last solution was adjusted to 4.0 with acetic acid before adding the silane. After 1 h hydrolysis with constant stirring, the obtained solution was diluted with 81.3 mL of the same methanol-distilled water solution. MTMO final concentration was 4% v/v. The samples were immersed in the hydrolyzed MTMO solution for 1 min and vertically cured in an oven at 80 ± 1 ºC for 10 min [Bexell et al. (2007)]. Samples were kept in desiccators until being painted. All the samples were coated with a three-component water-based polyurethane paint developed at the CIDEPINT (Table 3). The thickness of the metal coating was calculated by gravimetry, and the corresponding to the on organic coatings by a magnetic probe, according to ASTM B 499 standard; their values are reported in Table 4. The silane film thickness was measured by SEM.

For a proper paint curing the painted samples were kept in desiccators at 25 °C for 72 h.

After the paint film curing, its adhesion to the substrate before and after accelerated tests was assessed using the Tape Test, ASTM D-3359 standard. Impact tests were performed too, taking the ASTM D2794 standard as reference. To simulate a failure in service, the organic coating of both types of samples were cut up to the substrate and then, by triplicate, exposed the humidity chamber (HC) (ASTM D-2247 standard) and salt spray chamber (SSC)