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Behavior of two eco-compatible duplex systems used in the construction industry against corrosion

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ABSTRACT

Two types of coated steels are currently competing in the construction industry: the hot-dip galvanized steel (HDGS) and the 55%Al–Zn alloy coated steel (HDZAS). Both systems are typically coated by a chromate-based conversion film, which is dangerous for human health and environment. Furthermore, for aesthetics purposes and/or to prolong their expected or planned service life, they are painted designing each paint system as a function of the service conditions to which they will be subject to. The present work reports on a comparative study of two duplex systems: steel/metal coating/organic coating. In both cases, the chromate-based pretreatment was replaced by another one that features γ-mercaptopropyltrimethoxysilane (MTMO) as an active element. The organic coating used was a water-based polyurethane. Behavior of this paint against corrosion was assessed by exposing the samples in salt spray or humidity chambers, and monitoring its evolution by electrochemical impedance spectroscopy, visual observation, scanning electron microscopy and energy dispersive X-ray analysis. The results revealed that: MTMO was suitable for promoting adhesion both in HDGS and HDZAS; in humidity chamber, both duplex systems provided good protection; the presence of corrosion products of the base steel and paint blistering was detected in the HDGS/paint system seventy-two days after exposure; however, 150 days after that, none of these effects were observed in the HDZAS/paint system; differences in behavior were significant in Salt spray chamber: speed of paint delamination from the mark done and the bulk of corrosion products generated was much higher in HDGS/paint system than in HDZAS/paint.

1. Introduction

Corrosion is a major problem since it not only reduces the resistance of the structural materials and directly leads to potential harm to humans but also indirectly affects conservation of natural resources. In metals, corrosion depends on several factors including properties of the surface metal, the metal/protection film interface, physical, chemical and electrochemical properties of the protection film and the environmental conditions under which the system is exposed. To delay and/or reduce this natural thermodynamic metal tendency, metal and organic coatings, which form a protective layer onto metal surfaces, have been developed. Among the metal coatings used to prevent steel corrosion, those based on zinc or its alloys have become the most used due to their low cost and mainly to the fact that zinc is electrochemically more active than steel and therefore it protects steel cathodically. Also, corrosion products formed under certain exposure conditions can protect the surface providing a barrier effect [1–3]. Zinc alloys composed of 55% of Al, 1.6% of Si and Zn are among the alloys that provide excellent galvanic protection.

When a higher degree of protection is required, properly selected paint systems can be added to the metal protection. The combination of both protection systems (metal + organic coating), known as “duplex”, has shown to provide a synergistic effect when compared with individual coatings. This higher protection against corrosion is attributed, on the one hand, to the galvanic coating layer (cathodic protection + blocking of its defects by the corrosion products) and on the other hand, to the barrier effect provided by the paint system [4–6].

It should be noted that in spite of the formation of the barrier, at least to some extent, water and oxygen can penetrate the film, even in the absence of structural defects. Therefore, adhesion between paint and metal surface also plays a major role in the system protection; the type of bond in the substrate/paint interface depends both on the chemical nature and the degree of the crosslinking of the polymer and on the type of metal substrate and its surface treatment. Basically, paint adhesion may be improved

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by applying a pretreatment to the substrate. The most widely used, to improve paint adhesion onto zinc or its alloys, are those based on chromate and phosphate. These pretreatments have long been used and are highly effective and easy to apply, however they are harmful for human health and the environment [7]. For this reason, environmentally friendly pretreatments have been lately developed, and among them, silanes are one of the most investigated [8,9]. The general formula of these compounds is R-Si-$(R'O)_3$, where R is a carbon chain, functionalized or not and R′O is a ethoxy o methoxy group, which is easily hydrolysable. γ-aminopropyltrimethoxysilane ($NH_2(CH_2)_3Si(OCH_3)_3$), glycidoxypropyltrimethoxysilane ($CH_2OCH(CH_2)_3Si(OCH_3)_3$) and mercaptopropyltrimethoxysilane ($HS(CH_2)_3Si(OCH_3)_3$) are among the most studied silanes. They form a protective film onto the substrate, which adheres to the substrate by covalent bonds of the Si–O–Metal type formed by the products of hydrolysis of the R′O-groups and the oxi-hydroxides film present on the metal [10,11], Fig. 1.

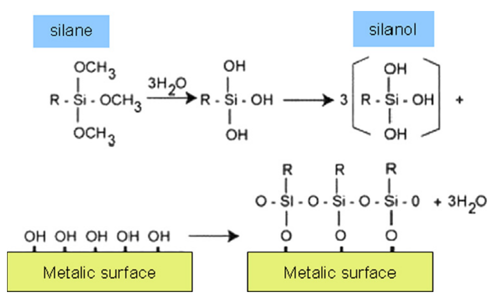

Fig. 1. Scheme of the silanes reaction.

Table 1
Coatings thickness.

Sample	Galvanic layer thickness (μm)	Paint film thickness (μm)
HDGS	26	115
HDZAS	35	120

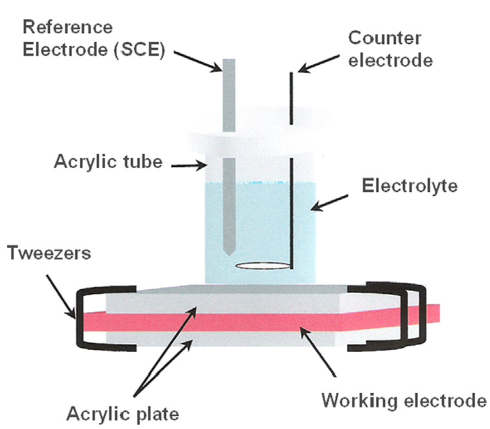

Fig. 2. Scheme of the electrochemical cell.

Strictness of the environmental regulations designed to protect the public health and the environment needs systems which are developed on the base of cleaner technologies both regarding the pretreatment and the paint. Therefore, replacement of organic solvents used in paints and pretreatments is a major requirement.

The present work reports on the behavior of two "duplex" systems against corrosion: steel galvanized by hot immersion/paint and steel coated with 55%Al–Zn alloy/paint. γ-mercaptopropyltrimethoxysilane (MTMO) was used as a pretreatment since, although it is used as a steel pretreatment, few works are available on its use on zinc as adhesion promoter. The protective ability of the systems was evaluated by two standardized accelerated assays, salt spray (SSC) or humidity and temperature controlled (HC) chambers. The deterioration level was assessed by visual observation, scanning electron microscopy (SEM), optic microscopy and electrochemical impedance spectroscopy (EIS).

2. Materials and methods

Samples of carbon steel SAE 1010 of commercial origin coated with zinc or 55%Al–Zn alloy by continuous hot-dip process were used as substrates. All the samples ($15 \times 7.5 \times 0.70$ cm) were subjected to electrochemical cleaning by immersion in a 10% p/v NaOH solution for 20 s and application of a 9 A current. To assess the effect of γ-mercaptopropyltrimethoxysilane (MTMO) as an adhesion promoter, some samples were pretreated with silane.

The pretreatment solution was prepared as follows: 3.6 mL of MTMO were mixed with 5.4 mL of a 60% (v/v) methanol solution and 40% v/v of distilled water. The pH of this solution was adjusted to 4.0 with acetic acid prior to addition of silane [12]. After 1 h of hydrolysis with constant agitation, the solution obtained was diluted with 81.3 mL of the methanol-distilled water solution. The final concentration of MTMO was 4% v/v. The samples were immersed in a solution of hydrolyzed MTMO for 1 min, cured in vertical position in a furnace at 80 ± 1 °C for 10 min [12], and kept at room temperature until painted. The untreated samples (without

Table 2
Adhesion test results.

Sample	Classification (ASTM D-3359)	Percentage of delaminated area
HDGS	1B	64
HDGS+MTMO	4B	4
HDZAS	3B	12
HDZAS+MTMO	5B	0

Classification of the adhesion degree according to the delaminated area.