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A silane pre-treatment for improving corrosion resistance performances of emeraldine base-coated aluminium samples in neutral environment

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Abstract

An aluminium–magnesium alloy AA5182 substrate pre-treated with a 3-aminopropyl-triethoxysilane (APS)-based solution and coated with emeraldine base (EB) showed improved corrosion resistance to neutral salt spray test, compared to samples pre-treated with phosphoric acid-based solutions prior to the EB coating. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) characterisations of samples pre-treated with APS showed the presence of an uneven silane coating on the aluminium surface according to the surface microstructure. The potentiodynamic study performed on the EB-coated samples showed a noticeable reduction of corrosion current of coupons pre-treated with APS, while no relevant difference in corrosion behaviour was observed between APS and phosphoric acid pre-treated samples prior to the EB coating. The coupling activity of APS between the AA5182 surface and EB coating at the most sensitive corrosion sites could be responsible of an improved adhesion of the EB coating at these points and could explain the observed improved corrosion resistance.

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Keywords: Corrosion protection; Aluminium; Polyaniline; Silane; Adhesion

1. Introduction

Polyaniline may exist in different oxidation states. The emeraldine base form (EB) corresponds to the most stable state of polyaniline in atmosphere conditions and in neutral environment (Fig. 1) [1,2]. It has been demonstrated that, in neutral environment, emeraldine base (EB) provides good corrosion protection on aluminium, iron and cold rolled steel [3–14]. This was partly attributed to its intrinsic barrier properties that make it a good inhibitor towards oxidative reactions [3–5]. However, recent studies have highlighted the capability of EB to positively polarise different metal substrates [9–14]. This ennobling effect combined with its low ion permeability and its low electronic conductivity has been evoked to explain its high corrosion protection properties on aluminium in neutral environment [13,14]. It is well known that in order to improve the corrosion protection performances of a coating, adhesion is an essential requirement and this notably depends on the affinity between the coating and the substrate as well as the surface pre-treatment. Several studies have shown how some silane compounds can be used as adhesion promoters between an organic coating and a metallic substrate [15–19]. These silane-based compounds used as primers of adhesion are organo-functional silanes, of general formula: $(R_1O)_3$–Si–$(CH_2)_n$–R_2. The principle of the adhesion of organo-silane on mineral substrates is based on the reactivity of the siloxane function (Si–OR_1) [15]. This group is hydrolysed to silanol and reacts with the metal hydroxide groups on the surface. The latter reaction is currently called ''silanization'' and it occurs in competition with the silanol/silanol condensation reaction. When the rate of hydrolysis is sufficiently high compared to the

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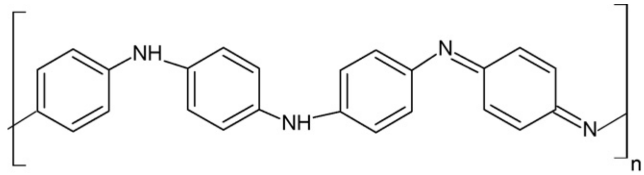

Fig. 1. Chemical structure of emeraldine base (EB).

silanol/silanol condensation, many Si–O–M bonds can be formed between small-sized silanols and the metal. In the opposite case, few Si–O–M bonds are formed between large-sized hindered silanols and the substrate. The first condition corresponds to a more adherent silane coating and this is preferred in order to obtain the best silane coupling activity [20]. The R_2 group is an organo-functional group (vinyl, amine, epoxy, mercapto, etc.) whose role is to establish a chemical bond with the organic coating.

The aim of the present work is to study the performances of an amino-silane compound, 3-aminopropyl-triethoxysilane (APS), as a primer of adhesion between an aluminium substrate and an emeraldine base (EB) coating in order to improve the corrosion protection properties of the EB coatings on aluminium. Due to its double affinity to the hydrated metal surface and to the EB film, APS could act as a coupling agent across this organic–inorganic interface. On one hand the silanol group is able to ensure the adhesion to the metallic substrate through Me–O–Si bonds. On the other hand, the amino group of the APS is expected to establish a chemical interaction with the imine and amine sites of the emeraldine base, according to the mechanism suggested in Fig. 2.

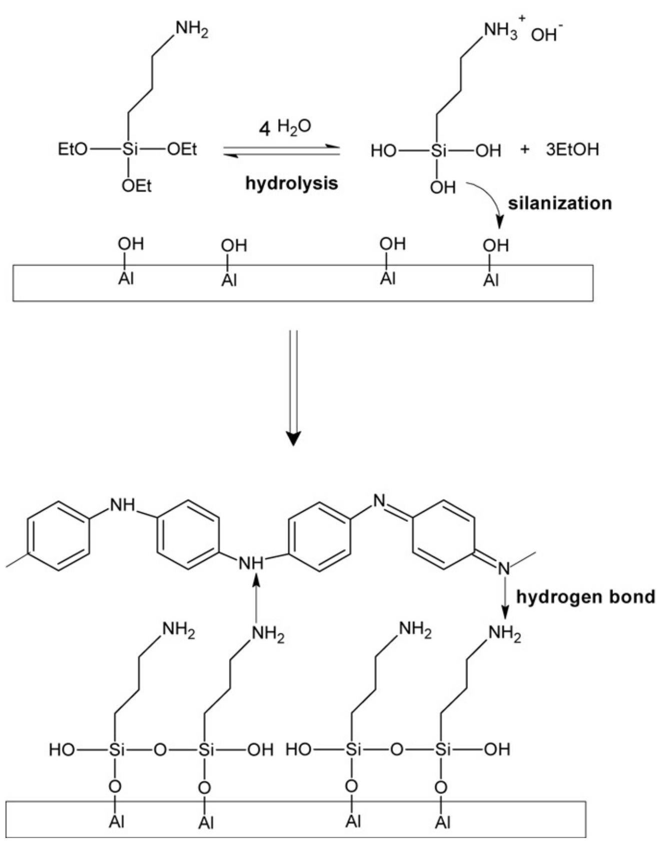

Fig. 2. Schematic mechanism proposed to describe the APS coupling action between an aluminium surface and an EB coating.

2. Experimental section

2.1. Substrate

ALCAN (France) supplied the AA5182 aluminium substrate. This was an aluminium–magnesium alloy of intermediate magnesium content (4–5%). Its chemical bulk composition is reported in Table 1. The samples were cut from 0.224 mm thick bands after industrial cold rolling. Prior to the coating the substrate material was chemically treated either with a phosphoric acid-based solution or with a silane solution, in order to clean the surface and improve adhesion of the polymer to the surface. It is in fact well known that proper and thorough cleaning of the aluminium surface is one of the most important steps in the finishing processes in the aluminium industry. Both alkaline and acid-based cleaners are used, however, the phosphoric acid degreasing is preferred when preparing surfaces for organic finishing because it makes it possible to achieve better adhesion [21]. This is the reason why we decided to study the adhesion promoter effect of the APS treatment towards the organic emeraldine base coating, compared to the conventional phosphoric acid treatment.

The phosphoric acid treatment consisted in dipping the material in a 100 g/l phosphoric acid solution at 70 °C for 10 s. For the silane-based treatments, different parameters must be controlled in order to obtain reproducible results. It has been shown that improving the quality of the silane/substrate interface requires an optimisation of the silanization process by enhancing the hydrolysis step and minimising the silanol/silanol condensation reactions [20]. This depends on different parameters varying according to the nature of the substrate and of the silane solution. Normally weakly concentrated solutions of APS are preferred (0.1–2 vol.% solutions) for the silanization of aluminium [20,22]. The ageing of the APS solution before metal treatment, as well as the dipping time of the substrate into the mixture, must be controlled in order to avoid the formation of hindered and less-strongly bound structures which would be eliminated when washing the substrate after silanization. Various conditions for silanization of aluminium with APS can be found in the literature [20,22,23]. For the present study, we decided to test the efficiency of an APS (3-aminopropyl-triethoxysilane by FLUKA) 1 vol.% solution in water as promoter agent. The choice of using an aqueous solution, instead of mixture of alcohol and water, was mainly motivated by the fact that, if its efficiency was proved, this could avoid using solutions containing volatile organic

Table 1
Typical bulk composition of the AA5182 aluminium alloy

AA5182	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
Addition elements (wt.%)	0.2	0.35	0.15	0.2–0.5	4–5	0.1	0.25	0.1