INVESTIGATING THE ANTICORROSIVE PERFORMANCE OF WELDABLE PRIMERS BY EIS

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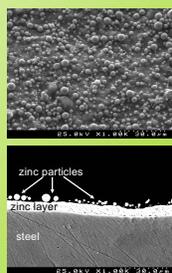
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Introduction

Weldable primers (WPs) were introduced in Europe, in 1995, by the automotive industry, as a means to improve the corrosion resistance of regions in the car body that cannot be reached by pretreatments or cathodic electro-paints after joining processes. WPs consist of an epoxy paint containing zinc powder applied to electrogalvanised steel. The function of the zinc powder is to make the primer weldable by providing electrical contact between the welding electrode and the metal substrate. Anticorrosive protection is achieved mainly via the barrier effect provided by the primer and can be further enhanced through the addition of anticorrosive pigments. This poster presents an EIS investigation on the anticorrosive performance and degradation of WPs when immersed in NaCl aqueous solutions.

Weldable primer.

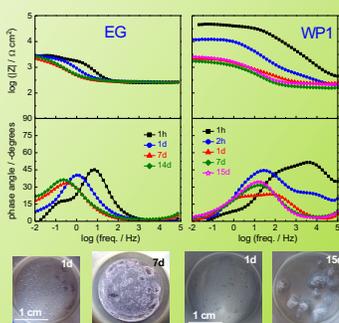Flanges and car body with hollow inaccessible parts.

Experimental

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY: The electrochemical cells were prepared by gluing PMMA tubes to the surface of the samples with epoxy glue. The tubes delimited an area of 3.46 cm^2 and were filled with the testing solution, 0.05M NaCl. A three-electrode arrangement was used with a saturated calomel electrode as reference, a platinum counter electrode and the exposed sample area as working electrode. The cell was connected to an Autolab PGstat 302N (Eco Chemie, The Netherlands) and all measurements were performed at room temperature with the cells inside a Faraday cage and the solution quiescent and exposed to air. Impedance measurements were done in the 100 kHz to 10 mHz frequency range with 7 points per decade distributed logarithmically; the sinusoidal perturbation was 10 mV rms at open circuit potential.

SEM: A Hitachi S-4100 Scanning Electron Microscope was used to study the surface morphology.

SVET: Measurements were performed with Applicable Electronics Inc. (USA) equipment. The samples were insulated with a mixture of beeswax + colophony except for a window of a few squared millimeters that was exposed to the testing solution. The vibrating microelectrode had a 10 μm spherical platinum black tip and vibrated with amplitude of 10 μm at an average distance of 200 μm from the surface of the sample. Each scan comprised 50 x 50 points.

SAMPLE	TYPE	DESCRIPTION
EG	Metal substrate	Low carbon DC06 steel sheet, 0.8 mm thick, with electroplated zinc layer of 7 μm (nominal thickness).
WP1	Weldable primer	Chromate-free pretreatment + epoxy paint with 73 wt% zinc powder in the dry film and nominal thickness of 3.5 μm.
WP2	Weldable primer	Same as WP1 but zinc powder replaced by powder of 55AlZn alloy.
WP3	Weldable primer	Same as WP2 but thickness of 6.5 μm.

Results and Discussion

1 The impedance of EG is around 1 kΩ cm^2 with two time constants (τ). The one at higher frequencies is ascribed to the corrosion process (C_{dl} and R_{ct}) and changes placement, from 10 Hz at 1 hour to 0.5 Hz after 7 days of immersion. The other, at low frequencies, is attributed to a mass transfer process. The impedance of WP1 has a fast drop, from ~$10^{4.5}$ Ω cm^2 at 1 hour of immersion to values close to the bare substrate after a few hours. Three τ are detected after just 1 hour of immersion: in addition to the two τ observed in EG, another appears at high frequencies (~10^3-10^5 Hz) due to the paint response. It rapidly vanishes and is replaced by another τ at medium frequencies (10-10^3 Hz). After a few days only one τ (C_{dl}, R_{ct}) dominates the spectrum. Visual inspection shows that corrosion occurs in a localized manner, with pits down to the steel in EG and the formation of blisters in WP1.
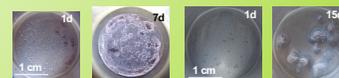
2 SEM micrographs of WP1 after 15 days of immersion in 0.05M NaCl. **a)** In the less corroded area of the sample, corrosion appears mainly on the zinc particles. There is no continuous film of corrosion products and the image suggests that most particles corrode isolated from the others. The inset shows the corrosion products covering the top of the particles, which is the area most accessible to solution. **b)** A thick layer of corrosion products appears on the top of the paint film close to the blisters. Cross section inspection indicates that blisters come associated with the undermining of the zinc layer that dissolves completely exposing the steel base underneath and extends about 100 μm away from the blister limit.
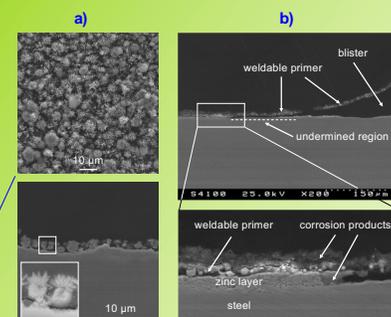
3 After 1 hour of immersion, SVET detects intense corrosion activity on the bare substrate and it is already possible to detect activity in WP1. Local anodes (in red, positive currents) are surrounded by larger cathodic areas with smaller current density (in blue, negative currents). After 1 day, the SVET map of EG shows anodic activity, coincident with round shaped pits observed on the zinc coating. The remaining area is cathodic. Corrosion spots (blisters) are observed in WP1, most of them coincident with the anodic spots measured by SVET at 1 hour. After 7 days, EG presents severe attack with nearly half of the area without zinc layer. The SVET map shows small currents on the exposed steel, strong anodic currents in the zinc close to the exposed steel and strong cathodic currents in the remaining zinc layer. WP1 has strong attack in both pictures and maps. The signals measured by SVET come from the corrosion of the metal substrate and not from the zinc particles, which are too small (~11 μm) to generate currents strong enough to be detected 200 μm above in the solution.
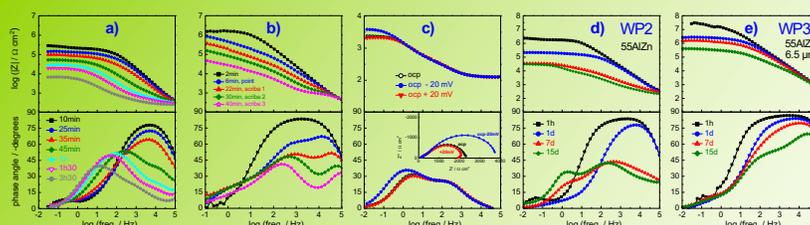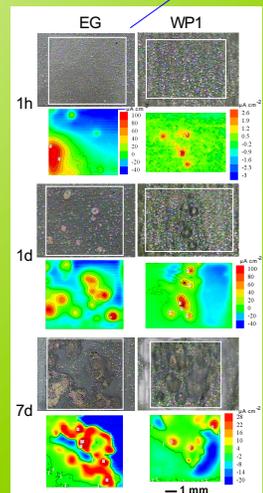
4 **a)** A single time constant response turns into a two time constant response in less than 1 hour of immersion. This is interpreted as a result of rapid water absorption and, due to the small film thickness, film saturation and water accumulation at the metal-paint interface. **b)** Small defects were produced in the paint film down to the substrate. This induced a rapid separation of the responses from the paint film and from the processes occurring at the metal surface. **c)** Response of WP1 after 1 day of immersion when subjected to small polarization tests in order to correlate the two time constants with the active and passive circuit elements in the corroding system. The time constant at high frequencies remains unchanged. It is not the response of the paint film, as concluded from a) and b). Its nature is not clear but it may be related with the accumulation of corrosion products on the top of the active metal areas (inside the blisters?), introducing an extra impedance to the flow of signal during the EIS measurement. **d)** WP2 is similar to WP1 except for the particles used (it has the same film thickness), but the corrosion rate is noticeably slower. **e)** Doubling the thickness of WP2 increases the impedance more than one order of magnitude.

The results suggest that the zinc particles-binder interaction in WP1 is weak and the particles' surfaces rapidly become wetted and oxidized. It seems that water reaches the metal substrate and ionic pathways are created through the entire surface mainly across the particles-matrix interface. This explains the rapid water uptake, low barrier properties and fast corrosion of the systems with zinc powder. Replacement of zinc powder by 55AlZn particles leads to good corrosion resistance. The 55AlZn alloy is known to have better anticorrosive performance compared to pure zinc due to the presence of aluminium that renders passive the metallic surface. The reduced corrosion of the 55AlZn particles preserves the integrity of the particles-matrix interface, thus retarding the ingress of water and aggressive species and ultimately leading to a slower degradation process. The mechanism, however, is the same as found for primers incorporating zinc particles.

Conclusions

- The corrosion of WPs follows the same pattern as the bare substrate (EG) but at a lower rate.
- The metallic particles incorporated on the paint seem to play a critical role.
- The low corrosion resistance of WPs is related mainly with the high corrosivity of zinc powder.
- Replacing Zn powder by 55AlZn powder provides superior corrosion resistance (but poorer weldability).
- Thicker films provide better protection (but weldability still requires thin films).

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