# LEIS to study corrosion protection of AA 2024 by smart coatings containing encapsulated inhibitors

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# Introduction

The organic coatings currently used in aerospace industry present very high corrosion protection. However, since the beginning of the 1990s, the high toxicity associated with Cr(VI) has imposed restrictions on their use in industrial applications and particularly in surface treatments (chromic acid anodizing or conversion coatings) and in organic coatings. In a previous work [1-3], a chromated water-borne primer (epoxy-amine) was tested by comparison to a traditional organic solvent-based coating. It was observed that the high protection provided by chromates is not only due to their healing effect but also to their ability to increase the barrier properties of the coating [2]. In addition, painting aircraft requires a surface treatment to improve the adherence of the coating. Recently, it was shown that aluminium alloy 2024 anodised in dilute sulphuric acid containing tartaric acid presented interesting corrosion protection performance [4]. Today, the replacement of chromates in coatings remains an important challenge and, during the last decades, numerous studies were devoted to the incorporation of corrosion inhibitors to provide an active corrosion protection [5-7]. The inhibitive compounds can be incorporated directly in the coatings or by using different kinds of reservoirs. With direct incorporation, corrosion inhibitors are released rapidly whereas the entrapped inhibitors can diffuse more slowly from the host material. The major purpose of the present work is to contribute to a better understanding of the self-

healing properties of encapsulated inhibitors (Inhibispheres<sup>TM</sup>) by using local electrochemical impedance spectroscopy (LEIS). An epoxy-amine water-borne paint containing Inhibispheres<sup>TM</sup> was deposited on a 2024 aluminium alloy (unclad), previously anodised in a tartaric-sulphuric acid bath.

# Experimental

Aluminium 2024 T3 alloy plates (125 x 100 x 1 mm) were used as substrate. The samples were treated in alkaline and acid baths followed by a tartaric-sulphuric acid anodizing treatment before the application of the coating. The encapsulated inhibitors (Inhibispheres<sup>TM</sup>) were incorporated in the water-borne paint. The liquid paints were applied by air spraying and cured at 60 °C for 3h. All samples were prepared at the same temperature and humidity conditions. Table 1 reports the two studied paint systems. For confidentiality reasons, details relative to the nature of the inhibitors can not be disclosed.

**Table 1:** Composition of the paint systems

Paint systems	Composition
P0	Waterborne primer without Inhibispheres <sup>™</sup>
P1	Waterborne primer with Inhibispheres <sup>™</sup>

All experiments were performed using analytical grade chemicals as received. The corrosive medium was a 0.1 mol/L NaCl solution. Local electrochemical impedance spectroscopy (LEIS) was carried out with a Solartron 1275 localized electrochemical impedance system, a Solartron 1287 electrochemical interface and a Solartron 1250 frequency response analyzer in a five-electrode configuration controlled by the software LEIS 270 (UNISCAN). A dual element probe (or bi-electrode) was placed in the solution. A saturated calomel reference electrode and a graphite counter electrode were also used.

An artificial defect was created in the work electrode to expose the substrate (200  $\mu$ m in length across the sample) (Fig. 1) using a cutting knife. The defect had a V-shaped profile. For local electrochemical impedance mapping (LEIM) the probe was stepped across an area of 1 cm x 1 cm (Fig. 1a). The step size was 300  $\mu$ m in the *X* and *Y* directions. The excitation frequency chosen was 1 kHz. For clarity, admittance was plotted rather than impedance. The LEIMs were obtained at 24 h and 168 h of immersion.



**Fig. 1.** Schematic representation of sample preparation (a) and optical micrograph of the defect in one of the samples (b).

## **Results and Discussion**

Figs. 2a and 2b present local impedance maps obtained for P0 after 24 h and 168 h of immersion in NaCl solution. The defect is clearly visible at the beginning of immersion, represented by the higher admittance values (smaller resistance values). After 168 h of immersion, the admittance values slightly increased (resistance values decreased). Corrosion products are visible in the scratch.

Figs. 2c and 2d present local impedance maps obtained for P1 after immersion in the NaCl solution. After 24 h of immersion, the defect is hardly seen. There is almost no difference between the defect and the coating. After 168 h of immersion, the admittance values have slightly increased (resistance values decreased). However, these values were much smaller than the values observed for P0. Visually, no corrosion products were observed in the scratch for this immersion time. These LEIM results indicate that the encapsulated inhibitors present in the P1 system are gradually released into the scratch to limit the corrosion process. Further work is in progress to investigate in more detail the release process.



**Fig. 2.** LEIM plotted at 1 kHz for P0 (a and b) and P1 (c and d) after 24 h and 168 h of immersion in 0.1 mol/L NaCl solution.

## Conclusions

Local electrochemical measurements performed on scratched paint samples confirmed the release of inhibitors from the Inhibispheres<sup>TM</sup> and corresponding limitation of the corrosion process. Understanding of fundamental protection mechanisms remains to be elucidated and is necessary for optimisation to meet end-user specifications.

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