

## **Assessment of the susceptibility of lacquered tinplate cans to corrosion in different solutions using electrochemical methods**

## **Evaluación de la susceptibilidad a la corrosión de recipientes de hojalata en diferentes soluciones usando técnicas electroquímicas**

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### **Abstract**

Corrosion of lacquered tinplate cans in different solutions was assessed using electrochemical methods. Samples with and without lacquer coating were exposed to different solutions and their susceptibility to corrosion was evaluated using cyclic voltammetry, Tafel curves and electrochemical impedance spectroscopy. The possible formation of a passive layer on the container surface was evaluated according to the kind of hysteresis presented in the first cycle of voltammeter measurements. Tafel plots showed how the behaviour of the tin layer can change from anodic to cathodic depending on the nature of the solution in contact with it, revealing the risk of localized corrosion. The effect of one additive in the solutions on the electrochemical performance containers was evaluated by electrochemical impedance. The impedance showed a deleterious effect of the additive, and corrosion processes appeared more quickly in containers packed with solutions modified with additive.

----- *Key words:* Tinplate, electrochemical techniques, corrosion in containers.

### **Resumen**

La corrosión de recipientes fabricados en hojalata expuestos a diferentes soluciones fue evaluada usando técnicas eletroquímicas. Los recipientes con y sin la aplicación de

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barniz fueron expuestos a diferentes soluciones. La susceptibilidad a sufrir corrosión se evaluó utilizando voltametría cíclica, curvas de polarización y espectroscopía de impedancia electroquímica. La posibilidad de formación de películas pasivas en la superficie de los recipientes se evaluó según la histéresis presente en el primer ciclo de las medidas de voltametría. Las curvas de polarización revelaron que el comportamiento del recubrimiento de estaño puede cambiar de anódico a catódico según la naturaleza de la solución en contacto con el recipiente, alertando sobre el riesgo de corrosión localizada. Mediante impedancia electroquímica se evaluó el efecto del uso de un aditivo en las soluciones o productos empacados en dos recipientes. Las medidas de impedancia mostraron un efecto perjudicial del aditivo utilizado y una rápida aparición de procesos corrosivos cuando se usó la solución modificada con el aditivo.

----- *Palabras clave:* hojalata, técnicas electroquímicas, corrosión en contenedores.

## Introduction

Tinplate is widely used by the packaging industry. Frequently, this material is employed to make cans for packing food, beverages and aerosol products. The tinplate cans are fabricated from low carbon mild steel sheet with a thin coat of electrodeposited tin. The surface of the tinplate is normally coated with a lacquer to improve the corrosion resistance of the container.

The anti-corrosion performance of lacquered tinplate cans depends on the barrier properties of the lacquer and on the nature of the canned products [1, 2]. When the lacquer used does not produce an effective barrier action, the corrosion of tinplate depends on the electrochemical interaction between tin and canned products. According to potential-pH diagrams [3], tin can form very stable oxides and hydroxides in natural environments which can protect the metal from further corrosion. Additionally, the high hydrogen over-voltage of tin leads to very low corrosion rates of the metal when exposed to a reasonable pH range [4]. However, tin has the ability to form soluble complexes with certain anions [5]. When this occurs the corrosion of tin is accelerated.

The performance of lacquered tinplate containers is commonly tested using a pack test, which involves long-term storage and high costs, and provides limited information. Electrochemical techniques have also been used as alternative assessment methods for corrosion studies for coated metals [6, 7]. Evaluation of lacquered tinplate by electrochemical methods reduces the cost and time of the test. Additionally, these methods provide more quantitative and qualitative information about corrosion processes [8-10]. This study assesses the behaviour of lacquered tinplate in different solutions using electrochemical methods. The influence of some additives in the test solutions on tinplate corrosion is analyzed using three different electrochemical techniques.

## Experimental

Two different types of containers were used for the measurements, with and without a lacquer coating. Materials used and specifications of the test solutions are shown in table 1. Cyclic polarisation (CP) and electrochemical impedance spectroscopy (EIS) were carried out in a three electrode cylindrical cell. The working electrodes ( $3.2 \text{ cm}^2$  of area) were made from the lateral portion of the container, a Hastelloy C ring was used as auxiliary electrode, and the reference electrode was a Hastelloy C rod. This kind of electrodes can be used due to high corrosion potential stability in the test solutions [11, 12], this was proved experimentally. The electrolytes were solutions traditionally packed in aerosol containers, namely (SD), (SE) and (SF). Solution (SE) was the same solution as (SD) but modified with an additive; this additive was supposed to improve the durability of the containers and decrease the corrosivity of the solution. Cyclic polarisations were performed with a sweep rate of  $8.06 \times 10^{-4} \text{ V.s}^{-1}$ , starting in an anodic direction, from 100 mV below the open circuit potential (OCP) to 1000 mV of anodic over potential, then the cycle was reversed until the initial point was reached. All measurements were taken after 60 minutes of immersion once the potential had stabilised. The impedance measurements were made at the OCP, 10 mV of amplitude and the frequency was varied from 60 kHz to 10 mHz.

In order to assess the electrochemical behaviour of materials used for fabrication of the tinplates cans, which are low-carbon steel, copper and tin, Tafel polarisation measurements were made using a conventional cell of three electrodes. Working electrodes were constructed with rods of copper, steel and tin. The metallic rods were embedded in an epoxy resin in order to isolate the lateral part of rods, and only a circular area of  $0.5 \text{ cm}^2$  was in contact with the solutions. An electrode of Ag/AgCl was used as reference, and a platinum mesh as counter electrode. Measurements were made with a sweep rate of  $1.666 \times 10^{-4} \text{ V.s}^{-1}$  in

the anodic direction, starting from 300 mV of cathodic overpotential with respect to the OCP, up to 300 mV of anodic overpotential. Measurements

began after 60 minutes of OCP stabilisation. Each electrochemical measurement was made in triplicate in a BAS ZAHNER potentiostat.

**Table 1** Specification of the materials

Material	Codification	Description
Container 1	C1	With lacquer coating over the surface
Container 2	C2	Without coating
Steel rod	s	Low-carbon steel
Tin rod	t	Pure tin
Copper rod	c	Pure copper
Solution D	SD	Citric solution without additive, pH = 8.7
Solution E	SE	Citric solution with additive, pH = 4.2
Solution F	SF	Lavender solution, without additive, pH = 8.7

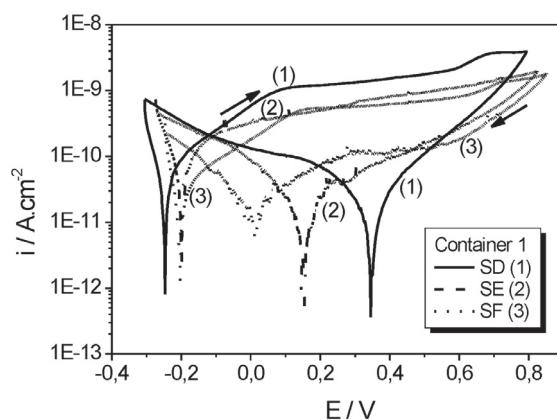
## Results and discussion

### Cyclic polarisation (CP)

Figure 1 shows the cyclic polarisation curves for container 1 in the three solutions tested. As can be seen in the CP curves, container 1 shows a negative cycle of hysteresis in the three solutions evaluated. This means that these solutions could be innocuous to the material. However, important differences in the cycle characteristics are observed, and the solutions can be classified according to the potential degree of corrosivity for container 1.

The amplitude of the negative hysteresis presented by the material in the three solutions can be placed in the following order: SD > SE > SF. This is an indication that container 1 may generate a passive layer, shown by the negative hysteresis; the passive layer would be thickest in SD and thinnest in SF. An important difference was also observed in the change of the corrosion potential (CCP) of the material in the three solutions evaluated. CCP is the difference between the corrosion potential observed during the anodic scan and the corrosion potential observed in the cathodic scan. The CCPs for solutions SD, SE, and SF were 0.592 V; 0.354

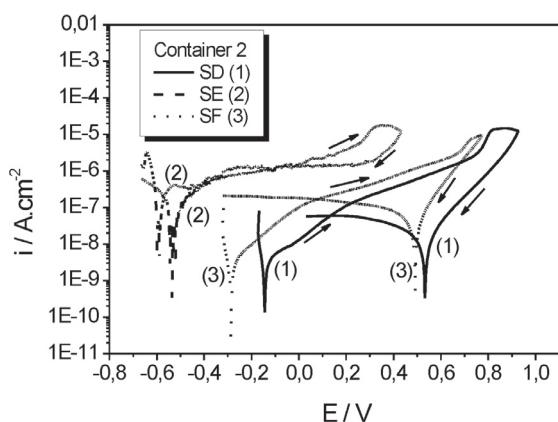
and 0.214 V respectively. A large CCP indicates the existence of a more resistant passive layer formed during the anodic scan. For this reason, the possibility of corrosion failure appearing in container 1 would be greater in solution SF than in solutions SE and SD.



**Figure 1** Cyclic polarisation of container 1 in the 3 solutions tested

Figure 2 shows cyclic polarisation for container 2 in the three solutions tested. Container 2 also presented a negative hysteresis in the CP curves for the solutions. As already stated, this means that these three solutions could be innocuous

for the material. Nevertheless, as with container 1, important differences in the CP curves are observed, and solutions can be classified according to their corrosivity. The amplitudes of the negative hysteresis presented by container 2 in the three solutions were different. Greater amplitude was observed in solution D, whereas in solution E amplitude is insignificant. This indicates that it is more likely that container 2 forms a passive layer during the anodic scan in SD solution than in solutions SF and SE. Additionally, the CCPs for solutions SD, SE, and SF were 0.676 V; 0.053 and 0.779 V respectively; this means that corrosion failure in container 2 may be more likely to occur with solution SE than with solutions SD or SF.



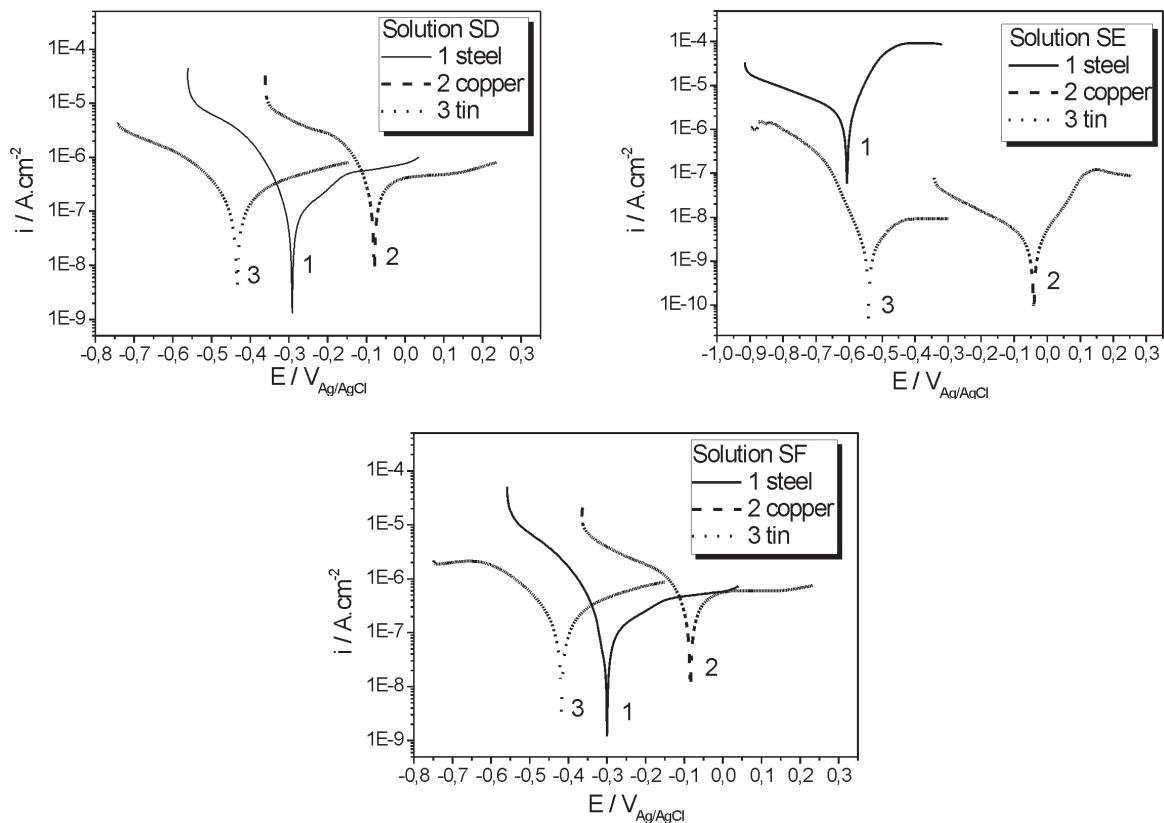
**Figure 2** Cyclic polarization of container 2 in the 3 solutions tested

#### Tafel Plots

Figure 3 shows Tafel polarisation curves made individually for low-carbon steel, tin and copper in the solutions tested; these materials are commonly used to fabricate tinplate for different kind of cans. As can be observed in the Tafel plots in solutions D and F, the materials can be ordered from more cathodic to anodic as follows: copper > low-carbon steel > tin. In contrast, in solution E the order is copper > tin > low-carbon steel. The corrosion potential of copper in the three solutions was approximately -0.070 V, while the corrosion potential of low-carbon steel

was approximately -0.3 V in both solutions SD and SF, and -0.6 V in solution SE. Tin showed a corrosion potential of approximately -0.425 V in solutions SD and SF, whereas in solution SE corrosion potential was -0.542 V. As can be seen in the figures and from the values, solution SE changes the potentials of tin and steel, causing the steel to behave as an anode with respect to tin. In consequence, in solution SE tin would not act as a sacrificial anode if corrosion processes appear in the steel substrate due to pores in the lacquer or tin coatings. This means that the additive added to SE solution neither improves the durability, nor decreases the corrosivity of the solution. In contrast, the corrosivity of solution SD would be increased by the addition of this additive.

Concerning the corrosion processes in tinplate cans, the cathodic process that consumes the electrons is often rate controlling [4]. For the dissolution and complexation of tin, an effective cathodic depolarisation is needed. As tin has a high overvoltage in the hydrogen evolution reaction, protons are unlikely to form useful depolarisers [13]. This situation can be seen in figure 3, in the Tafel plots for solution SD and SF. However, in solution SE with a pH of 4.2, the situation is different. In this solution the cathodic reaction may consist mainly of hydrogen reduction but, due to the high slope seen in the cathodic part of the tin curve, this reaction proceeds with great efficiency on the tin surface. This result indicates that in the solution SE there is one cathodic depolariser. Reduction of hydrogen can proceed easily on low-carbon steel with the presence of one cathodic de polarisen. This can explain the high corrosion current of the steel observed in solution SE. When tin acts protectively, as in the case of solutions SD and SF, the steel corrosion is suppressed and the corrosion reaction results in loss of tin at low rate. This is not a great problem because of the large area of tin coating and small cathodic area (pores). However, when the tin cannot act protectively, as is the case for SE solution, the cathodic/anodic area ratio is large and the localised attack on the steel would produce a rapid failure of the containers.

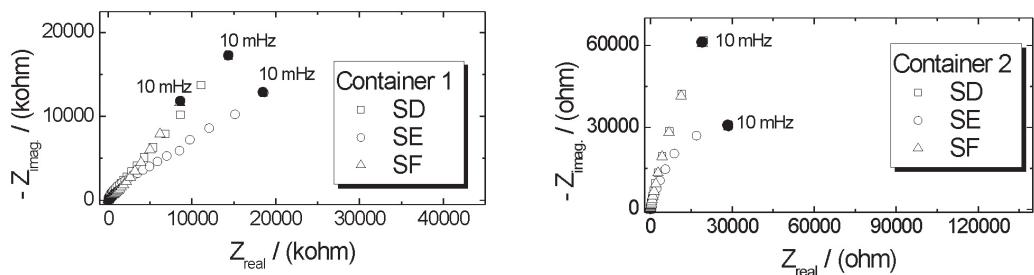


**Figure 3** Tafel polarisation of low-carbon steel, copper and tin in the 3 solutions tested

#### **Electrochemical impedance**

Impedance diagrams of containers 1 and 2 in the three solutions, made after 4 hours of immersion, are shown in figure 4. In all cases the impedance diagrams show one capacitive loop totally open. As expected, the impedances in container 1 are higher than impedances in container 2 due to the lacquer coating. In container 1, due to the presence of the polymeric coating, the capacitive

loop is related to the coating resistance in parallel with the lacquer capacitance. However, a small curvature at high frequencies likely indicates the confluence of multiple time constants, one of these being the time constant of corrosion processes under the lacquer coating. In container 2, which is made of unlacquered metal, the capacitive loop is related to charge transfer resistance, in parallel with double layer capacitance [8, 9].

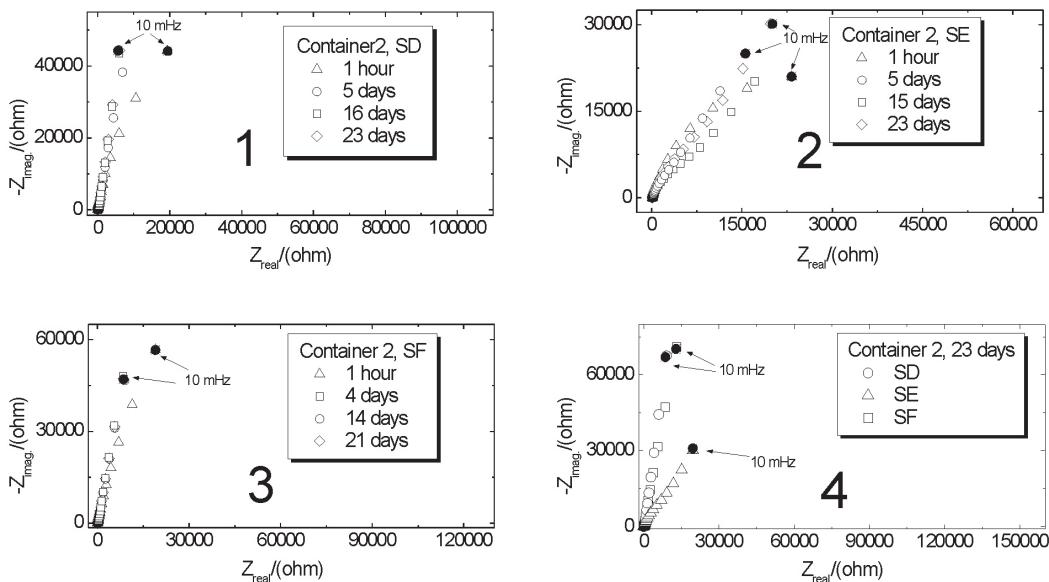


**Figure 4** Impedance diagrams for containers 1 and 2 in the 3 solutions tested

As can be seen in figure 4, the capacitive loop of container 1 in contact with solution SE tends to close at the real part of the impedance axis at the limit of zero frequency; this is true for both container 1 and 2. In contrast, the capacitive loop in the impedance diagrams obtained using solutions SD and SF for both containers remains open even at very low frequencies. This behaviour indicates a lower resistance either associated with the lacquer in container 1, or with the charge transfer resistance for container 2 in solution SE, while in solutions SD and SF both resistances remain higher. These results agree with the results shown by cyclic polarisation and Tafel plots, indicating that solution SE is more deleterious for both kinds of container than solutions SD and SF. The appearance of corrosion processes and early container failure is more likely in solution SE than in solutions SD or SF.

Figure 5 shows the impedance diagrams obtained for container 2 at different exposure times in the three solutions studied. Again, higher impedances are observed during the entire exposure period in solutions SD and SF (figures 5-1 and 5-3). In the impedance diagrams obtained using solutions

SD and SF a completely open loop is observed; this behaviour is indicative of an almost perfect capacitor at the end of exposure time. This means that the exposure of tinplate containers in contact with solutions SD and SF probably stimulates the formation of a passive layer with good protective properties on the tinplate surface. In contrast, in solution SE the impedance diagrams show a more defined loop, tending to close at the real part of impedance axis at the limit of low frequencies, with few changes during the time of exposure (see figure 5-2). These results indicate lower corrosion resistance of the metal in solution SE. This can be corroborated by comparing the impedance diagrams of the metal after 23 days of exposure in the three solutions (figure 5-4), in which a smaller loop is observed for solution SE than for solutions SD and SF. It can be seen that on the final day of exposure, day 23, the impedance in solutions SD and SF resembles the impedance of a perfect capacitor or the impedance of an RC circuit with a high resistance. This indicates that container 2 would perform well when solutions SD or SF are used. Additionally, impedance corroborates that the additive employed in solution SE produced the opposite of the intended effect.



**Figure 5** Impedance diagrams of container 2 at different exposure times in solutions: 1) SD, 2) SE, 3) SF, 4) Impedance at 23 days of exposure in the 3 solutions tested

## Conclusions

According to the results obtained in this study, the aggressiveness of the solutions evaluated for the tinplate containers is, in descending order, SE > SF > SD. The use of additives in products that will be packed in tinplate containers has to be carefully considered, with knowledge of their performance and the reactions that will take place between chemicals and metal surfaces. In the present study, the use of an additive in SE Solution was detrimental to the anti-corrosion performance of tinplate. In the SE solution a reversal of cathodic/anodic behaviour was observed in the galvanic couple between low-carbon steel and tin. This means that the tin coating no longer acts as a sacrificial anode, and consequently rapid corrosion of the tinplate occurs. Electrochemical impedance and polarisation measurements yielded concurring results. Electrochemical techniques can yield rapid results, and are useful tools for evaluating the behaviour of lacquered tinplate cans with different canned products.

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