Impedance measurements on lacquered tinplate: fitting with equivalent circuits

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Experimental impedance data previously obtained for various kinds of lacquered tinplate are fitted using two different equivalent electrical circuits, with the aim of assessing the advantages/disadvantages of this procedure for quality control of the material as compared to direct evaluation of the impedance diagrams. It is shown that for screening purposes the same conclusions can be obtained either by fitting or by qualitative analysis of the diagrams. The physical meaning of parameters obtained from the impedance measurements is also discussed. The results are interpreted on the basis that the lacquer is characterized by intact and porous areas which are associated with a capacitance in parallel with the pore resistance in the high frequency range. At lower frequencies other processes occur in series with the resistance of the pores. For short immersion times, the passivation film present on tinplate is detected, whereas for longer immersion times, faradaic processes are detected.

Keywords: coatings, equivalent circuits, impedance, quality control, tinplate

1. Introduction

Tinplate is considered one of the best alternatives for canning because it maintains the integrity of the canned food for a long time. Depending on the kind of food, additional protection with lacquers is very often used. However, in order to lower costs, a reduced thickness of the metallic coating is desirable. Thus, the quality of the deposit and lacquering must be improved and a better knowledge of the system is needed.

In this context parameters such as capacitances, resistances and constant phase elements (CPE) have been correlated with the corrosion behaviour of lacquered tinplate [1–7]. These parameters have been obtained directly from experimental impedance diagrams or after fitting the data with equivalent electrical circuits (EECs). In general, when EECs are used a physical meaning is attributed to each component by considering the coherency of its magnitude and its variation with time.

In previous work [7] the performance of tinplate lacquered under different conditions was monitored using electrochemical impedance. At the start of the tests the diagrams were characterized by a single capacitive loop. As time elapsed, a second loop appeared at higher frequencies. At longer times, a third time constant was observed in a low frequency range. The loop at higher frequencies is usually related to the coating [4, 5, 8, 9], whereas the interpretation of the second loop is not clear; it may be due to a faradaic process or to the presence of defects in the lacquer.

Hollaender, Ludwig and Hillebrand [4] correlated the three loops with three different areas in the lacquer itself. This physical situation is represented by the EEC in Fig. 1, where each area corresponds to one branch. As electrolyte simultaneously contacts the three areas, the branches are arranged in parallel.

The aim of this paper is to compare parameters obtained directly from the loops observed in the experimental EIS diagrams with those obtained by fitting the same results with two different EECs, namely the circuit presented by Hollaender et al. [4] and that proposed by Mansfeld [9] with an additional time constant. Thus, the eventual advantages of using EECs for screening purposes can be evaluated. Based on the results, the physical meaning of the parameters is discussed in more detail.

2. Experimental

2.1. Test conditions

Experimental results were obtained previously [7] for several lacquering conditions and pretreatments commonly used in the packaging industry. In the present study only those concerning the lacquering conditions and the effect of the sterilisation pretreatment are analysed. The sterilization consisted of total immersion of the samples in a 3 wt % acetic acid + 1 wt % sodium chloride solution at 120°C.
for 1 h in an autoclave. The features of the tinplate have been described previously [7]. Two lacquers were tested: an epoxy-phenolic 36% solid content (EP) and a phenolated epoxy urea 37% solid content (EU). The lacquering conditions are given in Table 1.

The performance of the various samples in total immersion conditions was monitored by impedance measurements in a solution containing 10^{-2} \text{ M} \text{ citric acid, 10}^{-2} \text{ M sodium citrate and 1.5} \times 10^{-1} \text{ M sodium chloride (pH 4). The samples were approximately 24 cm}^2.

2.2. Fitting

Two circuits were used for fitting the experimental results; namely circuit 1, presented by Hollaender et al. [4], which is shown in Fig. 1 and circuit 2, a modified Mansfeld circuit [9], shown in Fig. 2.

In both cases, the CPE formalism is adopted for the elements represented as capacitors in accordance with the software developed by Boukamp [10], which was used for fitting. The criterion adopted for the fits admitted a relative error [10] of less than 5% for the real and imaginary parts of the impedance. To simplify the discussion, Fig. 3 shows the convention adopted for the parameters and their correspondence with schematic impedance diagrams for the three cases: experimental results, fitting with circuit 1 and fitting with circuit 2. Only the parameters for the two first capacitive loops will be analysed because, as previously shown [7], they are related to the quality of the lacquers. The third process was only detected at low frequencies when the samples were already markedly damaged and therefore the respective parameters were not taken into consideration.

3. Results and discussion

3.1. Experimental parameters

The main conclusions from previous work [7] were: (i) EP in all conditions has better performance than EU; (ii) EP is better cured at 205° C than at 180° C and (iii) The effect of cure temperature can only be observed on EU after the sterilization. These conclusions were reached by visual inspection of the samples and were associated with the variation of \( C_2 \) with immersion time. The samples with the best performance were characterized by smaller changes of \( C_2 \). In the present work the analysis will be extended to the other parameters: \( C_1, R_1 \) and \( R_2 \). As these are obtained by direct evaluation of the diagrams, the values plotted in the following figures correspond to test times when only one loop is detected, or the loops \( R_1C_1 \) and \( R_2C_2 \) are well separated. The acquisition of the respective parameters is inaccurate whenever the loops are coupled and this is one limitation of the graphical procedure adopted.

In Fig. 4 the relative performance of EP and EU under condition B (see Table 1) is assessed by the variation of \( C_1, R_1 \) and \( R_2 \) with immersion time, which is compared to the variation of \( C_2 \). Curves for two samples of each lacquer are presented to show the reproducibility of the results. As can be seen, the values of \( C_2 \) start around 2 \times 10^{-8} \text{ F} for EU changes to 10^{-6} \text{ F} in 72 h of immersion, while for the EP samples, \( C_2 \) is lower than 10^{-6} \text{ F} even after

Table 1. Description of lacquering conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Number of coats</th>
<th>Cure temp. °C</th>
<th>Coating weight for EP g/m²</th>
<th>Coating weight for EU g/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>180</td>
<td>4.57 (2-3 µm)</td>
<td>4.44</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>205</td>
<td>4.35</td>
<td>3.90</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>180</td>
<td>8.51</td>
<td>7.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>205</td>
<td></td>
<td></td>
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</tbody>
</table>