

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

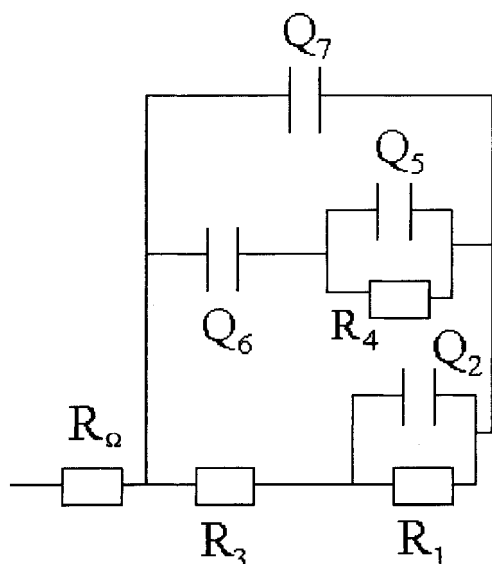


Fig. 1. Equivalent electrical circuit proposed by Hollaender *et al.* [4]: circuit 1. Pore area: (R_1) metal charge transfer resistance; (Q_2) metal charge transfer capacity; (R_3) pore resistance. Affected lacquer area: (R_4) metal charge transfer resistance; (Q_5) metal charge transfer capacity; (Q_6) affected lacquer capacity. Intact coating: (Q_7) Intact lacquer capacity. Solution: (R_Ω) electrolyte resistance.

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} M citric acid, 10^{-2} M sodium citrate and 1.5×10^{-1} 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

Table 1. Description of lacquering conditions

Condition	Number of coats	Cure temp. /°C	Coating weight for EP / g m^{-2}	Coating weight for EU / g m^{-2}
A	1	180	4.57 (2–3 μm)	4.44
B	1	205	4.35	3.90
C	1	180	8.51	7.26
	+			
	1	205		

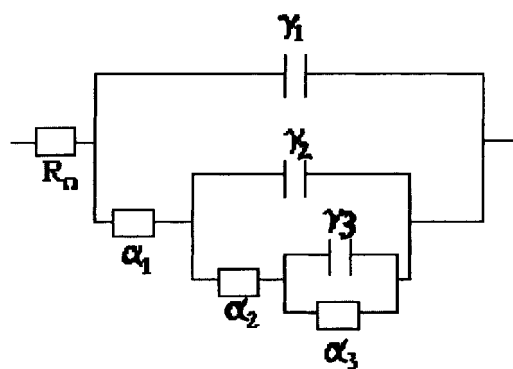


Fig. 2. Modified Mansfeld equivalent electrical circuit: circuit 2. Terms: (R_Ω) electrolyte resistance; ($\gamma_1, \gamma_2, \gamma_3$) capacitance of first, second and third loops; ($\alpha_1, \alpha_2, \alpha_3$) resistance of first, second and third loops.

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 2×10^{-8} F. However, C_2 for EU changes to 10^{-6} F in 72 h of immersion, while for the EP samples, C_2 is lower than 10^{-6} F even after

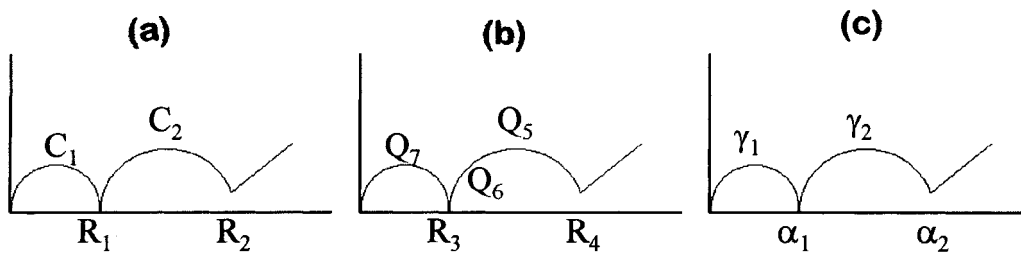


Fig. 3. Correspondence of the various parameters with impedance diagrams for: (a) experiment, (b) circuit 1 and (c) circuit 2.

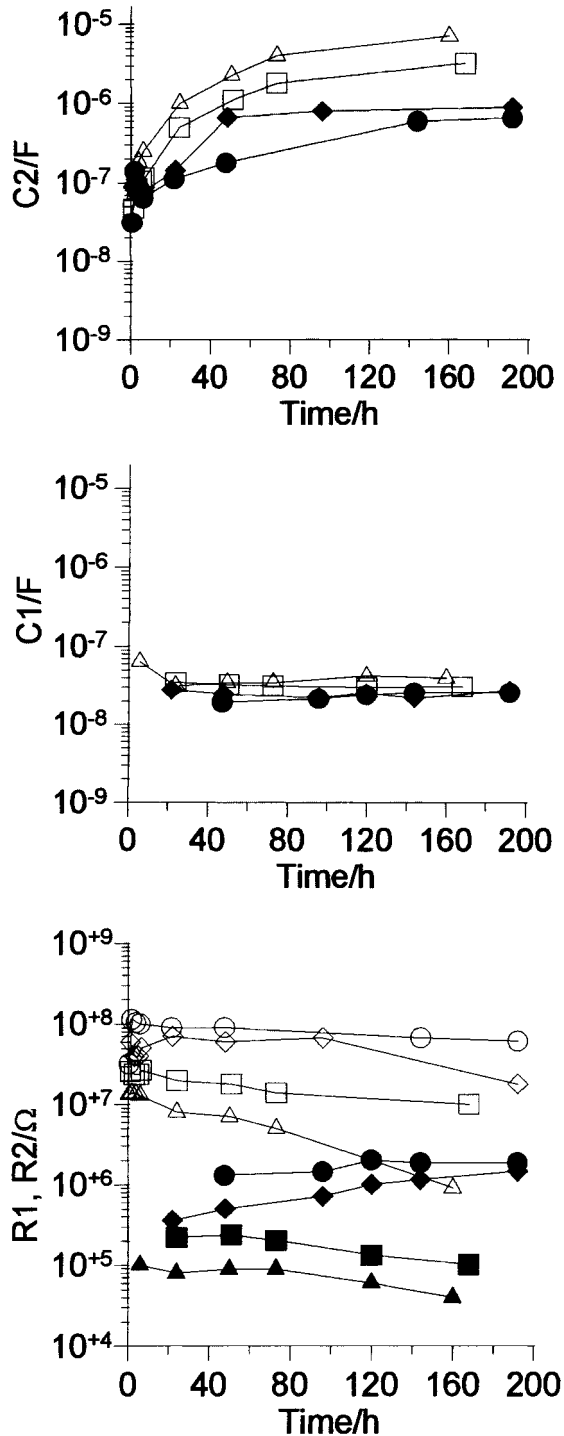


Fig. 4. Evolution of parameters C_2 , R_1 , R_2 and C_1 with immersion time. Samples EP and EU with one coat cured at 205°C (condition B). Key for R_1 : (●) EP-1; (◆) EP-2; (▲) EU-1; (■) EU-2. For R_2 : (○) EP-1; (◇) EP-2; (△) EU-1; (□) EU-2. For C_1 and C_2 : (●) EP-1; (◆) EP-2; (△) EU-1; (□) EU-2.

160 h. Coincidentally, samples EP-1 and EP-2 exhibited fewer spots of corrosion than samples EU-1 and EU-2. Therefore, using the plot of C_2 against time it is possible to classify the lacquers and to predict the differences in corrosion performance. The same classification is obtained from the plots of R_1 and R_2 ; in this case, the best performance is associated with the higher resistance values. As shown, not only R_1 , but also R_2 have higher values for EP conforming with its better behaviour. In Fig. 4, values obtained for C_1 are also given and their stability around 2×10^{-8} F is noteworthy for all immersion times. Although the same value is found for both lacquers, the higher frequency loop (R_1C_1) is only defined clearly for the EP samples later than for the EU ones. Thus, the elapsed time until the definition of the higher frequency loop (C_1) may also be used as a parameter to classify the lacquers.

In Fig. 5 the effect of the cure temperature (conditions A and B) will be analysed for lacquer EP. At the beginning of immersion, for both kinds of samples, C_2 has values of around 10^{-7} F. As time increases, these values remain lower for the samples cured at 205°C, meaning better performance when compared to the samples cured at 180°C. Parameters R_1 and R_2 , being higher for the samples cured at 205°C, are also indicative of better behaviour. Again parameter C_1 remains almost constant during the test time. However, for samples cured at 180°C the values are a little higher and can be estimated from the plots over shorter times when compared to 205°C cured samples, also denoting better performance for EP when cured at the latter temperature.

In Fig. 6, the effect of the cure temperature (conditions A and B) on the parameters C_2 , and C_1 is analysed for EU. In both cases C_2 starts at around 3×10^{-8} F and no significant difference was detected between the two kinds of sample. The same happened for R_1 and R_2 , which are not shown in the figure. For C_1 it can be seen that both the values of capacitance ($\sim 2 \times 10^{-8}$ F) and the time at which the loop at high frequencies becomes defined seem to be independent of cure temperature. The definition of the first loop (C_1), being so premature, suggests that the performance of EU with only one coat is so poor that the effect of cure temperature could not be detected.

In Fig. 7 the results for both lacquers applied under condition C are shown for nonsterilized,

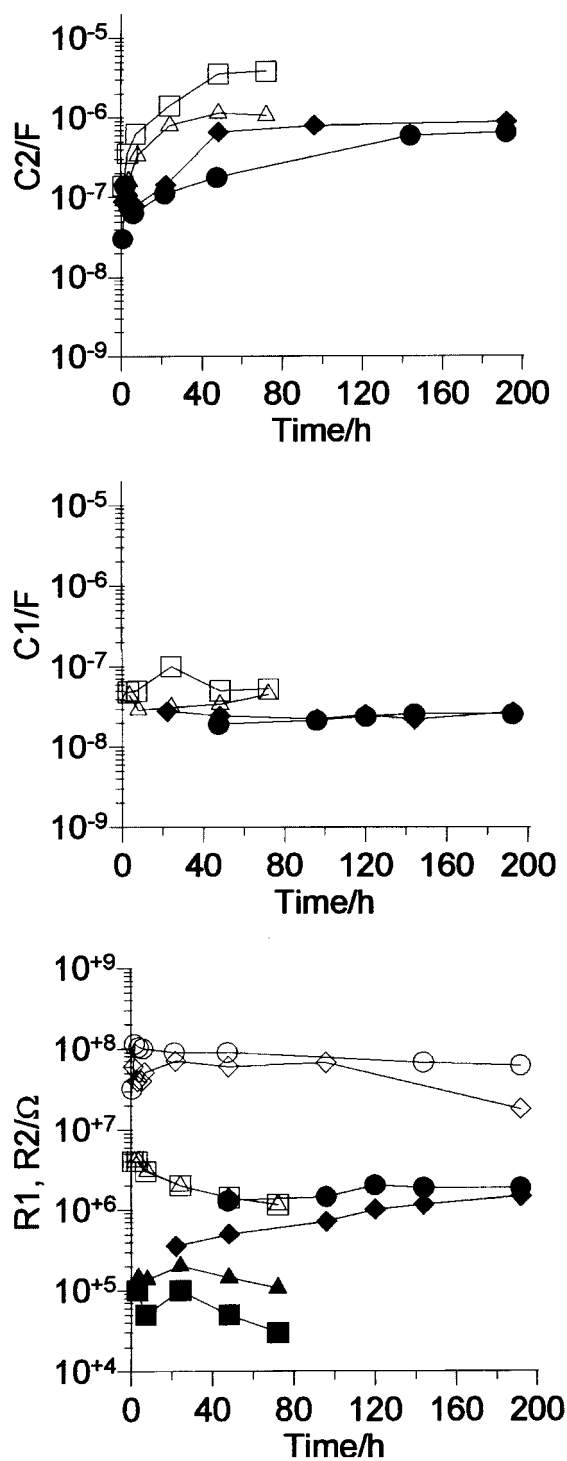


Fig. 5. Evolution of parameters C_2 , R_1 , R_2 and C_1 with immersion time. Samples EP with one coat cured at 180°C and 205°C (conditions A and B). Key for R_1 : (●) EP-1 (205°C); (◆) EP-2 (205°C); (■) EP-3 (180°C); (▲) EP-4 (180°C). For R_2 : (○) EP-1 (205°C); (◇) EP-2 (205°C); (□) EP-3 (180°C); (△) EP-4 (180°C). For C_1 and C_2 : (●) EP-1 (205°C); (◆) EP-2 (205°C); (□) EP-3 (180°C); (△) EP-4 (180°C).

Fig. 7(a), and sterilized samples, Fig. 7(b). In this case the analysis is restricted to C_2 because the other parameters showed the same behaviour as for the other experimental conditions. In Fig. 7(a) the better performance for EP is once again clear. The values for C_2 are almost constant at 2×10^{-8} F during the first 15 days of immersion and only later does this

value increase to 1×10^{-7} F. For EU, the values of C_2 also start at 2×10^{-8} F, but during the first hours of immersion increase rapidly to 1×10^{-6} F.

The destructive effect of sterilization on lacquers EP and EU is identified by comparing Fig. 7(a) and Fig. 7(b). Higher values of C_2 were obtained after 24 h of immersion for presterilized samples. After sterilization, the values of C_2 also show that the differences between EP and EU diminish, although EP still resists better.

Summarizing, the analysis of the parameters obtained directly from the experimental diagrams correlates well with the performance of the samples in the various test conditions. In accordance with previous observations for C_2 [7], resistances R_1 and R_2 have a meaningful variation with time, distinguishing EP and EU under the different lacquering conditions. The elapsed time for the accurate definition of capacitance C_1 can be used as a control parameter, while the capacitance value in itself does not allow one to distinguish between the experimental conditions, since it does not vary with time.

3.2. Fitting results

In Fig. 8 typical fitting results are given using circuit 1 (Fig. 1) and circuit 2 (Fig. 2). As indicated, the quality of the fits is similar for both circuits, with errors [10] of less than 5% and a reasonable distribution over the frequency range studied. The results shown in Fig. 8 correspond to an EU sample, prepared according to condition B after 336 h of test, but the quality of fit found is identical for all the data analysed.

The elements represented in both circuits as capacitors (Q and γ) were fitted as CPEs. Thus, a dissipation factor (n) is associated with Q and γ . Only when $n \approx 1$ are Q and γ really capacitors [10]. In Fig. 9 typical values of n obtained for the corresponding CPEs are shown for samples EP and EU under condition B.

In the left column of the figure the values for n related to the elements of circuit 1 are shown. It can be seen that Q_7 , corresponding to the intact fraction of the lacquer, gives $n \approx 1$. So, this parameter actually has a capacitive behaviour. The values for n associated with Q_6 were found by Hollaender *et al.* [4] as $n \approx 0.5$ (a diffusion process), nevertheless in the present paper the values found are near zero. In this case, Q_6 is frequency independent and $1/Q_6$ has dimensions of resistance. This is considered in the following figures and the values given correspond to the reciprocal of Q_6 . Q_5 shows $0.6 < n < 1$, being close to 1 most of the time. Thus, it can be envisaged as a capacitor in most of the cases and in a few cases as a Warburg element ($n = 0.5$).

In the right column of Fig. 9 the values for n related to the parameters of circuit 2 are analysed. It can be seen that γ_1 , as for Q_7 , has n very close to 1 (a capacitor) and γ_2 , as for Q_5 , gives $0.6 < n < 1$. The behaviour of the n values, shown in Fig. 9, was

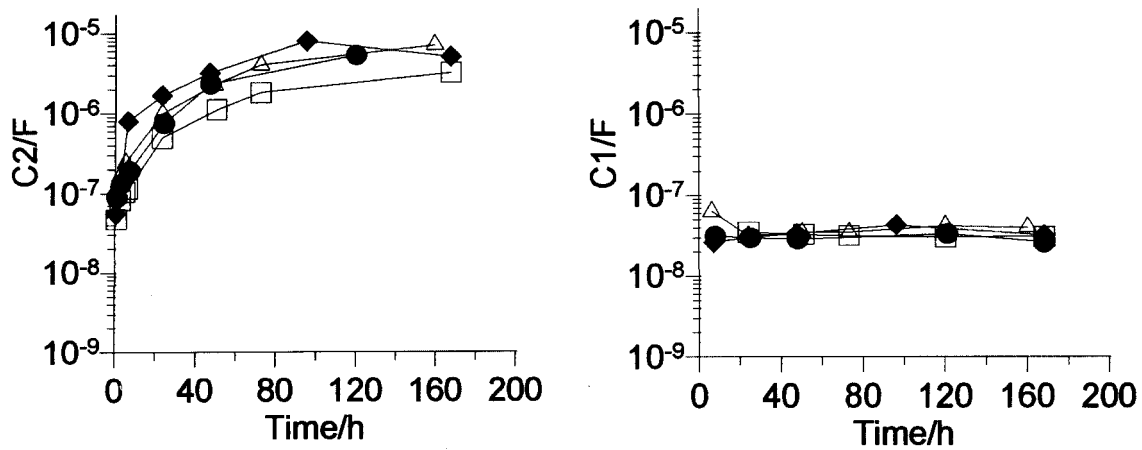


Fig. 6. Evolution of parameters C_2 and C_1 with immersion time. Samples EU with one coat cured at 180 °C and 205 °C (conditions A and B). Key at 205 °C: (Δ) EU-1; (\square) EU-2. At 180 °C: (\bullet) EU-3; (\blacklozenge) EU-4.

identical for all experimental conditions and will not be discussed further.

Figure 10 shows the evolution with time of the parameters obtained from circuits 1 and 2 for lacquered samples under condition B. Parameters γ_1 and Q_7 are always stable, giving values similar to C_1 in Fig. 4. The values for γ_1 and Q_7 were obtained even when the processes associated with the first two loops were coupled. It is thus assumed that the separation of the coupled loops has a physical meaning that justifies the numerical adjustment [11]. As previously mentioned, the value for parameter C_1 itself could not rank the lacquers, whereas the time at which C_1 was decoupled from C_2 was an important parameter. Indeed, by fitting, γ_1 and Q_7 can always be distinguished from the lower capacitive processes, and without special attention to the fitting procedure this time could not be detected. The behaviour of γ_1 and Q_7 , shown in Fig. 10, was identical for all experimental conditions and will not be discussed further. Still in Fig. 10, in the case of circuit 1, R_3 and R_4 do not give a clear difference between the lacquers while

by α_1 and α_2 (circuit 2), the two lacquers can be distinguished, in accordance with consideration of R_1 and R_2 obtained directly from the experimental diagrams (Fig. 4). The magnitudes of the fitted values (α_1 and α_2) are also in agreement with the experimental ones (R_1 and R_2 , Fig. 4). Thus, the lacquers can be differentiated by α_1 and α_2 in circuit 2 but not by R_3 and R_4 in circuit 1. Figure 10 also shows that Q_6 (as a resistor) and Q_5 give different values for EP and EU. It is interesting to observe that the Q_5 values match the γ_2 values well in circuit 2 and C_2 in Fig. 4.

In Fig. 11 the behaviour of EP in conditions A and B is analysed using parameters fitted with circuits 1 and 2. The corresponding experimental parameters are shown in Fig. 5. For Q_5 , the scatter in the values obtained for 180 °C does not allow easy identification of the influence of the cure temperature as was determined by the experimental values (Fig. 5) or by γ_2 (circuit 2) in the same Figure. In this last case, it was even possible to rank the cure temperatures from the first hours of immersion. This was not possible with the direct determination of C_2 from the experimental

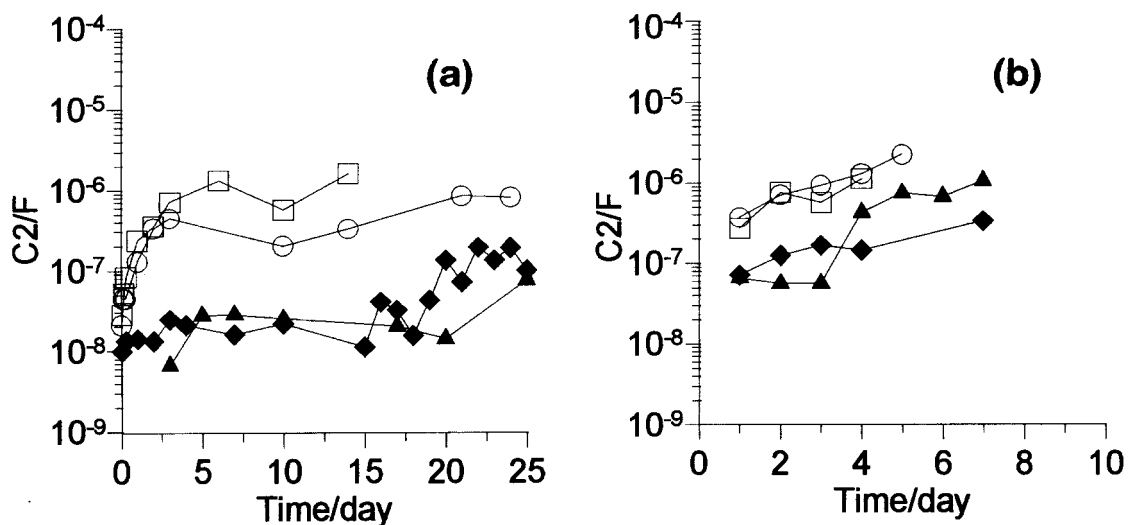


Fig. 7. Evolution of the capacitance C_2 before (a) and after (b) sterilization treatment with immersion time. Samples EP and EU with two coats (condition C). Key for (a): (\blacklozenge) EP-5; (\blacktriangle) EP-6; (\circ) EU-5; (\square) EU-6. For (b): (\blacklozenge) EP-7; (\blacktriangle) EP-8; (\circ) EU-7; (\square) EU-8.

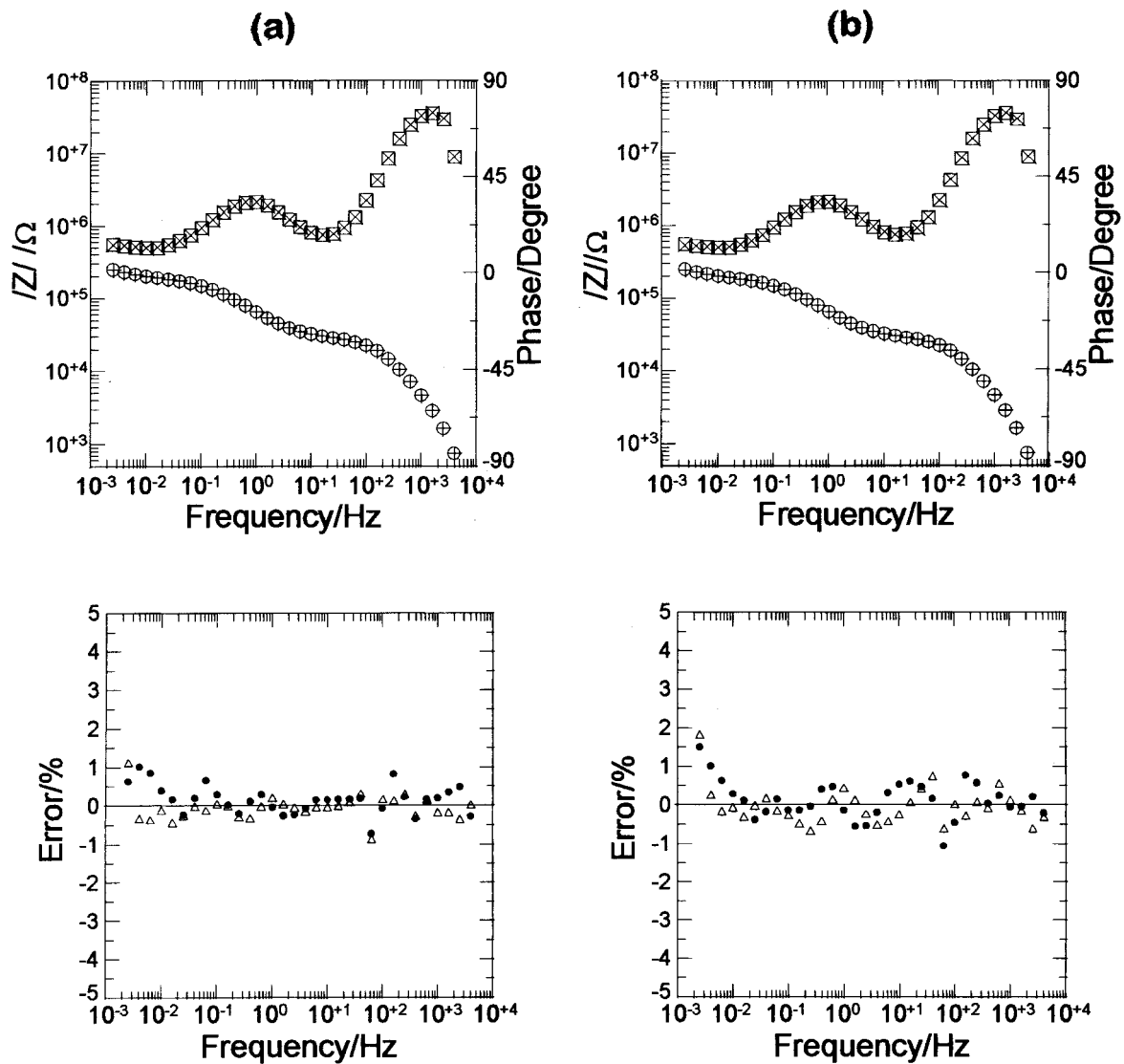


Fig. 8. Bode plots (upper diagrams) and relative error (lower diagrams) for EU with one coat cured at 205°C (condition B), after 336 h of immersion. Left pairs (a): fitting with circuit 1. Right pair (b): fitting with circuit 2. Key for $|Z|$: (○) experiment; (+) simulation. For phase: (□) experiment; (×) simulation. For relative errors: (●) real; (△) imaginary.

diagrams, because in the first hours of immersion the influence of C_1 could not be separated graphically from that of C_2 . In Fig. 11, R_3 was characterized by a large scatter, so the ranking of the samples using this parameter was not possible. However, the same did not occur with α_1 , which matched R_1 (Fig. 5) very well.

The fitting results for EU under conditions A and B are not given, but agreement with the results given in Fig. 6 was again observed.

In Fig. 12 the values of Q_5 and γ_2 are given for EP and EU under condition C after sterilisation of the samples. Comparing the behaviour of these parameters with C_2 in Fig. 8, it can be seen that the same ranking of the samples is possible with γ_2 , whereas Q_5 has a misleading behaviour.

As a summary of the fitting results, it can be said that both circuits are able to simulate the impedance diagrams obtained for lacquered tinplate under different experimental conditions. However, the kinetic parameters obtained from circuit 2 have a better

match to the experimental parameters (C_1 , R_1 , C_2 and R_2) to classify the lacquering conditions. In the following section, the physical meaning of each parameter is discussed.

3.3. Physical meaning of the parameters

3.3.1. First loop. The capacitance values associated with the first loop (C_1 , γ_1 or Q_7) were constant for all experimental conditions. As a general hypothesis it is possible to assume $C = \frac{\epsilon\epsilon_0 A}{d}$, where A is the area of the sample related to the intact lacquer, ϵ_0 is the vacuum dielectric constant, d and ϵ are, respectively, the lacquer thickness and the relative dielectric constant. In consequence of the absorption of electrolyte, ϵ is expected to increase with the immersion time, d is constant and A will only change after long periods of immersion, when a significant area of the lacquer is damaged. Thus, the constancy of the capacitance associated with the first loop implies that part of the lacquer has constant ϵ . According to the literature [4],

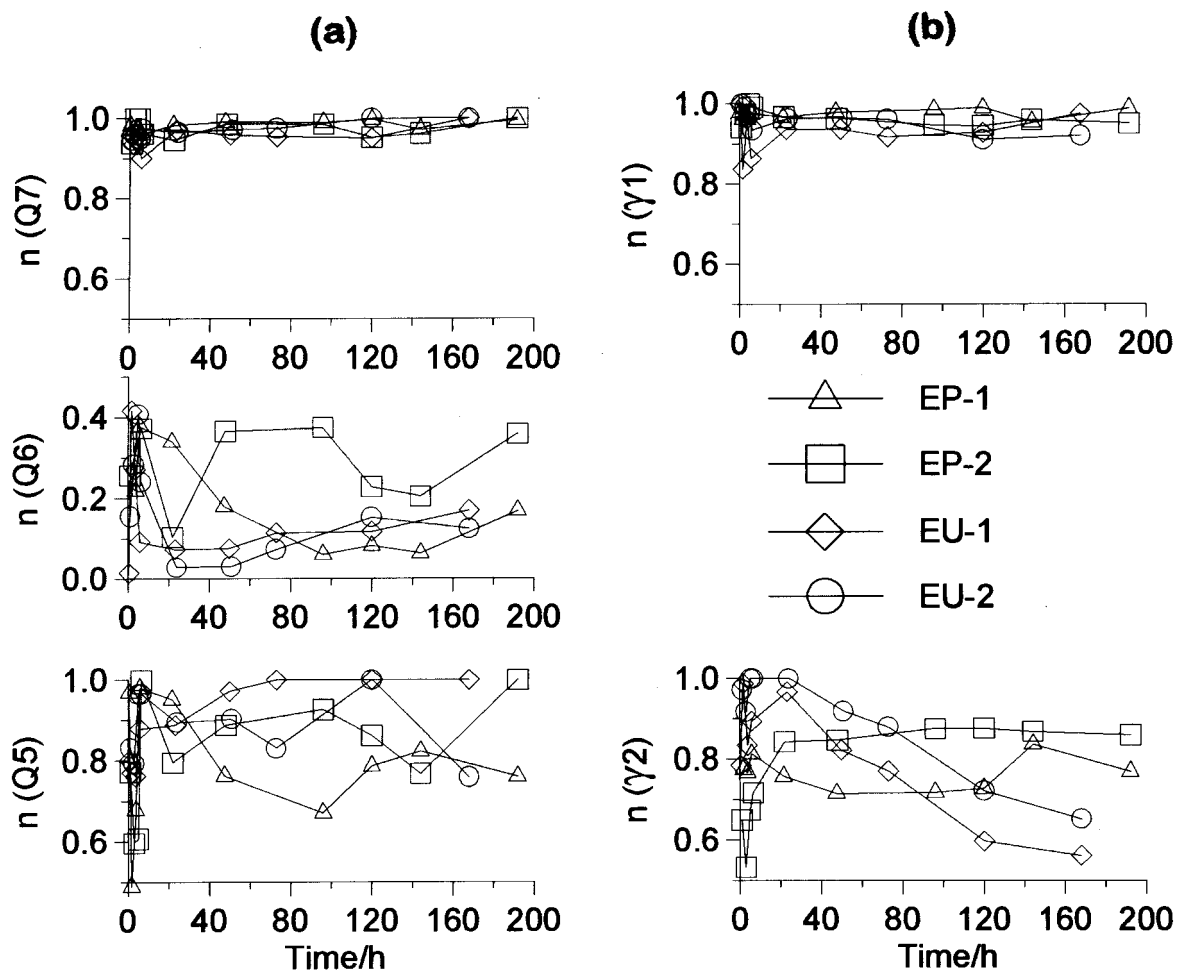


Fig. 9. Evolution of coefficient n for the various constant phase elements. (a) values refer to circuit 1. (b) values refer to circuit 2. Results obtained for EP and EU with one coat cured at 205°C (condition B).

it is supposed that this capacitance is actually representing the ‘intact’ part of the lacquer. In this case, what is the physical meaning of the resistance determined by the diameter of the first loop (R_1 , α_1 or R_3)? It is assumed that this resistance is $R = \rho d/A$, where ρ is the resistivity of the lacquer associated with C . From the results obtained, it is apparent that this resistance changes when the test conditions change, in contrast to C . However, as ϵ is constant, ρ is probably also constant. Therefore, the value of A related to R is not the same as that given in the equation for C . This leads to the conclusion that R is related only to weak areas of the lacquer (pores, low crosslinking). The resistive properties of these areas are, thus, expected to deteriorate with time, in agreement with the decrease in the experimental and fitted values of R_1 , R_3 and α_1 given above.

3.3.2. Second loop. Considering the differences between circuits 1 and 2, the question to be discussed is whether the process leading to the second loop occurs in series or in parallel with the first RC. The experimental results show that the second time constant is related to a process whose contribution becomes significant with time. In fact, there is an elapsed period of time before the existence of a second time

constant is perceivable. This period was correlated with the corrosion protection offered by each system. Whatever the process described by the second loop, it may take place either through the lacquer macro-defects, or through areas of weak linkage in the lacquer matrix. For circuit 2 this ambiguity is not possible. On the contrary, for circuit 1 the process concerned may take place at the bottom of the pores giving rise to R_3 and in parallel through $Q_6(R_4//Q_5)$. However, this last assumption is only possible when Q_6 is frequency dependent, but the fitting results show that, in the present case, Q_6 is a resistor. Moreover, with the progress of deterioration these weak areas will most probably become true pores. Thus, it can be assumed that R represents all the defective areas of the lacquer and the second process occurs in series with it. This latter process is discussed below in more detail.

As described in [12], a transverse section of the metal sheet surface allows the identification of the following layers in the system studied: lacquer, passivation film, electrolytic tin, tin–steel alloy and finally the steel base. The passivation film results from an additional treatment after the tin electroplating, usually made in a sodium dichromate bath, resulting in a layer about 1 μm thick. Considering the

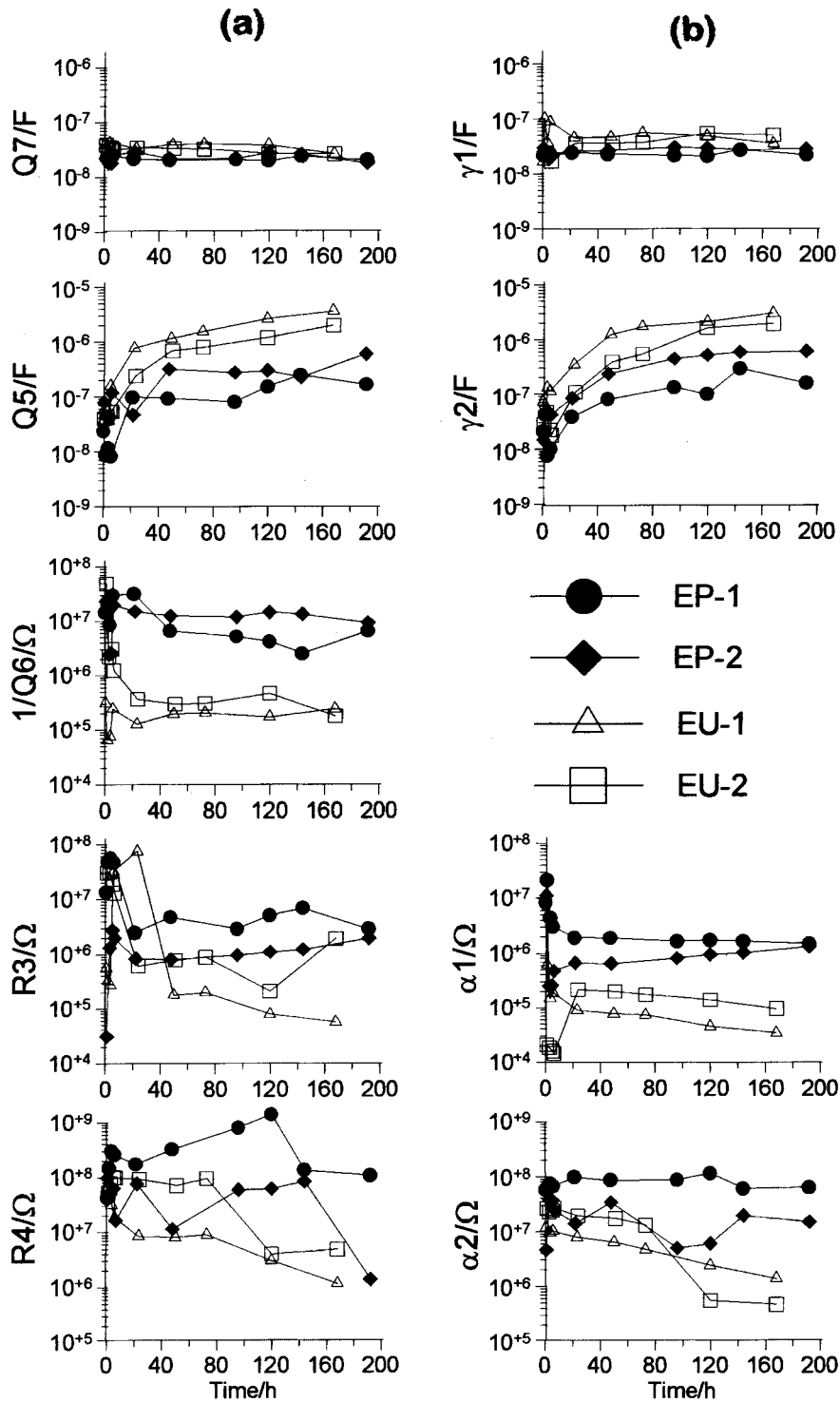


Fig. 10. Evolution of the components of circuits 1 (a) and 2 (b). Results obtained for EP and EU with one coat cured at 205°C (condition B).

deterioration of this system with time, the second loop may be related to the relaxation of the passive layer, its deterioration by the electrolyte and the corrosion of the tin layer. In fact, this possibility is supported by the experimental observations. In the early stages of attack, no second loop can be seen, probably because permeation of the weak areas is not important or is coupled with relaxation of the passive layer. Afterwards a second loop appears, but no sign of attack can be detected at the sample's surface. As soon as other loops are sketched on the diagrams,

corrosion spots appear on the surface. At this time the second loop may be related to a double layer relaxation in parallel with the charge transfer resistance and the other loops to faradaic processes occurring on tin. Another experimental fact that supports this interpretation is the average value of C_2 (10^{-6} – 10^{-5} F) obtained at the end of the tests. These values cannot be attributed to a 3–4 μm thick polymeric layer.

The fitting results showed that both circuits are able to simulate the experimental diagrams. The

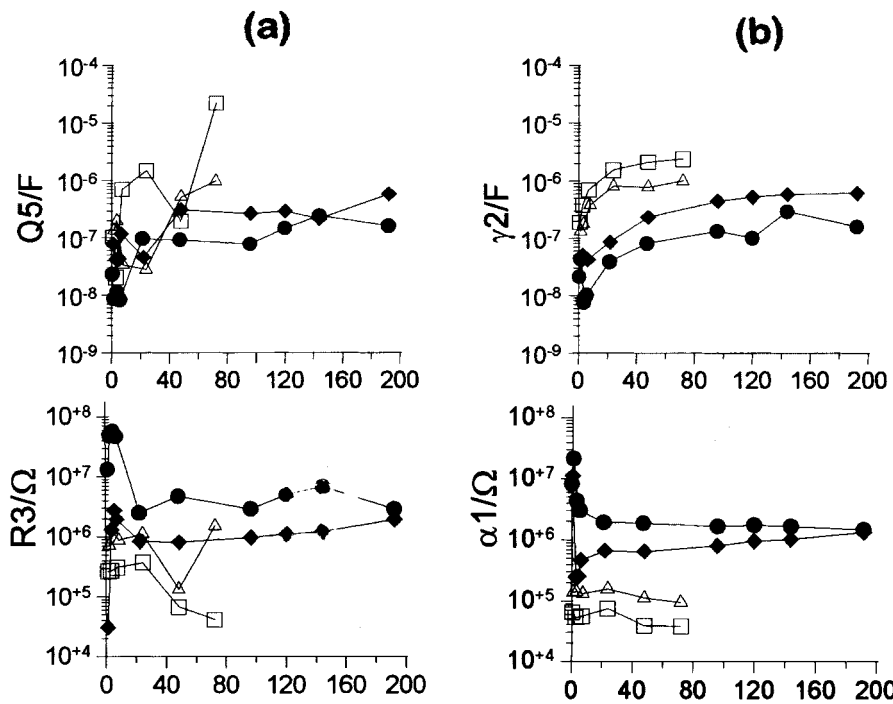


Fig. 11. Evolution of some components of circuits 1 (a) and 2 (b). Results obtained for EP with one coat cured at 180°C and 205°C (conditions A and B). Key at 205°C: (●) EP-1; (◆) EP-2. At 180°C: (□) EP-3; (△) EP-4.

equivalence between electrical circuits has already been addressed in the literature [13–15]. However, only circuit 2 had kinetic parameters that could distinguish between the test conditions. So, it may be concluded that the behaviour of lacquered tinplate is very well represented by circuit 2, which coincidentally gives parameters closely related to C_1 , R_1 , C_2 and R_2 determined directly from the experimental diagrams. In this case, the high frequency loop (γ_1) represents the intact part of the lacquer in parallel with weak areas (α_1). The second loop ($\gamma_2\alpha_2$) represents the process which occurs in these areas. Probably, in the early stages of attack, this time constant is related to the relaxation of the passivation layer and later, to the double layer in parallel with the charge

transfer resistance of faradaic processes which occur on tin.

3.4. Advantages/disadvantages of fitting

Finally, it is possible to discuss the two procedures used in this work: fitting and direct extrapolation of the loops in the impedance diagrams. The advantage of fitting is the possibility of decoupling the processes related to the first and second loops, assuming that this procedure has a physical meaning [11]. Another aspect is the work systematically done by the computer. It is important to emphasise that with the experimental approach adopted, the physical meaning of each parameter is better understood. A fitting

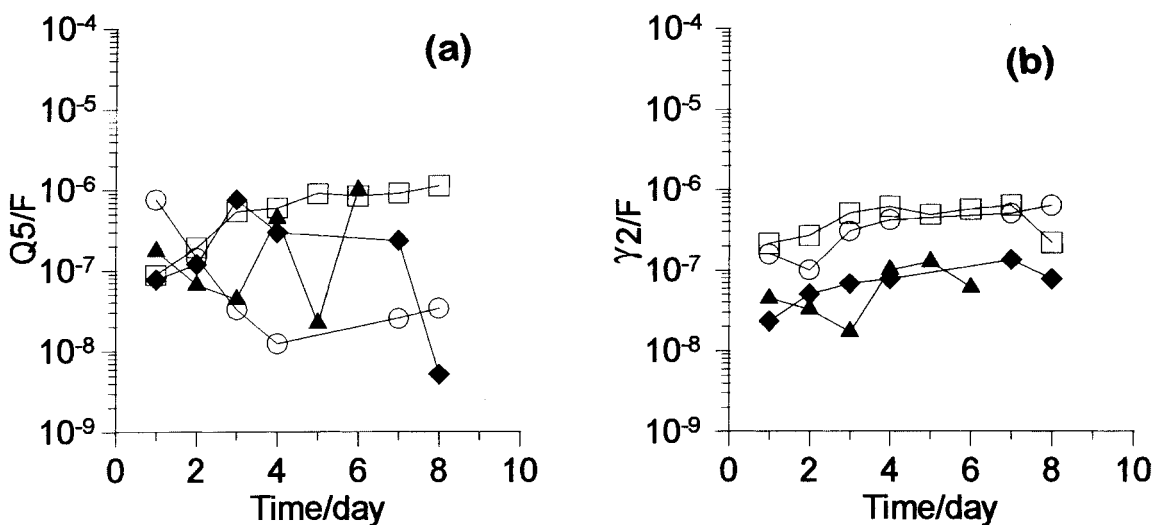


Fig. 12. Evolution of some components of circuits 1 (a) and 2 (b). Results obtained for EP and EU with two coats (condition C) after sterilization treatment. Key for Q_5 and γ_2 : (◆) EP-7; (▲) EP-8; (○) EU-7; (□) EU-8.

procedure is acceptable for quantitative purposes when a kinetic model is proposed, or to assess the error structure of impedance data [13–15]. However, in the present study, no electrochemical model was proposed. For instance, neither the rate of permeation, nor the reactions which occur through the pores were described. This is an important point because the equivalent circuits are often proposed as models when they are just one of the possible electrical descriptions of an electrochemical interface. In the present study, an approximate analysis of impedance spectra led to the ranking of various lacquered tinplates giving equivalent results to those obtained by fitting.

4. Conclusions

It was shown that by systematic analysis of impedance data it is possible to attribute a physical meaning to the kinetic parameters obtained from measurements. Direct evaluation of the loops on the impedance diagrams leads to the same conclusions as those obtained when equivalent electrical circuits are used. The behaviour of lacquered tinplate can be explained in terms of an intact part and pores on the lacquer.

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