Electrochemical Impedance Spectroscopy as a Tool for Investigating the Quality and Performance of Coated Food Cans

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In the present work, electrochemical impedance spectroscopy (EIS) is explored as a tool for evaluating the quality of coatings on food cans. The properties of the coating-metal interface are evaluated using an equivalent electrical circuit representing intact and defect coating areas. The element corresponding to the charge transfer capacitance under pores, proportional to the wetted metal surface, is found to be the most useful element for quality evaluation. It is shown that with EIS, differences can be detected between new and filled cans from different suppliers, as well as between different product formulations. Three measurement techniques, i.e., initial state characterization, rapid dc aging, and long-term electrolyte aging, are applied to a series of petfood and beverage cans, and the results compared with the performance of the same cans after filling and storage. It is shown that all three measurement techniques give basic guidance as to the long-term performance of the filled cans. However, the electrolyte-aging test was found to give the best precision in the performance prediction.

INTRODUCTION

One important application for coated tinplate is in metal packaging (e.g., food). Tinplate food cans are generally quite complex in structure. The metal substrate is usually a mild steel base that has been subjected to the surface pre-treatment producing an $FeSn_2$ layer, a tin layer, and a passivating tin oxide layer.[1] The flat substrate is then coated with a food grade organic coating before it is transformed into a can by forming and/or welding operations. Finally, this can is filled, seamed, and sterilized. The coating, applied to prevent the metal base from corrosive attack by the packed food, further increases the complexity of the system due to the introduction of electrical and electrochemical coating properties such as dielectric behavior, ionic resistance, and hindrance to the diffusion of chemical species.

Since the reactions between food and metal substrate of a can are mainly electrochemical in nature, it appears that electrochemical methods should be well suited for characterizing lacquer protective properties. While traditional direct current (dc) methods, such as potential-time or polarization curves, do not provide sufficient information on poorly conducting layers, alternated current (ac) methods such as electrochemical impedance spectroscopy (EIS) have proved useful in studying the properties of polymer-coated metals and their changes during exposure to corrosive environments.[2,3] In EIS, the complex impedance of the system is measured over a wide frequency range. The data can be interpreted using equivalent electrical circuits, where resistive and capacitive circuit elements are combined and evaluated in order to give the best agreement between experimental and computed (simulated) spectra.[2,4-6]

Previous work using EIS on coated tinplate has focused on the development of equivalent circuits permitting the evaluation of coating properties such as permeability and porosity. Various models, representing the intact coating as well as different types of defects, such as pores, blisters and delaminated areas, have been proposed.[2,4,7-10] The intact coating capacitance can provide information on the insulating effect of the coating and on water uptake during the measurement in aqueous electrolyte solutions.[2] Moreover, by measuring the value of the coating capacitance and its change over time, the effect of different can production steps such as cure temperature and time, mechanical deformation, and sterilization on the coating properties can be studied.[11]

The amount of disbonded, free or wetting metal surface, related to the amount of coating defects, has been identified as an important parameter.[4,7-9] Depending on

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the model used, the area of the wetting metal surface can be estimated either from the pore resistance of the coating or the interfacial capacitance of the exposed metal surface.[2,12] The pore resistance is the most commonly used parameter,[7-9] but has the disadvantage of not permitting the distinctions between differences in coating resistivity and differences in free metal surface. Furthermore, it is generally only possible to obtain qualitative measures using this parameter.[2] Through measurement of the interfacial capacitance some workers have reported quantitative values of wetted metal surface.[10,12]

It should be kept in mind that the free metal surface is not a property given for a certain substrate-coating combination, but something that changes both during can manufacturing and as the coating interacts with water and various food components during sterilization and storage. Both deformation of the substrate and sterilization weakens the interface and induces defects.[7,9,13] Permeated water can cause a loss of adhesion and initiate blisters under the coating. The sensitivity to this process is known as "wet adhesion."[14] The subsequent corrosion reactions can very rapidly lead to further loss of adhesion of the coating. Furthermore, these changes occur not only over the lifetime of the can but also during the actual EIS experiments. Consequently, the experimental protocol has to be designed to take such effects into account.

A distinction should be made between initial wetted metal area (mainly due to pores) and the increase in wetted metal area during exposure, related to the sensitivity of the interface to delamination of the coating promoted by corrosion reactions. Different experimental approaches have been suggested in the literature. One common method is to expose the sample to an electrolyte solution for a period of up to several months, while measuring the pore resistance, the interfacial impedance, or resistance.[7,8,10,15] Such tests have shown a general correlation between free metal surface and metal uptake measured either directly in the electrolyte[8] or in the product.[4] Another method is to accelerate the corrosion process, comparing the properties of the system before and after short dc-treatment. This approach has been used successfully to evaluate the quality of aluminum-polyethylene laminates,[4] and has shown promise also for coated tin plate systems.[10]

In the present work, EIS is explored as a tool for can quality evaluation with the aim of finding a rapid technique that can replace the time-consuming traditional filling and storage tests. The properties of the coating-metal interface are examined using a model comprising intact and defect coating areas proposed by Hollaender.[4,10] The suitability of the different elements of the equivalent electrical circuit as measures of can quality is evaluated. Then three different measurement techniques, i.e., initial state characterization, rapid dc aging, and long-term electrolyte aging, are applied to new (empty) pet food and beverage cans with different coatings from different suppliers, and the results compared with the performance of the same cans after filling and storage.

EXPERIMENTAL

Materials

Five types of pet food cans and two types of beverage cans were examined. For each type of can, unfilled, i.e., new cans, as well as cans stored for 12 months with different product recipes, were examined. Not all can-product combinations were available for testing. The characteristics of the different can types as well as the can-product combinations included in the tests are given in *Table* 1. As can be seen, all cans except the first pet food can are three-piece welded cans. Whereas drawn, two-piece cans are uniformly coated, welded cans have a separately applied coating on the weld line, which is a known source of defects.[1,4] The interior coatings of the

Table 1—Can Samples and Coating Characteristics

	Can	Samples	Coating Type	Coating Thickness (μm)
1.	2-piece drawn tinplate pet food can	New Filled with product A	PVC-organosol	6.0
2.	3-piece welded tinplate pet food can	New Filled with product B	Epoxy-phenolic, solvent based	5.8
3.	3-piece welded tinplate pet food can	New Filled with product B Filled with product C	Epoxy-phenolic, solvent based	5.1
4.	3-piece welding tinplate pet food can	New Filled with product B Filled with product C	Epoxy-phenolic, solvent based	3.6
5.	3-piece welded tinplate pet food can	New Filled with product A Filled with product B Filled with product C	Epoxy-phenolic, solvent based	7.5
6.	3-piece welded tinplate beverage can	New Filled with product I Filled with product II	Epoxy-phenolic, water based	3.6
7.	3-piece welded tinplate beverage can	New Filled with product I Filled with product II	Epoxy-phenolic, solvent based	5.4

different cans were identified using FTIR spectroscopy and found to be a thermoplastic PVC-organosol for Can 1 and thermoset epoxy-phenolic (bisphenol-A-based) coatings for the others. The coating thicknesses were all in the range of 3-10 µm. No information on the process of coating application and curing could be obtained from the suppliers.

EIS Measurement Routines

Three different EIS routines were used: (1) initial state characterization without any aging treatment (initial state test), (2) the dc aging routine (dc test)[10] and (3) the electrolyte-aging routine (long-term test).[4,9] The initial state test consists of a single ac measurement.

The dc test consists of two ac measurements with a dc treatment in between. During the dc treatment, the can is polarized to a cathodic potential of –2V against the reference electrode for 120 sec. This means an accelerated weathering of the system that can be regarded as a very rapid simulation of the corrosive interactions between food can and packed products during the shelf life of the can. The dc affects, in particular, the interface metal/coating resulting in further delamination of the lacquer. The nondestructive first ac routine registers the initial scale of the can, whereas the second nondestructive ac routine, identical with the first one, characterizes the final state and thus provides information on the influence of the dc treatment. Details on the measurement parameters are given in the next section.

The long-term tests are repeated ac measurements carried out with new cans that are filled with electrolyte for 10-100 hr. During this time, electrolyte solution may penetrate through the lacquer, especially through the pores in the lacquer, leading to further delamination. Between the ac measurements, the cans filled with electrolyte were stocked at room temperature. The properties of the new, unaffected cans are obtained at the beginning of long-term measurements whereas the subsequent measurements provide information on the interfacial sensitivity to corrosion.

Methods

The electrochemical impedance measurements were performed using a Zahner-Elektrik (Kronach, Germany) IM6 Impedance Spectrum Analyser. The THALES software from Zahner-Elektrik was used for the computerized control of the measurement and for the interpretation of the experimental impedance spectra through equivalent electrical circuits, working with a non-linear least square fitting technique.

Impedance measurements were carried out by applying a sinusoidal potential signal (5 mV for pet food cans, 10 mV for beverage cans) in the frequency range of 100 mHz to about 500 kHz. Beverage cans generally showed fewer coating defects and better isolating properties than pet food cans and therefore, a higher perturbation signal was chosen in order to improve the signal quality of the ac measurement. Resolution parameters were adjusted to 10 steps per decade with an accuracy of 10 measure periods for f > 66 Hz and 10 steps per decade with an accuracy of 5 measure periods for f < 66 Hz. A phosphate buffer solution prepared from ortho-phosphoric acid and sodium hydroxide adjusted to pH = 6 served as electrolyte solution. A classical three electrode cell consisting of a can filled with 150 ml of electrolyte solution as working electrode, a pointed graphite rod (Ø 10 mm) as counter electrode and a saturated calomel glass reference electrode (SCE) was employed. Reference and counter electrode, had a distance of 25 mm from each other, centered in the cell. It should be mentioned that the use of calomel electrodes might lead to the observation of an artificial peak in phase at frequencies above 100 kHz. However, close examination of the experimental data showed no such effect to be present in this work. All impedance measurements were carried out in a Faraday cage in order to minimize the effect of electromagnetic field disturbances on the system being studied.

The initial state tests and the first ac routine of the dc tests were carried out at the free corrosion potential of the system after waiting for five minutes for potential stabilization. Single scans from low to high frequency were performed. In order to check the stability of the system, a scan from high to low and back from low to high frequencies was also carried out. The dc treatment at the dc test consisted of a polarization to –2V (potential at reference electrode) for 120 sec. A relaxation of the corrosion potential for several minutes was necessary before starting the second ac routine. For the long-term experiments, measurements were started directly after filling the cans with electrolyte solution, and repeated at regular intervals during the entire time of the experiment (up to 100 hr). The frequency range was always scanned from high to low and back from low to high frequencies. The initial state tests and dc tests were repeated three times on different cans for each sample type, whereas long-term tests were performed once on one can per sample type. All results given for dc tests base on the mean value of three measurements.

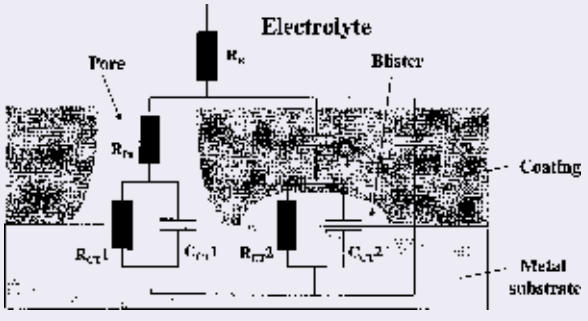

Figure 1—Model and equivalent electrical circuit representing intact areas, pores and blisters of the coating-substrate system. R_E = electrolyte resistance, R_{po} = coating pore resistance, $R_{CT}1$ = charge transfer resistance under pore, $C_{CT}1$ = charge transfer capacitance under pore, C_C' = coating capacitance above blister, $R_{CT}2$ = charge transfer resistance under blister, $C_{CT}2$ = charge transfer capacitance under blister, C_C = coating capacitance.

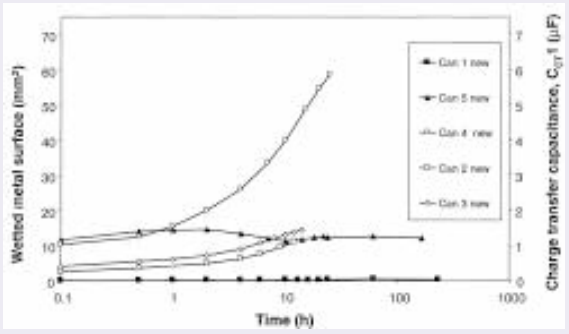

Figure 2—Interfacial capacitance $C_{CT}1$ and calculated initial wetted metal surface under pores in the coating of pet food cans as a function of immersion time in electrolyte solution (long-term test).

For the determination of the charge transfer capacitance per unit tinplate area, the coating of can pieces with a known macroscopic surface area was removed electrolytically by applying a dc current of around –1 $mAcm^{-2}$ for several minutes in a solution prepared from 5 g sodium carbonate in 1000 ml distilled water. EIS measurements were then carried out on the bare can pieces with the same parameters as for the other ac experiments.

Coating thickness was determined by optical microscopy on embedded sections of the cans. Diffuse reflectance infrared spectroscopy was performed on the coatings using a Nicolet 560 Magna IR spectrometer. In addition to the EIS measurements, the interior of the filled cans was evaluated for defects and corrosion by visual inspection.

RESULTS AND DISCUSSION

Evaluation of the Equivalent Electrical Circuit

A model of the coating-substrate system with a corresponding equivalent circuit proposed by Hollaender was used.[10] The model and the circuit are presented in *Figure* 1. While this circuit is flexible enough to fit the impedance data of different can and lacquer types, its eight impedance elements can be directly related to the physical properties of the metal/lacquer system which is a basic condition to be met for any fitting technique.[2] The circuit consists of three parts connected in parallel: (1) an insulating coating capacitance C_C for the unaffected regions of the lacquered metal; (2) a pore resistance R_{Po} in series with an RC element (charge transfer capacitance C_{CT} in parallel with charge transfer resistance R_{CT}), representing the pore regions of the system; and (3) a part for the blister regions consisting of a coating capacitance for the remaining coating in series with another RC element. An electrolyte resistance R_E is connected in series of these three parts. The description of the tinplate surface as an RC element is a simplification, but by using constant phase elements for the charge transfer capacitances, good results can be obtained. It may be noted that from a theoretical point of view, the quantification of the RC element in series with a coating capacitance (i.e., tinplate surface under the blister) appears difficult due to the low current passing through. However, previous work has shown that reasonable and reproducible results for this RC element can be obtained.[10]

As outlined in *Table* 2, the different elements in the circuit in *Figure* 1 can all be related to the characteristics of the coating-substrate system. Thus R_{Po} is related to the amount of pores (pore area) in the coating. A higher pore area will lead to lower values for R_{Po}. C_C is inversely proportional to the thickness of the lacquer, and also depends on its water content. Furthermore, the change in C_C over time can be used to determine the water uptake of the coating. $R_{CT}1$ describes the corrosion state of the metal surface under the pores. It is related to the active metal surface, and its reciprocal value is a measure of the corrosion current. $R_{CT}2$ has the same meaning for the delaminated metal area under blisters. R_E describes the ohmic resistance of the electrolyte between reference electrode and working electrode. From $C_{CT}1$ and $C_{CT}2$ the wet metal surface (surface in contact with electrolyte solution) under pores, A, and be derived according to

$$A = \frac{C_{CT}}{C_{CT\,Ref}} \quad (1)$$

where C_{CTRef} is the specific capacitance of the free metal surface.

C_{CTRef} was determined by fitting impedance data measured on an uncoated tin plate sample with a simple equivalent circuit consisting of an RC element, representing a pure metal surface (neglecting any oxides), with an electrolyte resistance connected in series.[2] In

Table 2—Description and Evaluation of Circuit Elements

Element	Description	Related To	Typical Value	Comments
R_E	Electrolyte resistance		1-2 Ω	
R_{Po}	Pore resistance	Pore area in coating	5-50 Ω	Interference of corrosion products
$R_{CT}1$	Interfacial resistance, pore	Corrosion state of metal	10^4-10^6 Ω	Interference of corrosion products
$C_{CT}1$	Interfacial capacitance, pore Constant phase element	Amount of delaminated metal area under pores	10^{-8}-10^{-6} F, a = 0.3-0.7	Low scattering and reliable Characteristic of coating quality
$R_{CT}2$	Interfacial resistance, blister	Corrosion state of metal	0.1-100 Ω	Low scattering
$C_{CT}2$	Interfacial capacitance, blister Constant phase element	Wet metal surface	10^{-10}-10^{-9} F, a ≥ 1	No change with aging
C_C'	Coating capacitance above blister		10^{-7}-10^{-5} F	Large scattering
C_C	Unaffected coating capacitance	Coating thickness, water content	10^{-8}-10^{-7} F	No clear correlation with water uptake

spite of the simplicity of the model, a good fit was obtained, yielding an average value of 10±3 μF/cm² for C_{CTRef}. It can be argued that the method used for preparing the reference metal surface (electrolysis) could lead to a modification of the capacitance compared to the surface under an organic coating. Therefore, the surface area values provided by equation (1) should be regarded as approximate.

Evaluation of impedance data showed that $C_{CT}1$, a measure for the delaminated area under pores and exhibiting high reliability and low scattering, appeared to be the most appropriate circuit element to investigate the quality of lacquered tinplate cans. In *Figure* 2, $C_{CT}1$ is shown as a function of time as obtained from long-term experiments (discussed later). Measurements with three cans yielded a standard deviation for $C_{CT}1$ of around 20%. Also $C_{CT}2$ could be used for analysis, but since the values were found to remain almost equal for new and filled cans, this element proved to be less useful as a measure of adhesion properties and can lacquer quality.

As can be seen in *Figure* 3, C_C shows an increase for some cans, presumably related to water uptake of the lacquer, but no clear correlation between water uptake and lacquer quality could be established. The coating capacitance of Can 1 in *Figure* 3 is lower than for the other cans due to its PVC-organosol coating.

$R_{CT}1$ proved to be strongly influenced by the corrosion reaction and its products. In long-term experiments, some pet food cans showed an initial decrease of $R_{CT}1$ followed by the rapid increase after about 10 hours (*Figure* 4). It is believed that this behavior is due to the formation of corrosion products, leading to a passivation of the metal surface and higher values for $R_{CT}1$. Therefore, the interpretation of $R_{CT}1$ can be misleading. In the initial state tests, filled cans showed lower $R_{CT}2$ values than new cans due to the higher amounts of active metal surfaces of the former, as shown in *Figure* 5. It seems that the metal surface under blisters is not passivated by corrosion products as for the delaminated areas under pores. Probably a different mechanism for the delamination process under blisters occurs compared to the pore regions with a direct contact between metal and electrolyte.

R_{Po} also showed a strong influence of the corrosion products. Higher values were observed for filled than for new cans in initial state tests. *Figure* 6 presents long-term experiments with new beverage cans. As can be seen, after an initial short decrease, R_{Po} exhibits a continuous increase. This is believed to be due to the penetration of electrolyte solution, lowering the resistance of the initially dry lacquer, followed by the formation of corrosion products that block the growing pores and produce higher pore resistances. It has been shown that corrosion products in defects dominate the impedance characteristics of these regions.[16] The increase of R_{Po} with time could be used as an indicator of the intensity of the corrosion reaction. Thus, Can 7 in *Figure* 6 is believed to undergo very severe corrosion.

C_C' showed the largest scattering of all circuit elements. Furthermore, the a-value of $C_{CT}2$ was sometimes found to be higher than 1, which clearly is unphysical. This, together with the previously mentioned uncertainty in quantifying the RC-element in series with the coating capacitance, indicates that the use of the blister part of the model could be doubtful. However, the other values obtained for $R_{CT}2$ and $C_{CT}2$ exhibited low scatter and high reproducibility. Also, a good overall fit could only be obtained by including the part of the equivalent circuit representing the blister points to the relevance of these elements to the general model.

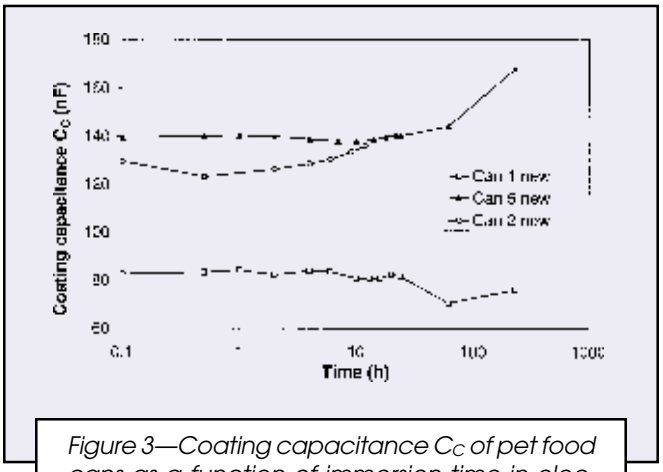

Figure 3—Coating capacitance C_C of pet food cans as a function of immersion time in electrolyte solution (long-term test).

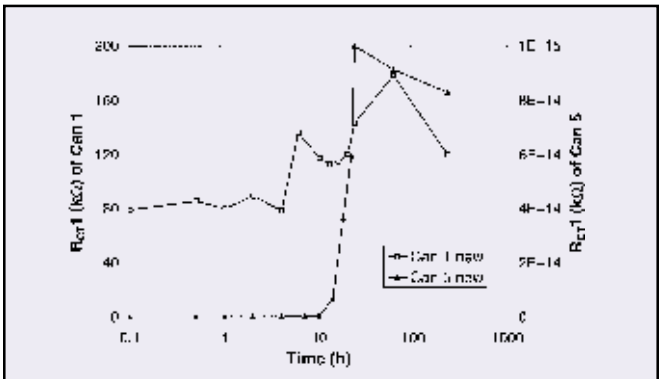

Figure 4–Charge transfer resistance $R_{CT}1$ of pet food cans as a function of immersion time in electrolyte solution (long-term test).

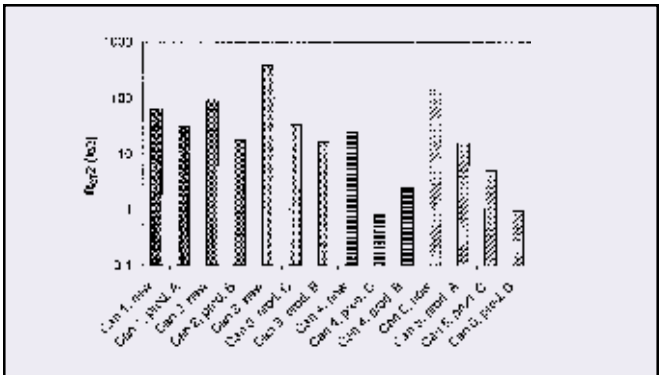

Figure 5—Charge transfer resistance $R_{CT}2$ of new and packed cans as obtained from EIS measurements.

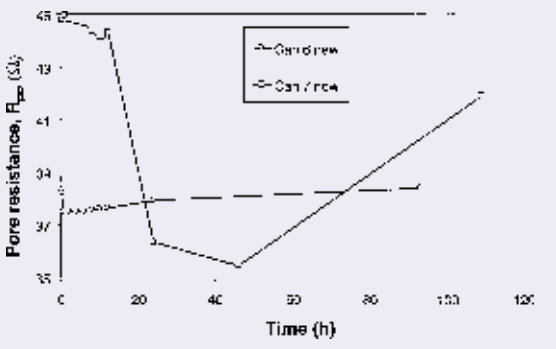

Figure 6—Coating pore resistance (R_{Po}) of beverage cans as a function of immersion time in electrolyte (long-term test).

A summary of the observations regarding the different circuit elements, together with typical values obtained for each element, is given in *Table* 2. Since $C_{CT}1$ was found to be the most reliable measure of the quality of the cans, describing the amount of delaminated metal area under pores, further evaluation was focused on this circuit element. Also, $R_{CT}2$ could be useful for the interpretation of results. However, *Table* 2 shows a factor of 1000 between $C_{CT}1$ and $C_{CT}2$. Consequently, the delaminated metal surface under pores is roughly 1000 times larger than the delaminated surface under blisters. It is doubtful that the evaluation of $R_{CT}2$ as a measure of the corrosion state of the metal surface under blisters is representative of the coating quality of the total can.

Initial State Characterization and dc Tests

In *Figure* 7, ac data before and after a dc-treatment for a pet food can is presented (dc test). In the second ac routine a lowered impedance, due to the weathering treatment, can be noted. Two phase maxima can be seen, the one at higher frequencies mainly influenced by C_C, and the one at the lower frequencies related to C_{CT}. In the second ac routine, the phase at high frequencies is lowered due to water uptake of the coating. The phase maxima belonging to C_{CT} are shifted to lower frequencies and higher values as a result of the larger delaminated metal area compared to the first ac routine.

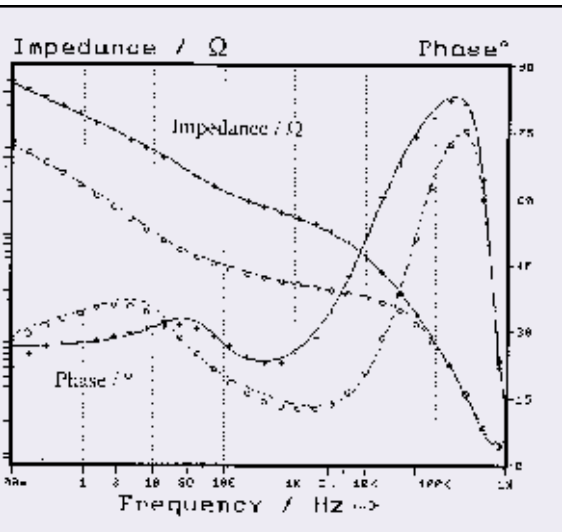

Figure 7—Impedance data (Bode plot) and fitted curves for a coated tinplate can (Can 5 new) before (+ data, —fit) and after (O data, …… fit) a dc aging treatment (dc-test).

Figure 8 presents initial state tests, as well as the results of dc tests on different pet food cans. The dc test is expressed as increase on dc treatment, i.e., the difference between the first and second ac routines. All data is shown both as capacitance and as wetted metal area calculated according to equation (1). In *Figure* 8 it can be seen that, as can be expected, in general a higher initial wetted metal surface is measured for filled cans than for new cans. The measurements also permit a classification of the aggressiveness of different recipes to be made. *Figure* 8 also shows that, within the data set for each can type, the values are consistently higher for cans filled with product B compared to cans filled with product C, which indicates that product B is more aggressive than C. Furthermore, the fact that the cans filled with product A exhibit the highest values (see the data for Can 5) points to an overall aggressiveness ranking of product A > product B > product C.

For new cans, a higher initial wetted metal surface (initial state test) always correlates with a stronger damaging influence of the dc treatment, resulting in larger additional delaminated area (dc test). This indicates that dc tests can provide useful information on the coating adhesion quality for new cans. For filled cans, however, it is found that a high initial wetted metal surface in general coincides with a lower added delamination during the dc polarization. This is believed to be due to the fact that the free metal surface in the filled cans has become partially passivated by corrosion products as a result of corrosive interactions with the food during storage. Thus, the passivation leads to lower currents during the dc treatment and, consequently to a lower additional delamination. These results indicate that the dc test is only justifiable for new cans, since for the filled cans the interpretation is complicated by corrosion products.

Long-term Measurements

An example of a long-term measurement with a pet food can is presented in *Figure* 9. A continuous decrease with time of the impedance at frequencies below 10 kHz, as well as of the phase between 100 Hz and 100 kHz, can be seen. This is related to a steady deterioration of the metal/coating system induced by the penetrating electrolyte solution.

Figure 2 presents the results of long-term tests on pet food cans. Again the data is shown both as capacitance and as wetted metal area calculated according to equation (1). As can be seen, the behavior varies dramatically between the cans. Can 1, with very low initial values, exhibits minimal increase over time, indicating a high coating stability. Can 4 starts out with a fairly high value

that then increases strongly as the measurement continues. Cans 2 and 3 show an intermediate behavior with a gradual increase of the wetted metal surface with time. Can 5 is different from the others, with an initially high value that increases during the first hours of the experiment and then decreases, finally leveling out close to the initial value after about 10 hr.

Accelerated Tests vs. Performance of Filled Cans

The results of the tests on filled cans are presented in terms of wetted metal area in *Table* 3. Examining the data on the pet food cans (Cans 1-5), it can be seen that the cans exhibit quite different performances. Can 1 is excellent, showing a very low value of wetted metal surface, especially considering it was filled with a more aggressive product than the others. Cans 2 and 3 then show an intermediate behavior with moderate values of wetted metal surface, whereas Cans 4 and 5 exhibit higher values. Regarding the beverage cans (Cans 6 and 7), it is clear that Can 6 is better than Can 7. It is worth noting that the values of wetted metal surface are quite low for both beverage cans, on par with the best pet food can. This is remarkable, considering the fact that the beverage cans are welded whereas Can 1 is drawn. However, it is well known that beverages are much more sensitive products than pet food, thus requiring a better coating quality. The results of the visual inspection of the filled cans in general agree quite well with the electrochemical evaluation. Thus Cans 1 and 2 were found to be excellent, without any visible defects and quite intact coating surfaces. Cans 3, 4, and 5 showed slight changes, particularly along the weld line, with Can 3 exhibiting the smallest and Can 5 the largest number of defects. No defects could be seen in Cans 6 and 7.

Inspecting the data provided by the different tests on new pet food cans, it is clear that none of the three tests are able to exactly predict the behavior of the filled cans (see *Table* 3). The initial state measurement and dc test both produce the same performance ranking, and this ranking follows the same overall trend as the real behavior. However, these tests grossly underestimate the performance of Can 5 and slightly underestimate the performance of Can 3. The long-term test gives a different ranking, where the best (Can 1) and the worst (Can 4) cans are clearly identified, but the performance of Can 5

Table 3—Results of Tests on New and Filled Cans, Wetted Metal Area Under Pores (mm²/can)

Can Type	Initial State	New Cans After DC Aging, Total	After Electrolyte Aging[a]	Filled Cans[b] (after 12 (Months)
1	0.1	0.1	0.2	0.5
2	1	6	10	4
3	3	40	13	3
4	4	80	40	20
5	10	300	10	13
6	0.3	0.3	0.1	0.2
7	0.6	1.4	1.3	0.6

(a) Value after 10 hr.
(b) Prod. A for Can 1, prod. B for cans 2-5 and prod. I for Cans 6-7.

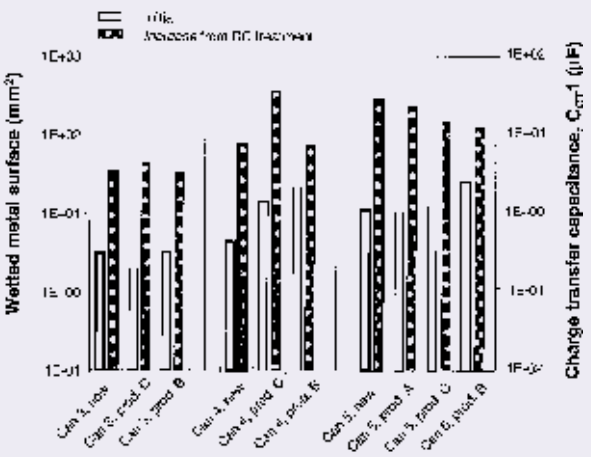

Figure 8—Interfacial capacitance and initial wetted metal surface under pores in the coating from initial state and dc tests of new and filled pet food cans. The results of the dc tests are expressed as increase on dc treatment, i.e., the difference between the first and second ac routines.

is overestimated. It is reminded that Can 5 exhibited an anomalous behavior in the long-term test, with values of wetted metal surface that decreased towards the end of the test. By either ignoring Can 5, or taking the results of the long-term test after 2 rather than 10 hr (which reverses the ranking of Cans 4 and 5, see *Figure* 6), the long-term test provides a correct performance ranking. However, it is reminded that for Cans 4 and 5 the result of the visual inspection of filled cans was not in perfect agreement with the ranking obtained by the EIS tests. It is clear that further work, possibly involving a larger number of samples and statistical evaluation, is required in order to develop a measurement protocol that accurately predicts the long-term behavior. It is also worth mentioning that the quality differences between the cans

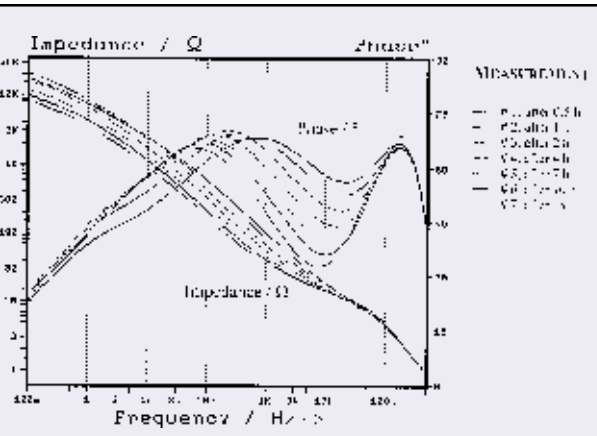

Figure 9—Impedance data (Bode plot) for a pet food can (Can 4 new) measured at different times after immersion in electrolyte solution (long-term test).

appear quite small in absolute terms. Although the EIS measurements shows the cans to be different, they are all quite acceptable from a practical point of view. Thus the product was found to be without visible change for all cans, and the observed defects were small in all cases.

Regarding the beverage cans, *Table* 3 shows that all three tests on new cans provide the correct ranking of the performance of the filled cans.

CONCLUSIONS

The impedance data of coated tinplate cans were interpreted using an equivalent electrical circuit. The circuit was found to work well, and all elements yielded realistic values, although not all of the elements were useful for evaluating can quality. The charge transfer capacitance under pores, proportional to the wetted metal surface area, was found to be the most reliable and useful element for quality evaluation.

The EIS measurements allowed comparisons of coating quality between new and filled cans from different suppliers to be made. It was found that it was possible to characterize the aggressiveness of different product formulations packed in the same can. It was also observed that a dc treatment was useful for new cans, but less appropriate for examining filled cans due to the influence of corrosion products.

Although all tests on new cans, i.e., initial state measurement, dc aging and electrolyte aging, provided basic guidance as to the long-term performance of the filled cans, the electrolyte aging test gave the best precision in performance prediction. Differences in performance and quality between cans were found to be small, and all cans were of an acceptable quality.

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