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Research note

Evaluation of lacquered tinplated cans containing octopus in brine by employing X-ray microanalysis and electrochemical impedance spectroscopy

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Abstract

Investigation of metal can discoloration, lacquer adhesion failure and side seam steel corrosion in tin plated cans containing cooked octopus in brine was evaluated with X-ray microanalysis (energy dispersive X-ray spectroscopy, EDS) and electrochemical impedance spectroscopy (EIS). The effectiveness of EDS to analyze corrosion defects in metal food containers has been proven already in previous studies carried out in our laboratory. Complementary and/or alternative to sophisticated surface analysis methods, which require advanced and expensive instrumentation, simple and inexpensive quality tests based on EIS were also performed and results are discussed. Obvious alterations of the electrochemical properties of corroded and non-corroded samples (internal can walls and side seam) used as working electrodes in a common three-electrode compartment electrochemical cell can be used for rapid and simple evaluation of corrosion defects in tinplated food cans.

Keywords: X-ray microanalysis; Electrochemical impedance spectroscopy; Discoloration; Can corrosion

1. Introduction

A large portion of processed food products including meat and fish products, soups, fruit and fruit juices, condensed milk etc. reach the consumer annually in the form of canned products (Kraus and Tarulis, 1997; Robertson, 1993). Out of the several millions of canned products reaching the consumer worldwide, the overwhelming majority of which are of excellent quality, metal containers occasionally develop integrity problems which can lead to early failure through corrosion, loss of seal integrity, discoloration development, all resulting to canned product rejection by the consumer (Charbonneau, 1997).

Can integrity problems reported in the literature include: stress corrosion cracking (SCC) involving corrosion at stressed areas of the container, sulfide black corrosion involving the formation of a black body and occasionally discoloration on the product surface, pitting corrosion involving rapid iron dissolution at fractures or pores in the organic coating leading to product blackening, external (filiform) corrosion involving the formation of rust on the external surface of metal container due to scratch defects and enamel adhesion failure involving the chemistry of the organic coating, the application procedure of the coating or the nature of the metal substrate (Charbonneau, 1997; Resnik, 1997).

Tinplate corrosion depends on many factors including can material (tin coated steel, tin free steel), nature of the organic coating (epoxy, polyester, acrylic resins), enamel properties (adhesion, porosity and corrosion resistance), nature of the contacting medium (aqueous, fatty foodstuffs)

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and of course composition of the contained product (acid foods, sulfur and/or salt containing foods, etc.) (Barilli et al., 2003; Montanari et al., 1996).

Recently scanning electron microscopy (SEM) in combination with X-ray microanalysis (energy dispersive X-ray spectroscopy, EDS) have proven to be a powerful and effective tool to investigate the many causes of corrosion in metal food containers (Charbonneau, 1999; Charbonneau, 2001; Kontominas et al., 2006). Lacquer failure has also been studied using scanning Kelvin probe and scanning acoustic microscopy (Doherty and Sykes, 2004).

However, (1) the complexity of the tinplate/lacquer system (base steel, Fe–Sn alloy layer, passivation layer, overlaying of tin and organic coatings), (2) the difficulties encountered occasionally in obtaining reproducible results with both surface EDS or chemical analysis (atomic absorption spectroscopy, polarization methods) and (3) the low corrosion rate observed using lacquered tinplate sheets, have stimulated impedimetric studies using the whole lacquered can as an electrolytic cell and working electrode (Catala et al., 1998; Bastidas et al., 1997).

The objective of the present work is to show how the combination of SEM/EDS with Electrochemical Impedance Spectroscopy (EIS) can be used to determine the cause of both sulfide black discoloration and side seam steel corrosion development in tin plated cans containing octopus in brine.

2. Materials and methods

2.1. Materials

Five different types of samples (Fig. 1) of canned octopus in brine were provided by a local fish processor marked as follows: S_1 (good product; non-corroded side seam), S_2 (rejected product; corroded side seam), S_3 (good product; with no discoloration of internal can walls), S_4 (rejected product; with brown/black spots on internal can walls), and S_5 (rejected product; as S_4 bearing an "intact" linear region, located opposite the side seam of the can).

Cans were cylindrical (83 mm diameter × 38 mm high), made of tinplate internally lacquered (epoxy including phenolic and amino moieties), externally printed, bearing an easy open (EO) top, containing 104 g of octopus in 56 g brine. According to the food processor canned products were retorted at 121 °C for 30 min. Photographs of internal

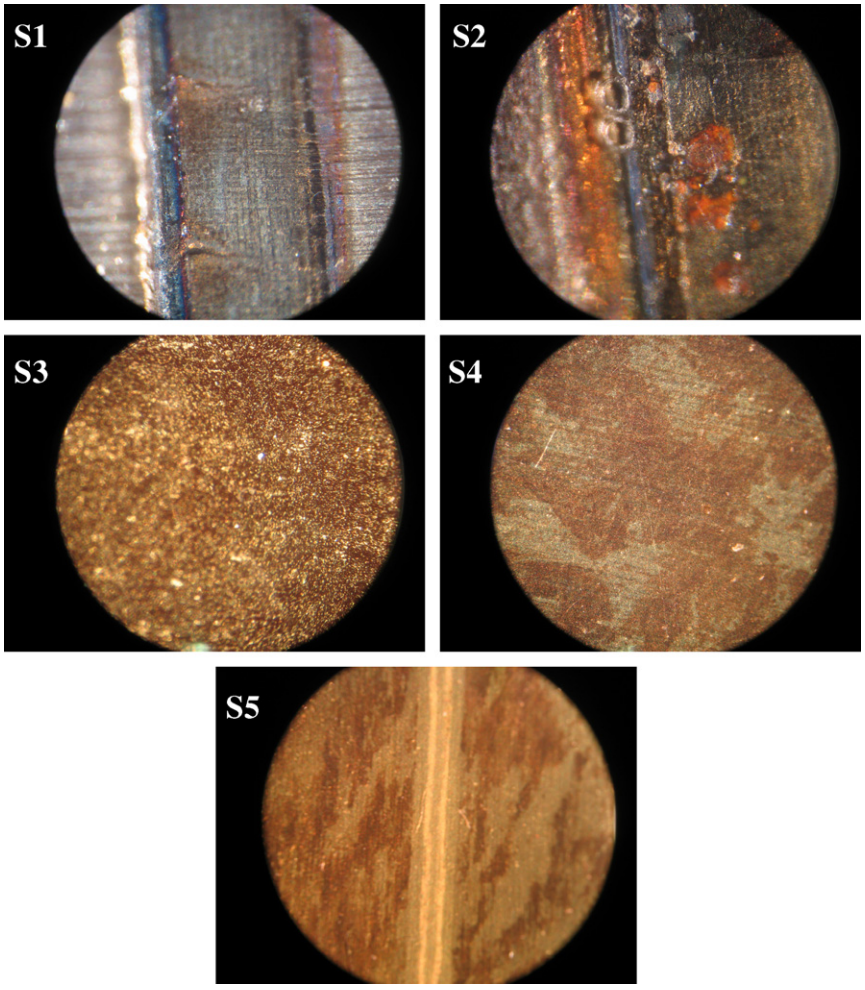

Fig. 1. Photographs of internal can walls (130×).

surface of cans were taken using a LEICA stereoscope model S8 APO (Wetzlar, Germany) at a magnification × 130 (Fig. 1). The cysteine test was carried out according to the method of Anonymous (1977).

2.2. SEM–EDS analysis

Samples were cut out of the respective can and mounted on bronze stubs using a colloidal graphite glue, followed by gold coating using a Polaron SC 7620 sputter coater by Thermo VG Scientific. Secondary electron images were obtained with a JEOL JSM-5600 scanning electron microscope with analysis carried out using a ISI-300 microanalysis system by Oxford instruments equipped with an Oxford detector to obtain X-ray spectra (magnification: 1600×). X-ray microanalysis was performed at an acceleration voltage of 20 kV, specimen tilt (0 °C), working distance (20 mm) and emission current (80 μA). Analysis was focused on the specific areas of interest with an appropriate zoom.

2.3. EIS analysis

Electrochemical impedance spectroscopy (EIS) experiments were performed with an Autolab Analyser (PGSTAT12/FRA2, Eco Chemie, The Netherlands) in a one-compartment three-electrode cell. Working electrodes were made as follows: the external wall of the each sample (S_1–S_5, of appropriate dimensions $1 \times 1\ cm^2$) was scratched with the aid of a file to remove the dielectric coating (lacquer) thus exposing the conductive base-metal surface. A lead wire was soldered onto the conductive area, and the whole construction was carefully covered with an insulating tape leaving an opening ($0.5 \times 0.5\ cm^2$) considered as the active surface of the working electrode. The reference electrode was a Ag/AgCl/3 M KCl (BAS, IN) and a large surface platinum foil ($1 \times 2\ cm^2$) served as the auxiliary electrode. Impedance spectra were recorded over a frequency range of 10–10^5 Hz using a single sinusoidal excitation signal, superimposed on 0.3 V. Excitation amplitude of 5 mV was used throughout the experiment. All potentials are referred to the Ag/AgCl/3 M KCl reference electrode. Measurements were conducted in a 50 mM phosphate, pH 7 buffer solution.

At least 10 specimen of each type of can samples were evaluated in each experiment.

3. Results and discussion

3.1. SEM/EDS study

Comparison of photographs S_1 and S_2 (internal area of side seam) clearly shows corroded internal surface of side seam in S_2 can (Fig. 1). Likewise comparison of cans S_3 and S_4 shows mostly brown spots on internal can walls of S_4 can. Finally the "intact" linear region opposite the side seam of can S_4 is clearly shown in S_5.

Results of the SEM/EDS analysis of the five different can samples are given in Table 1. A high value for C is owed to the carbon content of the organic lacquer itself. Carbon values for all can samples are comparable. At this point it must be mentioned that the values found for carbon represent rough estimates and not precise calculations simply presented in order to indicate their abundance.

Iron values are all low in the range between 0.22% and 0.29% with the exception of samples S_1 and S_2 which is almost 3–10 times higher indicative of the poor protection provided to steel by the organic lacquer close to the can seam, due to the mechanical stresses applied during the formation of the latter. Increased values of Sn in samples S_4 and S_5, compared with those of observed in sample S_3 (these three samples are coming from the same can) can be explained considering that any defects of the lacquer result in tin exposure. On the other hand, the extremely low Sn value observed in sample S_2 cannot be easily explained, actually expressing the risk of collection of non-representative data when local surface analysis methods are employed. Indeed, the exposure of tin in all of three "corroded" samples, S_2, S_4 and S_5 can be alternatively documented by the appearance of peaks corresponding to S in the EDS spectra (Fig. 2) and one can safely postulate that brown spots are the result of reaction of sulfur containing moieties coming from the product with tin to form brown SnS precipitate. Sulfur compounds such as sulfur containing amino acids are typical breakdown products of seafood protein during intensive thermal treatment (retorting). To further test the above postulation the cysteine test (Anonymous, 1977) was carried out on can samples S_2, S_3, S_4 and S_5 and brown/black spots composed of SnS/FeS were formed (photographs not shown) through the reaction of cysteine with exposed iron and tin on can internal walls due to lacquer failure. Good (S_3) can samples produced no discoloration at all due to adequate protection provided by the lacquer. Present iron and tin values do not pose a health risk to consumers but render the product sensorily unacceptable due to the black and brown spots formed on the internal surface of the can.

The presence of silicon can be attributed to the steel that is used for tin mill products. According to the European

Table 1
Elemental analysis using SED–EDS of can samples

Element	Atomic, %				
	S_1 good seam	S_2 corroded seam	S_3 good (no discoloration)	S_4 bearing brown spots	S_5 as S_4 with an "intact" region
C	96.15	98.05	99.55	97.93	98.17
Si	0.32	0.26	0.29	0.02	0.06
Fe	2.83	1.12	0.24	0.29	0.22
Sn	0.7	0.03	0.11	0.72	0.39
S		0.12		0.42	0.45
Zn				0.62	0.62
Na		0.24			
Cl		0.18			

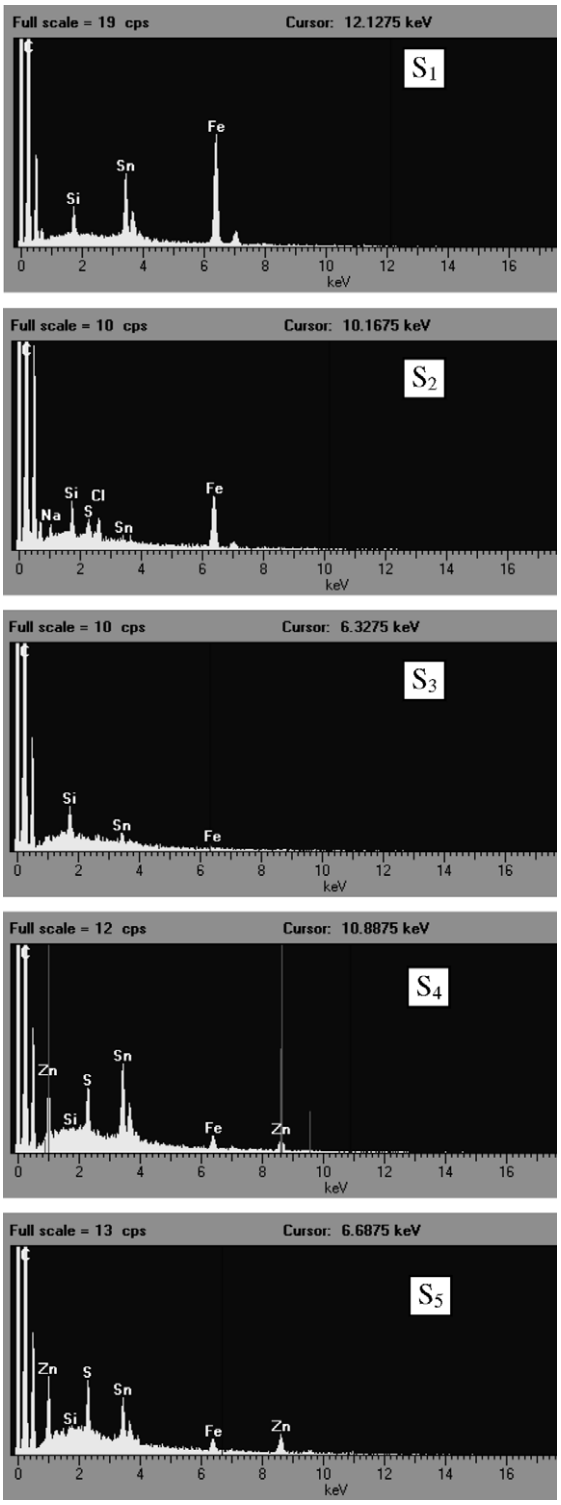

Fig. 2. EDS analysis of good (S_1, S_3) and defective (S_2, S_4, S_5) can walls.

Standard EN 10202, steel used for tin mill products normally contains various elements such as Mn, Cu, Ni, Sn, Cr, Mo and Si at different amounts (CEN, 2001).

With regard to Zn content, zinc paste is added to the epoxy-phenolic (E/P) or organosol type varnishes (in a proportion of 10 parts Zn paste to 100 parts of E/P lacquer) to increase the resistance to the sulfur containing protein products. The reason for the inclusion of zinc is that it reacts with the sulfur compounds to form zinc sulfide precipitates which cannot readily be detected against the background of the opaque lacquer (Warne, 1988).

Finally low values of Na^+ and Cl^- were recorded in the highly corroded seam (S_2) can samples, probably sorbed onto the corroded can wall surfaces while none of the two ions was recorded in the good and minimally damaged can samples. Given the presence of citric acid in the brine in this particular case of lacquer failure, steel corrosion is greatly enhanced.

3.2. EIS study

Electrochemical impedance spectra of all five can samples are given in Fig. 3 in the form of Bode plots. The principle behind this study is that a perfectly protected (lacquered) tin plate is expected to behave as a pure capacitor, due to the dielectric (insulating) properties of the lacquer. According to the ac theory (Macdonald, 1987), a

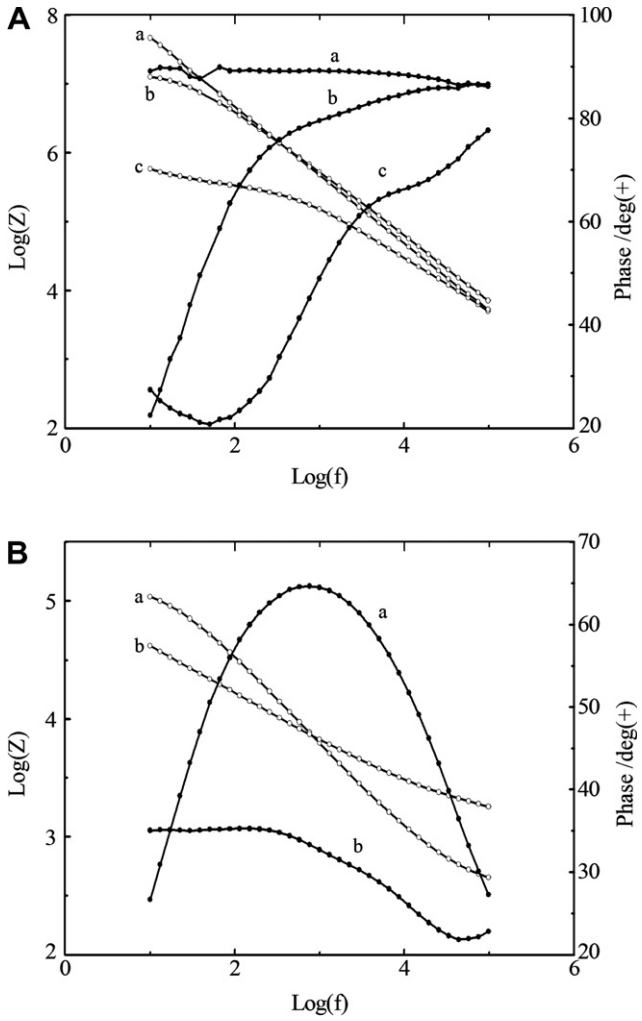

Fig. 3. Bode plots of (A) S_3(a), S_4(b), S_5(c) and (B) S_1(a), S_2(b) tinplated can-based electrodes. *Impedance values* (it empty circles); *Phase values* (*filled circles*).

metal covered with an undamaged coating exhibits has a high impedance and the bode blot of this sample (metal/dielectric coating) is a straight line with a slope of -1[Log(Z) = f(Log(f)) plot], whereas the phase angle [phase = f (Log(f)) plot] reaches 90° over a wide frequency range. This is the condition in the case of sample S_3 (Fig. 3A, curve a) indicating that undamaged lacquer on internal can walls provides an ideal protection of the base metal.

In the case of a damaged coating, water penetrates into the coating and forms a new liquid/metal interface under the damaged area with corrosion phenomena being initiated at this new interface. In this case the behavior of the system is not purely capacitive as a resistive element (R), parallel to the capacitor (C), is thus introduced. Each RC circuit with a specific time constant, $\tau = RC$, appears as a bell-shaped peak in the phase plot (the maximum value of phase angle does not reach 90°, as it would for a pure capacitive impedance) and also causes a change of the slope of the impedance plot. In case of rejected samples S_4 and S_5 (Fig. 3A, curves b and c, respectively) more than one time constants are visible and this behavior is characteristic of coating failure.

The effect of the mechanical stresses applied during the formation of the seam on the quality of the coating in the area of the side seam is clearly shown in the Bode plot in Fig. 3B, curve a. Even though visual and microscopic examination of the sample shows that the coating is uniform and compact, the pattern of the spectrum, as compared to that of Fig. 3A, curve a, indicates that it does not fully protect the base metal from the solution of the electrolyte. This situation is also reflected by comparison of Log(Z) values of S_1 and S_3 samples, that is, 5.2 vs. 7.8 Ohm, at 10 Hz, respectively. An extensive damage of the lacquer in sample S_2 is also confirmed by EIS data shown in Fig. 3B, curve b. Indeed, the behavior of the tested sample at the low frequency range ($f < 300$ Hz) is almost resistive. The recorded impedance plot is parallel to the x-axis (frequency) showing that there is no dependence of its value by any capacitive component according to the equation $Z = (2\pi fC)^{-1}$.

4. Conclusions

The present work shows that SEM–EDS along with EIS can be used very effectively to analyze can corrosion, lacquer failure and metal can doscoloration defects in enameled food containers. It is worth mentioning that this is the first time that EIS has been used for direct quality control of tinplated cans. Electrodes based on intact areas of the internal can walls exhibit an almost ideal dielectric behavior (impedance curve is a straight line with a slope of –1 and phase reaches 90° over the entire tested frequency range), which can safely be distinguished from those observed for electrodes based on defected areas. In addition, EIS succeeded in identifying the insufficient protection provided by the lacquer at stressed areas of samples that showed no evident defect after visual and microscopic examination.

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