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Investigation of fish product–metal container interaction using scanning electron microscopy–X-ray microanalysis

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Abstract

Scanning electron microscopy (SEM) and X-ray microanalysis (EDS) were used to investigate metal can discoloration and lacquer adhesion failure in enameled food cans containing tuna in vegetable oil and octopus in brine, respectively. Black and brown spots on the internal surface of the can body were caused by the formation of FeS and SnS, respectively. The source of metal can discoloration was traced to inadequate lacquering of the tin plated steel, exposing both tin and iron to sulfur containing amino acids originating from the tuna product. Enamel adhesion failure in canned octopus was also traced to local defects in the lacquer coating enabling both NaCl and citric acid contained in the brine to cause enamel blisters on the can body leading to lacquer peeling and in turn to local detinning and steel corrosion. The first defect known as "sulfide staining" is harmless to human health and does not usually affect the product. The second defect may cause extensive detinning and steel corrosion possibly affecting the safety of the canned product. This postulation is supported by iron and tin concentrations both in the product and liquid medium carried out by atomic absorption spectroscopy.

Keywords: Scanning electron microscopy; X-ray microanalysis; Discoloration; Enamel adhesion failure; Tin plated cans

1. Introduction

Despite the recent trend for consumption of minimally processed or "fresh" foods there is still a significant portion of foodstuffs that becomes available to the consumer in the form of canned products (meat and fish products, soups, mixed fruit salads, fruit juices, condensed milk, etc.) (Kraus & Tarulis, 1997). Scientists both in industry and government, through stringent quality control procedures ensure that billions of canned products reaching the consumer annually are in excellent condition. Occasionally, however, metal containers develop integrity problems while the can undergoes early failure through corrosion, loss of seal integrity or may develop discoloration problems that cause its rejection by the consumer (Charbonneau, 1997).

The parties involved in such instances are usually a food processor and a supplier of the food packaging material. It is of primary importance for both parties in cooperation to quickly determine the cause of such problems in order to prevent their recurrence.

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 black spots on both the internal surface of the can body and occasionally on the product surface, pitting corrosion involving

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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).

Degree of enamel failure, i.e., enamel blistering and subsequent peeling depends on numerous 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) and of course composition of the contained product (acid foods, sulfur and/or salt containing foods, etc.) (Barilli, Frangi, Gelati, & Montanari, 2003; Montanari, Pezzani, Cassara, Quaranta, & Lupi, 1996).

Recently scanning electron microscopy (SEM) in combination with X-ray microanalysis (EDS) have proven to be a powerful and effective tool to investigate the many causes of corrosion in metal food containers (Charbonneau, 1999, 2001). The objective of the present work is to show how SEM/EDS can be used to determine the cause of two recent cases of sulfide black corrosion development and enamel adhesion failure respectively in tin plated food cans.

2. Materials and methods

2.1. Materials

Two batches of canned tuna in soy oil were provided by a local fish processor marked as follows: A (good product; with no discoloration on internal can walls) and C (rejected product; with black spots on internal can walls and can bottom end). Cans were cylindrical (83 mm diameter × 38 mm high), two piece, made of tinplate internally lacquered (epoxy including phenolic and amino moieties), externally printed, bearing an easy open (EO) top containing 104 g of tuna in 56 g soy oil. According to the food processor canned products were retorted at 121 °C for 30 min.

Cans were opened and examined for sensory defects in the product (color, off-odor, off-taste) and visible defects in the can (discoloration, scratches, etc.) internally on both the walls and the top/bottom ends. Based on the above observations, four different can samples were prepared: A (sample with no defects on can or product), B (same as A which was intentionally scratched using a knife on the internal wall surface), C (can bearing large black and brown spots internally on can walls) and D (can bearing a series of small black spots on the internal surface of the bottom end).

Respective two batches of canned octopus in brine, provided by the same fish processor, were marked as follows E (good product; with no enamel adhesion failure) and F (rejected product; with internal enamel adhesion failure on can walls). Cans were of the same dimensions as above, made of tin plated steel, internally lacquered (epoxy including phenolic and amino moieties) externally printed, bearing an easy open top containing 96 g of octopus in 64 g natural brine (NaCl and citric acid). According to the food processor canned products were retorted at 121 °C for 30 min.

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°), working distance (20 mm) and emission current (80 μA). Analysis was focused on the specific areas of interest with an appropriate zoom.

2.3. Cysteine test (Anonymous, 1977)

A and C type can samples (12 samples of each) were filled with a test solution consisting of 0.5 g of cysteine chloride (Merck No. 2839) in 1 L of buffer solution (3.56 g KH_2PO_4 (Merck No. 4873) and $Na_2HPO_4 \cdot 2H_2O$ (Merck No. 6500) in 1 L of distilled water). Cans were sealed and retorted for 30 min at 125 °C. They were then left to cool down at room temperature for 24 h and were cut open and evaluated for color formation according to the following scale: 1 – very weak, 2 – weak, 3 – moderate, 4 – strong, 5 – very strong. Top, bottom and can walls were evaluated separately.

2.4. Atomic absorption spectroscopic analysis

Iron and tin were determined on a Perkin–Elmer model AAnalyst 700 atomic absorption spectrophotometer using graphite furnace accessories.

Standard curves for iron and tin were constructed, by fixed dilutions of a stock solution containing 20 μg L^{-1} for each metal yielding a linear range in the concentration region of 1–10 μg L^{-1} for iron and 1–20 μg L^{-1} for tin. In every case that the sample concentration exceeded the linear range, the sample was automatically diluted to bring its concentration within range.

3. Results and discussion

3.1. Sulfide black discoloration

Results of the SEM/EDS analysis of the four different can samples are given in Table 1.

Table 1
Elemental analysis using SEM-EDS of can samples

Element	Atomic, %			
	Sample A (good)	Sample B (intentionally scratched)	Sample C (bearing black and brown spots)	Sample D (bearing black spots)
C	81.4	0	97.5	97.0
Al	15.9	0	0.5	2.0
Sn	1.0	13.2	0.4	0.1
Ti	1.1	0	0.1	0.1
Fe	0.6	86.8	1.1	0.6
S	0	0	0.4	0.2
Total	100	100	100	100

Data in Table 1 clearly show very low values for Fe and Sn in the "good" (A) can sample obviously due to adequate protection provided by the lacquer. A high value for C is owed to the C content of the organic lacquer it self. It must be mentioned here that the values found for carbon represent rough estimates and not precise calculations simply presented in order to indicate their abundance. The value for Al is also owed to the lacquer, which contains Al based additives. Data recorded for the "scratched" sample support the above assumption, since values for C and Al become nil due to destruction of the lacquer. As a result of the destruction of the lacquer coating a 140-fold increase in iron was recorded due to its exposure. Respective increase in tin values was 13-fold.

The presence of a small amount of titanium should also be attributed to the lacquer, since it is totally absent in sample B, in which lacquer has been removed, and it exists at an almost 10-fold lower amount in samples C and D where the lacquer has been damaged. Titanium was probably used as a dopant in the lacquer, aiming

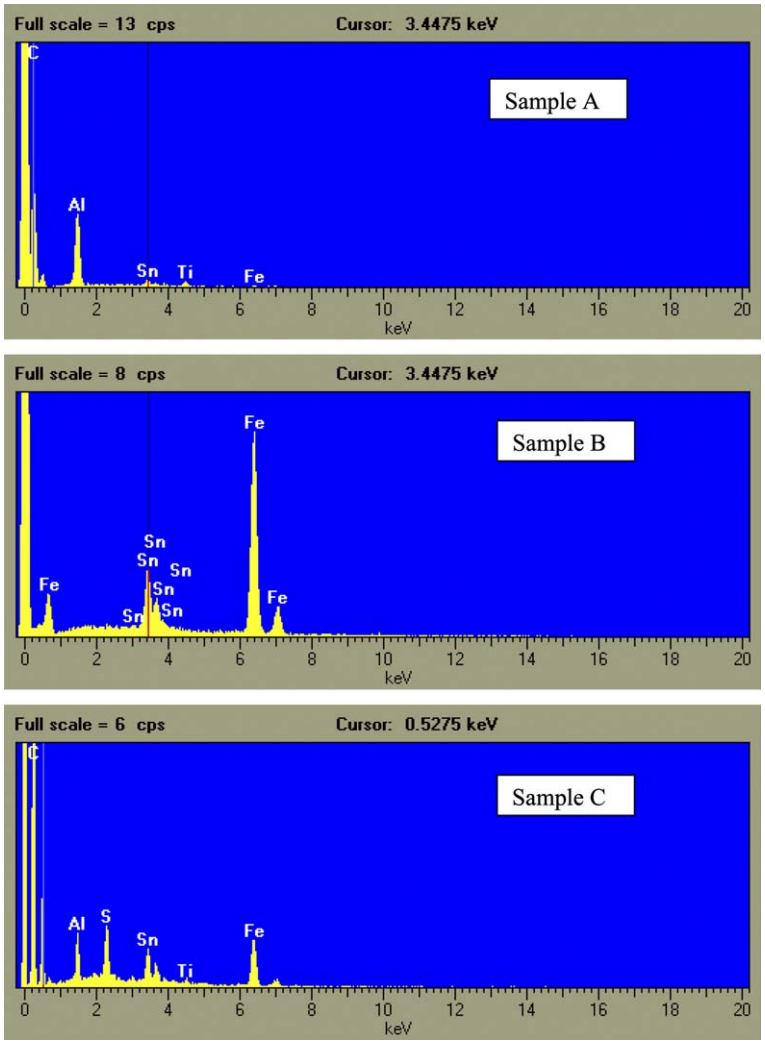

Fig. 1. SEM of images of (A) good, (B) intentionally scratched and (C) defective cans.

to the enhancement of the protective (insulating) properties of the latter, or in order to increase the adhesion of the lacquer to can walls, or for improving the mechanical strength of the coating.

The appearance of black and/or brown corroded areas on the internal wall may be attributed to lacquer failure, as in both C and D samples, Al value considerably decreased. Considering that any defects of lacquer result in iron and tin exposure, in combination with the appearance of an extra peak in the EDS spectra (Fig. 1), attributable to sulfur, we can safely support that black spots are the result of reaction between exposed tin from the container with sulfur containing compounds from the product to form black FeS precipitate. Similarly, brown spots are the result of reaction between exposed tin from the container and sulfur to form a brown SnS precipitate. Sulfur compounds such as sulfur containing amino acids are a typical breakdown product of fish protein during intensive thermal treatment (retorting). Increase of the C content (17–51%) over the black and/or brown corroded areas is an extra evidence for the presence of amino acids or breakdown product of proteins.

Above results, which are also presented as SEM images (Fig. 1) are further supported by microscopic data which clearly show black and brown corroded areas on the internal walls of the defective cans (C)

Fig. 2. Sulfide staining on internal walls of defective (C) cans.

Fig. 3. Intentionally scratched (B) can.

(Fig. 2). The results of scratching internal walls of intact cans is shown in Fig. 3.

To further test above postulation the cysteine test was carried out on A and C samples. Fig. 4 clearly shows black spots composed of FeS formed through the reaction of cysteine with exposed iron on can internal walls due to lacquer failure. Discoloration was noted only on can internal walls and was evaluated as "very strong". Good (A) can samples produced no discoloration at all due to adequate protection provided by the lacquer.

Iron and tin content of product packaged in samples A and C are given in Table 2. Values in Table 2 indicate that there is a 1.5-fold increase in iron content and a 2-fold increase in tin content of tuna fish and soy oil, respectively, in the rejected product owed to local destruction of internal can coating (enamel) exposing iron and tin, respectively, to the product environment. 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.

3.2. Enamel adhesion failure

Data in Table 3 clearly show low values for iron and tin in the "good" (E) can sample obviously due to

Fig. 4. Sulfide staining on internal walls of defective (C) cans using the "cysteine" test.

Table 2
Concentration of Fe and Sn in good and rejected product

Sample	Metal concentration	
	Fe	Sn
Tuna, good product (μg g^{-1})	62[a]	2.8
Soy oil, good product (μg g^{-1})	22	1.8
Tuna, rejected product (μg g^{-1})	90	6.0
Soy oil, rejected product (μg g^{-1})	38	3.6
Octopus, good product (μg g^{-1})	160	17
Aqueous brine, good product (μg g^{-1})	87	3
Octopus, rejected product (μg g^{-1})	750	122
Aqueous brine, rejected product (μg g^{-1})	520	20

[a] Mean of six determinations (2 batches × 3 determinations/batch).

adequate protection provided by the lacquer. High values for carbon are owed to the carbon content of the organic lacquer itself. The aluminum and titanium content are also owed to the lacquer containing aluminum- and titanium-based additives. Data also show approximately a 78-fold increase in iron and a 7-fold increase in tin content owed to the local exposure of iron and tin, respectively, due to enamel adhesion failure.

In this particular case it is postulated that due to incomplete enamel coating resulting in the formation of local pores or cracks, citric acid (known for its high detinning potential) made its way through such pores or cracks on the enamel surface and caused local detinning of the can wall resulting in tin migration into the contained product and solution. As tin is dissolved the underlying iron is exposed, initiating corrosion of the can wall and simultaneous migration of iron into the contained product and solution. This postulation is further supported by iron and tin content of the product (octopus) and brine shown in Table 4. That is, in the "bad" product (F) there was a 5–6-fold increase in iron content of both the product (octopus) and the brine as compared to the "good" (E) product. Respective increase for tin was 7-fold, with the tolerance level of tin in the EU being 200 mg/kg wet weight of product, for cans containing food (Commission Regulation 242/2004).

Table 3
Elemental analysis using SEM-EDS of good (E) and defective (F) can samples

Element	Sample E	Sample F
C	80.5	0.0
Al	16.5	0.0
Sn	0.7	4.5
Ti	1.1	0.0
Fe	1.2	95.5
S	0	0
Total	100.00	100.00

Loss in enamel adhesion may be rationalized as follows: enamel adhesion is owed to: (a) hydrogen bonds formed between enamel reactive groups (i.e. –OH) and oxygen present on the steel surface (Hamilton & Ibers, 1968; Resnik, 1993, 1997) that is, enamel

$$\mathrm{OH}\cdots\mathrm{O}-\mathrm{metal(Fe)}$$

and (b) secondarily to electrostatic attractions between enamel and metal. The canned product itself, high in sulfur containing amino acids creates a highly reducing environment liberating electrons (e^-) in the brine medium. Such free electrons react with water in the brine according to reaction (1) producing hydroxyl ions

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1)$$

Hydroxyl ions bind to both the enamel and the metal causing a reduction in electrostatic attraction between the enamel and the metal. In parallel Na^+ (originating

Table 4
Concentration of Fe and Sn in good (E) and rejected (F) product

Sample	Metal concentration	
	Fe	Sn
Octopus, good product (μg g^{-1})	160[a]	17
Aqueous brine, good product (μg g^{-1})	87	3
Octopus, rejected product (μg g^{-1})	750	122
Aqueous brine, rejected product (μg g^{-1})	520	20

[a] Mean of six determinations (2 batches × 3 determinations/batch).

Fig. 5. Enamel adhesion failure on internal walls of defective (F) cans.

from the NaCl in the brine) move towards the vicinity of the enamel failure and form NaOH in the presence of excess OH^-. The NaOH formed accumulates on the metal surface causing migration of water molecules from the brine to the metal (due to osmosis phenomena) causing the formation enamel blistering around initial pores or cracks on the enamel surface (Doherty & Sykes, 2004). As blistering advances, enamel adhesion failure is observed (Fig. 5). Given the presence of citric acid in the brine in this particular case steel corrosion is greatly enhanced.

According to Charbonneau (1997) 10 out of 15 incidents of enamel adhesion failure studied by National Food Processes Association (NFPA) involved canned fish, chicken, clams and cheese, all products rich in proteins (–SH). In this particular case incomplete lacquering of the can created a major enamel adhesion failure problem given the specific product composition (sulfur containing amino acids, NaCl and citric acid).

4. Conclusion

The above investigations indicate that SEM–EDS can be used very effectively to analyse can corrosion defects as well as enamel adhesion failure in enameled food containers especially when combined with other food analytical methods.

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