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APPLICATION OF SCANNING ELECTRON MICROSCOPY AND X-RAY MICROANALYSIS TO INVESTIGATE CORROSION PROBLEMS IN PLAIN AND ENAMELLED THREE PIECE WELDED FOOD CANS

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Abstract

Scanning Electron Microscopy (SEM) and X-Ray Microanalysis (EDS) have been used to investigate rapid detinning, pitting corrosion and cosmetic corrosion in plain tinplate food cans and pitting corrosion, underenamel corrosion, enamel flaking, sulfide black corrosion and stress corrosion cracking in enamelled food cans.

Through the use of SEM-EDS it was determined that $(SnL\alpha/FeK\alpha)^{1/2}$ X-ray line intensities are proportional to the tin coating weight on tinplate. The method was applied to a rapid detinning problem in canned grapefruit sections. The cause of the early corrosion failure was found to be reversed tinplate. An early pitting corrosion failure in apple sauce packed in plain tinplate cans was related to use of tinplate sensitive to pitting corrosion in combination with a product containing oxygen and nickel as corrosion accelerators. An internal rusting cosmetic corrosion problem present on the inside tinplate ends of canned mushrooms was caused by exposed steel at lightly tinned surface ridges of tinplate reacting with moisture and oxygen in the product. An early pitting corrosion problem in carrots packed in enamelled cans was related to excessive metal exposure at the side seam weld and at various areas on the can body. An underenamel corrosion and enamel flaking problem in canned pet food was caused by the inadvertent use of black plate instead of tin free steel. A sulfide black corrosion problem on the tin free steel ends of canned minced clams may be related to enamel fracture. A stress corrosion cracking problem in canned pet food may be related to can coating integrity and copper residues in the product.

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Key Words: Scanning Electron Microscopy, X-ray Microanalysis, Tinplate Food Cans, Early Corrosion Failure, Pitting Corrosion, Welded Food Cans, Enamelled Tinplate, Plain Tinplate, Tin Free Steel.

Introduction

The canned food industry has an excellent record of providing a safe and wholesome product to the consumer. This is no accident. Food technologists are attentive to the safety of the food supply and ensuring that canned food reaches the consumer in excellent condition is part of the responsibility of the packaging corrosion specialist.

Occasionally internal can corrosion develops within the metal food container and the container either undergoes early failure or develops discoloration of the can surface which is objectionable to the consumer. The corrosion specialist must try to determine the cause of the problem and take steps to prevent its recurrence. This involves both troubleshooting and research. When a corrosion problem develops in canned food, the NFPA is frequently asked to provide an independent third party evaluation of the cause of the problem. Some corrosion problems affect canned foods worldwide and cooperative international research investigations are needed to resolve the problem. The recently completed Can Manufacturers Institute-American Iron and Steel Institute-Foreign Steel Maker-National Food Processors Association Research Program addressing the cause of early failure of canned light colored fruits packed in cans fabricated from aluminum-killed continuous-cast steels, is an excellent example of mutual team work to resolve a highly complex corrosion problem (Kamm and Hotchner 1989).

Corrosion problems in canned food may be caused by a tinplate that is sensitive to corrosion, a can manufacturing practice that is faulty or a food product that is abnormally corrosive. The chemistry of the food product is the least understood cause of inside corrosion. This is because foods contain many compounds which have been largely untested for their corrosion promoting potential. Much better understood is the influence of ingredients that the packer may add to his product or the effect of canning practices that the packer uses to produce the canned product. Table 1 lists control actions that the packer should take to prevent corrosion losses from both internal and external can corrosion (FPI, 1990).

In a recent paper it was shown that SEM-EDS is a powerful investigative tool to diagnose the causes of canned food corrosion problems, especially when combined with food analytical procedures (Charbonneau, 1988). It is the intent of this paper to expand on that earlier paper by describing typical

corrosion problems that occur in canned food and, by giving examples through case histories, show how SEM–EDS can be used to explain these manifestations of corrosion.

Materials and Methods

Materials

Tinplate and Tin Free Steel. Tinplate, tin free steel and nickel plated steel are the materials used to manufacture metal food cans. Metal can making technology (types of cans, trends and selection factors) has been reviewed (Kopetz, 1978). In this paper, only corrosion processes that occur in three-piece welded cans (fabricated from plain and enamelled tinplate and tin free steel) will be considered.

Tinplate defined. (Beese and Ludwigsen, 1974; AISI, 1979) Tin cans are made from a special grade of low carbon, cold rolled steel which is generally referred to as a tin mill product. The base steel is cleaned electrolytically and plated with tin. It is then passed through a melting tower to melt and reflow the tin to form a shiny tin surface and tin–iron alloy layer. The plate is then chemically treated to prevent oxide growth and lubricated with a thin layer of a Food and Drug Administration (FDA)-approved synthetic oil.

In specialized "K" plate, a nearly continuous tin–iron alloy layer improves the corrosion resistance of tinplate for mildly acid products.

The tin coatings on tinplate can be purchased in thicknesses ranging from 0.31 to about 1.54 μm. Tinplate may be equally coated with tin on both sides or it may be differentially coated with a different tin coating weight on each side. Tin coating weight can be expressed in pounds per basis box or grams/square meter. As an example, 1.00 lb/bb equally coated tinplate carries 0.5 lb/bb (11.2 g/m^2) per side and 1.00/0.50 lb/bb differentially coated carries 0.50/0.25 lb/bb (11.2/5.6 g/m^2) per side. 1.00 lb/bb (both sides) is equivalent to 11.2 g/m^2 on each side which corresponds to 1.54 μm tin on each side.

Tinplate can be purchased in a wide range of tempers and thicknesses. Thicknesses ranging from 0.15 to about 0.38 mm are commercially available (ASTM A624M). The chemistry of the base steel is carefully regulated to control physical properties and corrosion resistance.

Tin Free Steel (TFS) Defined. (Beese and Ludwigsen, 1974) Electrolytic chromium coated steel is an alternate for tinplate. It is designated TFS–CT (tin free steel–chromium type) or TFS–CCO (tin free steel–chromium-chromium oxide). The chromium-chromium oxide coating is approximately 0.02 μm thick, a factor of about 10 thinner than the tin coating on tinplate. This material can be used for many products where the cathodic protection usually supplied by tin is not needed, but must be protected with an organic coating on both surfaces. Organic coatings adhere exceptionally well to TFS. TFS is used to fabricate can bodies and ends.

Tin Free Steel–Can Maker's Quality (CMQ). This is the basic tin mill product. CMQ is commonly referred to as black plate. The surface may or may not be passivated. It has borderline corrosion resistance before and after enamelling. Containers for dry products can be fabricated from CMQ. It also is always used with the additional protection of an organic coating.

Organic Coatings (FPI, 1990). The inside or outside of the food container may be coated with an organic coating or lacquer. The coatings are applied to cans for several reasons: (1) To prevent inside and outside corrosion; (2) To minimize cost of the container; (3) To serve as a lubricant in the production process providing mobility and fabricability; (4) To provide decoration to the can exterior.

Hundreds of coatings are available to the can maker. Coatings are selected for use on the basis of which will give the best performance for the lowest cost. Table 2 summarizes the types of coatings used on the inside of food cans and rates their product resistance and fabricability properties. (FPI, 1990) The combination of flexibility and hardness of the organic film and coating surface lubricity work together to make a coating fabricate well.

Table 1. Recommended Actions To Control Container Corrosion.

To Control Inside Corrosion

1. Avoid high temperature storage (where possible).
2. Minimize O_2 during can closing.
3. Minimize nitrates (water < 5 ppm NO_3).
4. Avoid sulfites, sulfur containing fungicides.
5. Acidify with the *right acid* at the *right level*.
6. Avoid heat abuse to products—Heat induced reactions produce corrosion accelerators.
7. Use correct level of azo dye food colors.
8. Minimize chloride levels in fruits packed in duplex cans.
9. Avoid metal contamination of product by copper and nickel.
10. Avoid scratches on lacquered cans and fractured die codes —use ink jet coding.
11. Q. C. incoming cans and lids for metal exposure. Develop mutually acceptable metal exposure limits with the can maker.
12. Retain unused material for future corrosion evaluation if a problem develops.
13. Do not reformulate the product without first checking with the can maker, NFPA, or other resources if the change will influence the corrosivity of the product.

To Control External Corrosion

1. Maintain seaming equipment to avoid scratches on cans and coatings.
2. Remove rust buildup in retorts and on retort baskets.
3. Dry cans thoroughly.
4. Store finished products in a non-corrosive, non-sweating environment.
5. Store empty cans and box board materials in a dry non-corrosive environment.
6. Treat high and low pH waters. Avoid water high in chlorine, chlorides and sulfates.

Methods

SEM–EDS Analysis. An Amray 1600 T SEM and a Kevex 8000 X-ray Microanalysis system equipped with a Kevex Extra detector were used to examine corroded and uncorroded specimens.

Qualitative Analysis of Corroded Specimens. Corroded areas were located, cut from the can, mounted and examined as is or sputter coated with carbon using a Polaron Sputter coater Model E5100. Either secondary or backscattered electron images were obtained. EDS analysis was performed at an acceleration voltage of 2OkV either in the beryllium or ultra thin window mode. The EDS spectrum was examined for the presence of corrosion accelerators.

Table 2. Summary of Interior Food Coating Types.

Type	Product Resistance	Fabricability
Oleoresinous	Fair to Good	Fair to Good
Phenolics	Superior	Poor
Oleo/Phenolics	Good to Excellent	Fair
Epoxy Amino	Good	Good
Epoxy Phenolics	Excellent	Good
Epoxy Acrylates	Good	Good
Epoxy Acrylate/ Phenolics	Excellent	Good
Solution Vinyls	Excellent	Excellent
Dispersion Vinyls (Organosols)	Good to Excellent	Excellent
Polyesters	Excellent	Excellent

Quantitative Analysis of Tinplate for Tin Coating Weight. When a corrosion problem develops, the tin coating weight on the inside of the can must be checked to see if it meets the specification. Too low a tin coating weight may result in an early corrosion failure. The usual way of determining the tin coating weight on a partially detinned can is to (1) measure the tin that has dissolved from the coating into the food; (2) determine the amount of tin from the original tin coating that remains on the plate; and (3) combine the amounts of tin in (1) and (2) and determine the initial tin coating weight. This procedure gives a good approximation to the original tin coating weight but it is time consuming.

SEM-EDS is particularly useful to determine tin coating weights on corroded samples because it is rapid and the determination can be made on small non-corroded areas, perhaps protected by a side seam stripe or under the can double seam on the body hook or on uncorroded areas in the headspace area of the can.

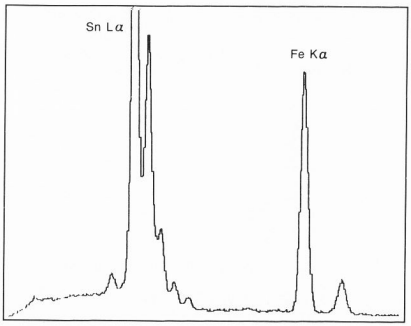

Figure 1. EDS Spectrum of 0.25 lb/basis box (2.8 g/m²) tin coating.

SEM-EDS Method For Tin Coating Weight

Sample Preparation

An uncorroded area inside the can was located. A striped area near the side seam weld is a good location to check for a suitable sample. The stripe was removed from the area being tested. Chloroform and methyl ethyl ketone were useful as solvents to remove the stripe. The unknown sample was cut from the can. Samples and tinplate standards were mounted on the same aluminum stub using sticky tape. Test areas were about 5 mm × 10 mm.

Standards. The standards were commercial tinplate samples with a range in tin coating weight from 0.25 to 1.0 pounds per basis box (2.8 to 11.2 g/m²). The standards were flat plate and were obtained from the tinplate industry.

Quantitation

An EDS spectrum was acquired for the unknown sample and each of the standards under identical conditions of specimen tilt (34°), working distance (12 mm), emission current (150 μa), and acceleration voltage (20 kV). The count rate was held at 3,000 cps to avoid the 2 × Si sum peak (Winstanley, 1986). The Kevex detector was operated in the Beryllium window mode. Figure 1 shows a typical EDS Spectrum for 0.25 pounds/basis box (2.8 g/m²) tin coating.

For the sample and each standard, the peak intensities of the tin Lα and iron Kα peaks including background acquired in 300 seconds was measured. A standard curve was constructed by plotting $(\text{Sn L}\alpha/\text{Fe K}\alpha)^{1/2}$ *vs.* standard values of tin coating weight. The concentration of the unknown was determined from the standard curve. Figure 2 shows a typical standard curve. The standard curve has good linearity.

In practice, a single standard close in tin coating weight to the unknown can be used instead of a standard curve. The procedure does not measure the actual tin coating weight directly but probably measures the screening effect that the tin coating has on the penetration of the electron beam into the steel base.

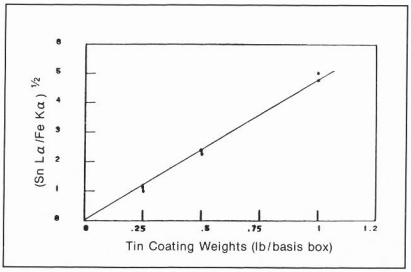

Figure 2. Standard Curve—
Tin coating weight *vs.* $(\text{Sn L}\alpha/\text{Fe K}\alpha)^{1/2}$.

Figure 3. Smooth continuous tin coverage on 1.00 lb/basis box (11.2 g/m²) tin coating. Bar = 100 μm.

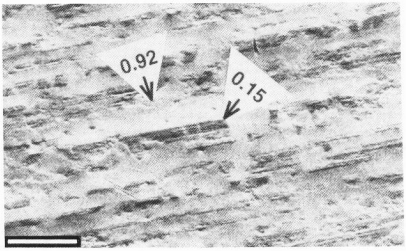

Figure 4. Areas of light and heavy tin coverage on 0.50 lb/basis box (5.6 g/m²) tin coating. Bar = 100 μm.

If the surface of the tinplate is smooth as in Figure 3, the determination of tin coating weight can be made at varying magnifications. However, if the surface is not smooth as in Figure 4, a magnification must be chosen to represent the entire surface. In Figure 4 areas like (0.15) are lightly tinned areas. A tin coating weight of 0.15 pounds/basis box (1.7 g/m²) was found at area 0.15. At area (0.92) the tin coating weight was found to be 0.92 pounds/basis box (10.3 g/m²). At 100× magnification a tin coating weight of 0.5 pounds/basis box (5.6 g/m²) was found, which agrees with the known tin coating weight. Working at 100× magnification appears to be a good choice for the samples that have been examined using SEM–EDS.

Tin Coating Weight. A Stannomatic V Electronic Tin Coating Analyzer (Wilkens Anderson Co., Chicago) was used to determine tin coating weight. The tin and the $FeSn_2$ alloy was electrolytically dissolved from a 6.5 cm² surface of tinplate. Two numerical counters compute the results as a function of the current used for the electrolysis. The results are displayed simultaneously by two four digit panel displays.

Trace Metals

The trace element content of the samples was determined using Inductively Coupled Plasma Spectrometry (ICP). The ICP used was an Instrumentation Laboratories Plasma sequential unit with an air path and vacuum monochromator allowing operation over the range 160–800 nm. Sample flow rate was 1.0 ml/min (peristaltic pump) into a cross-flow nebulizer.

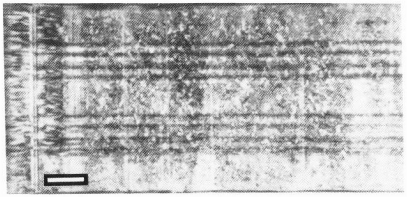

Figure 5. Inside surface of a No. 303 (8.1 cm in diameter) tinplate can during the first year of storage at 77 °F. The white areas are tin crystallites. Bar = 20 mm.

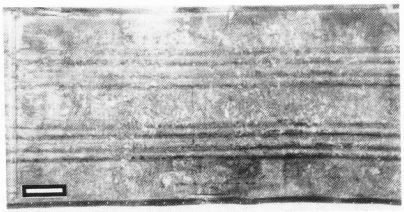

Figure 6. Inside surface of a No. 303 (8.1 cm in diameter) tinplate can after 1½–2 years of storage at 77 °F. Gray areas of exposed base plate are visible. Bar = 20 mm.

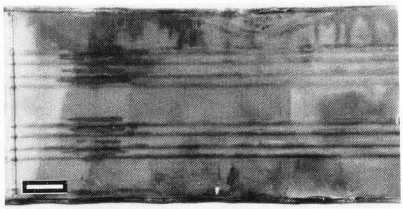

Figure 7. Inside surface of a No. 303 (8.1 cm in diameter) tinplate can after many years of storage at 77 °F. Nearly all the tin has gone from the container walls. Bar = 20 mm.

Results and Discussion

Case histories of typical corrosion problems that occur inside plain tinplate and enamelled tinplate cans are discussed. The samples examined were supplied by the canned food industry.

Part I.
Corrosion Investigations in Plain Tinplate Food Cans.

Normal Corrosion Process. The normal corrosion process inside plain tinplate food cans is slow, even detinning of the tinplate surface. Figure 5 shows how the can should look during the first year of storage at room temperature (77 °F). The tin crystal boundaries should become clearer during the first year of storage.

Gray areas of exposed base plate shown in Figure 6 should be visible only after 1½–2 years of storage at 77 °F.

Figure 7 shows how the inside of the can will look after many years of storage. Nearly all the tin has gone from the container walls. Note that the cans shown in Figures 5, 6 and 7 have soldered side seams. The detinning pattern on the body of the cans will be the same for cans with a welded side seam construction.

Rapid detinning and pitting corrosion are the two types of corrosion that cause early failure in plain tinplate cans.

Case History No. 1—Rapid Detinning

When rapid detinning occurs, tin quickly dissolves from the container walls. The inside of the can may be completely detinned and looks like Figure 7 in as early as 3 months. If hydrogen is evolved into the can headspace and the can vacuum drops as detinning occurs, the process is called rapid electrolytic detinning. If no hydrogen evolves and the vacuum remains unchanged during detinning, the process involves non-galvanic direct attack on the tin.

Nearly 20% of the corrosion problems that the NFPA has investigated during the 1980s have been rapid detinning in canned fruit and vegetables.

The causes of rapid detinning may be: (1) a fast corroding steel; or (2) an abnormally corrosive product. The presence of depolarizers like oxygen, nitrate, sulfites and organic acids like fumaric acid are known to promote rapid detinning problems; and (3) a tin coating weight that is too low.

In case history No. 1, too low a tin coating weight explained the cause of an early failure by rapid detinning.

Description of Problem. No. 303 (454g) canned grapefruit sections packed in 1987 developed hydrogen swells in less than a year. The inside of the cans were completely detinned and looked like Figure 7. There was no side seam stripe and the side seam area was also detinned. There were several packing dates involved in the problem. Conditions of underfilling, low fill temperature and side seam leakage which resulted in excessive oxygen inside the can explained the detinning in many of the containers. There was one particular packing date however where none of these factors explained the detinning. The can specification for the containers was: Type L steel, aluminum-killed-continuous cast (AK–CC), Continuous annealed, T-5 Temper, 75 pounds/nominal basis box (0.21 mm thick). The tin coating weight specified was 1.00/0.20 pounds/basis box with the heavier 1.00 (11.2 g/m²) side on the inside of the can.

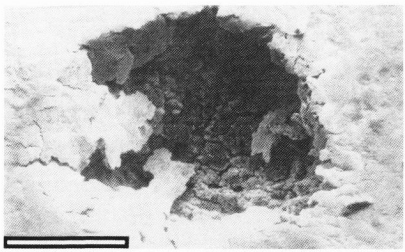

Figure 8. A typical corrosion pit on the inside body bead of a plain tinplate container undergoing early failure by pitting corrosion. Bar = 100 μm.

The outside of several of the cans was tested for tin coating weight using the Stannomatic procedure and found to be approximately 1.00 pounds per basis box (11.2 g/m²). A non-corroded inside area on the body hook under the double seam was located by inspection and analyzed for tin coating weight using SEM–EDS. A value of 0.33 pounds per basis box (3.7 g/m²) was measured. This is an example of *reversed tinplate* with the lighter coating being inadvertently used on the inside of the can. It's rare, but when it happens rapid detinning usually follows.

Case History No. 2—Pitting Corrosion

A second early failure mechanism inside plain tinplate cans is either pitting corrosion or partial detinning and pitting corrosion. Early failure may occur in as little as 3 months by either hydrogen swell or by perforation. If the failure mechanism is pitting corrosion, there is no detinning and the tinplate surface inside the can may be as bright as the day the product was packed. If the surface is examined with a microscope, corrosion pits may be seen on the body beads, on the bead crests or at the side seam weld, or perhaps a thin line of pitting may be seen on the can wall in the headspace area of the can.

Figure 8 shows an SEM photo of a typical corrosion pit. At the corrosion pits, iron dissolves into the product and hydrogen evolves into the can headspace.

If the failure mechanism is partial detinning and pitting, both the tin and the steel are attacked simultaneously and hydrogen is produced at the corroded areas.

About 6% of the corrosion problems investigated by NFPA since 1980 have involved early failure of plain tinplate cans by either pitting or partial detinning and pitting corrosion. The food industry worldwide can add many other incidences of pack failures with the light colored fruit.

The causes of pitting corrosion may be (1) a corrosion sensitive steel and (2) an abnormally corrosive product. Oxygen, sulfur dioxide, organic acids and trace metals are known to promote pitting corrosion. (FPI, 1990)

In case history No. 2, oxygen, a corrosion sensitive plate and nickel contamination of the product appear to explain the cause of a pitting corrosion problem in canned apple sauce.

Description of Problem. Early corrosion failure by pitting corrosion occurred in an 1989 apple sauce pack. Pinholes through the can body developed within 4 months from the date of pack. Several thousand cases of No. 303 (454 g) canned product were involved. The product was packed at two canning plants, one in New York and one in Michigan. The problem was more severe at the New York plant.

The can specification was: 0.50/0.25 pounds per basis box

(5.6/2.8 g/m²) K plate tin coating, plain tinplate bodies with a basis weight of 65 pounds/nominal basis box (0.18 mm thick). The covers were 80 pounds/nominal basis box (0.22 mm thick)

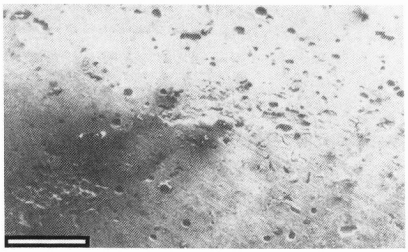

Figure 9. A typical pitted and stained area on the headspace walls of a can that contained apple sauce. Bar = 1,000 μm.

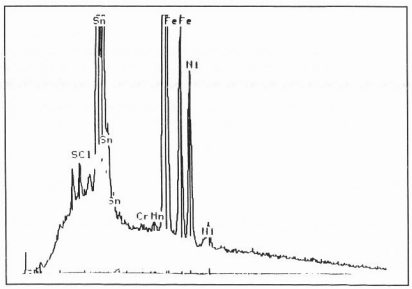

Figure 10. EDS spectrum of the corroded area in Figure 9.

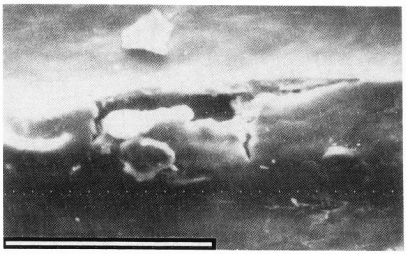

Figure 11. A pitted area on an enamelled tin free steel end that was in contact with apple sauce. Bar = 100 μm.

enamelled tin free steel. The bodies were made from DR8-batch annealed-aluminum-killed continuous cast steel.

The same lots of tinplate were used to make cans for both apple sauce packs. A second lot of tinplate from a different can supplier performed much better and had a very low incidence rate of pitting corrosion.

Oxygen. The puncture vacuums at the time of the corrosion exam varied between 0–10 inches Hg for samples from the New York plant and 11–15 inches Hg for samples from the Michigan plant. Samples with almost no pitting corrosion at the New York plant had puncture vacuums of 10 inches Hg and under. This indicates that the puncture vacuums at the time of pack were probably 10 in. Hg and under. This agrees with company records. The differences in puncture vacuum would suggest that the canned product at the New York plant would have had more dissolved oxygen and would be more at risk of pitting corrosion than the product canned at the Michigan plant.

Corrosion Sensitive Steel

Aubrun *et al.*, (1989) have reported that the deformation of tinplate by stretching during can making produces microcracks in the steel a few micrometers deep. The sensitivity to pitting is reported to be a function of microcrack density. The authors used SEM to measure the microcrack density. They define the microcrack density as the average number of microcracks present in 3 SEM fields in the steel in an area 10 mm × 0.05 mm (0.5 mm²) at 2,000× magnification. The area tested was either parallel to a bead in a formed can or at an area on unformed tinplate which had been stretched to simulate beading. Both the cans and the unformed tinplate used to produce the canned apple sauce have been tested for microcrack density and found to be sensitive to pitting corrosion. The microcrack density of the failed cans was approximately 100/0.5 mm².

Nickel Contamination

The cans were examined for corrosion using an optical microscope. Most of the pitting was characterized by a few deep pits on the body beads. These pits would have eventually pinholed through the container. Some of the code lots from the New York canning plant had multiple corrosion pits on the walls of the can in the can headspace. These pits occurred in clusters some of which were associated with partial detinning and black colored staining of the tinplate. Figure 9 shows a typical cluster of corrosion pits.

Tinplate samples were analyzed using SEM–EDS. The corrosion pits below the product line were mostly empty of corrosion deposits. Trace levels of sulfur and chloride were found in and around the pits. In contrast corrosion pits in the black stained areas in the can headspace were high in nickel. Figure 10 shows an EDS spectrum of the one of stained areas. Traces of nickel were also detected in corrosion pits on the enamelled tin free steel ends in complaint samples from both packing locations. Figure 11 shows a pitted area on one of the tin free steel ends.

Samples of the apple sauce were analyzed for trace metal content using inductively coupled plasma spectrometry (ICP). The results are listed in Table 3. Each sample represents a different code of product.

The level of iron and tin in the product is an indicator of the amount of corrosion inside the can. The results indicate that there is much more iron from pitting corrosion in the New York

Table 3. Trace Elements in Apple Sauce by ICP. Elements in Parts Per Million.

Sample	Ni	Fe	Sn	Na
	New York			
1	20.0	176	29	235
2	18.8	40	14	282
3	16.4	26	10	263
4	13.9	24	17	200
5	13.7	26	14	455
6	13.7	14	8	172
7	6.7	20	37	5
8	5.6	7	29	5
9	8.1	5	27	2
10	0.1	19	46	4
	Michigan			
11	2.8	7	33	96
12	2.5	4	34	99
13	1.8	3	18	56
14	1.1	12	34	8
15	0.9	8	21	6
16	0.6	2	21	4

samples compared to the Michigan samples. The tin content is relatively low for all samples which agrees with the visual finding that pitting corrosion was the main mechanism of early container failure.

The nickel content of the samples varied between 0.1–20.0 ppm. The higher nickel contents are associated with the higher iron levels. The New York samples were significantly higher in nickel than the Michigan samples. Sample #10 with 0.1 ppm nickel is a control sample from an apple sauce pack canned in 1988. This pack did not have early corrosion. When this sample was opened in 1989, after a period of somewhat longer than 1 year of storage, some pitting corrosion had evidently occurred based on the elevated iron content of the sample.

The sodium content of the samples is generally higher in samples with high iron and nickel. New York samples with low sodium were from a diet pack whereas samples with sodium levels >172 ppm were from the regular apple sauce pack. In preparing apple sauce for canning, apples are flumed from one product preparation station to another. The fluming solution was sodium chloride for the regular pack and ascorbic acid for the diet pack. The source of the high levels of sodium is likely the salt solution used during fluming.

The source of the nickel is likely the thermatator tube from the scrapped surface heat exchanger through which the apple sauce was conveyed during product processing. A nickel tube was used at the New York plant.

What appears to have happened is that the salt fluming solution attacked the nickel tubing and the nickel dissolved into the apple sauce. The sodium chloride fluming solution is more corrosive to nickel than ascorbic acid, and this probably explains why higher levels of nickel were found in the regular pack samples compared to the diet samples.

Significantly less nickel was found in the Michigan samples. A stainless steel tube, not nickel, was used at this plant and no corrosion of the stainless steel apparently occurred.

The reason why nickel should attack tinplate is not clear. It may be that like copper it plates out on tinplate surfaces and causes pitting of the steel. (Charbonneau, 1988).

In case history No. 2, pitting corrosion appears to be the result of a corrosion sensitive steel combining with a product of abnormal corrosivity. Product corrosivity was apparently increased by oxygen and nickel.

Case History No. 3—Cosmetic Corrosion

Cosmetic problems sometimes occur inside plain tinplate cans or rusting occurs on the outside of the cans that result in unsightly discolorations or stains on the tinplate. The main types of cosmetic corrosion that develop on plain tinplate cans are headspace detinning (Board and Steele, 1975), tin sulfide staining (Britton, 1975), milkplate staining and asparagus staining (Carter and Helwig, 1969; Laubscher, 1963), mushroom staining and internal and external rusting (FPI, 1990). These problems do not normally lead to early pack failure. They are costly because they often lead to consumer complaints.

About 5% of the problems that NFPA has investigated over the past decade have been cosmetic corrosion. This does not include cosmetic corrosion problems that occur in conjunction with early failure corrosion mechanisms.

In case history No. 3, excess oxygen reacted with lightly tinned areas on tinplate, causing a rusting problem inside canned mushrooms.

Description of Problem. No. 10 (1.93 kg) canned mushrooms developed rust deposits on the inside packer's end within about a month after canning. The problem occurred on a small percentage of the production. The can body and the packer's end were plain tinplate. The tin coating weight was 75/20 pounds per basis box (8.4/2.2 g/m^2). The can company ends were tin free steel.

Figure 12 shows rust on one of the tinplate lids. The rust covered a major portion of the lid surface. The pronounced parallel lines in Figure 12 are normal identification marks for differential tin coating weights. Figure 13 shows a rust stained area. Figure 14 shows the area with the rust removed. The site of rusting appears to be ridges in the tinplate that are lightly coated with tin compared to surrounding areas. (See Figure 4). The EDS spectrum of the stained area contained a major oxygen peak and trace levels of sodium, phosphorus, and chloride besides iron and tin from the tinplate. The source of these elemental components is the food product.

Figure 15 shows X-ray maps for a rusted area. The presence of white areas indicates the presence of a particular element. Oxygen, tin, and iron (many white areas) are distributed over the rusted surface, whereas sodium and chloride are localized in the rust (few white areas). Phosphorus is present at a low level and the phosphorus map is mostly background. The X-ray map in Figure 16 shows the distribution of oxygen (indicated by black rectangles) over the rusted surface. This internal rusting problem appears to be due to an excess level of oxygen in the can

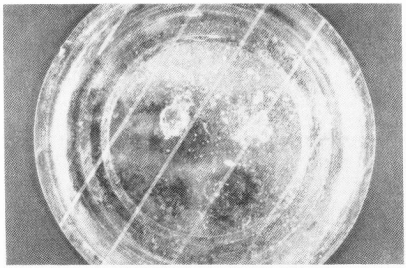

Figure 12. Rust deposits on the inside surface of a tinplate can end after contact with mushrooms for one month.

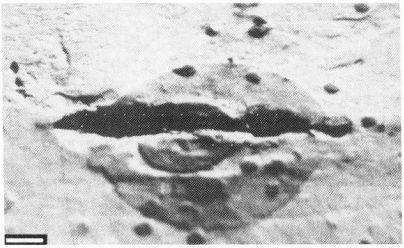

Figure 13. A rust stained ridge area in Figure 12. Bar= 10 μm.

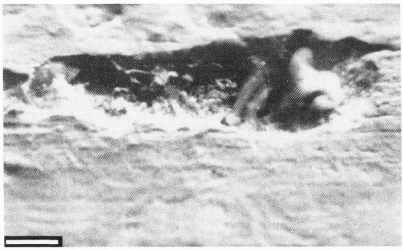

Figure 14. A corrosion pit under the rust in Figure 13. Bar=10 μm.

which attacked the tinplate. The point of attack was the lightly tinned ridges of the plate. The problem can be prevented by using enamelled tin free steel instead of tinplate and taking steps during canning to reduce oxygen.

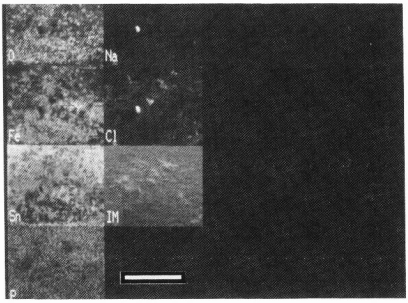

Figure 15. X-ray maps for oxygen, iron, tin, phosphorus sodium, chloride and the image at a typical rusted ridge in Figure 13. Bar=100 μm.

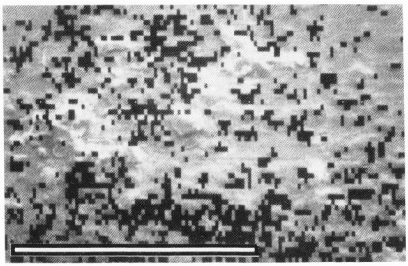

Figure 16. X-ray map for oxygen from Figure 15. Bar=100 μm.

Corrosion in Enamelled Cans

Normal Corrosion Process in Enamelled Cans

The normal corrosion process in enamelled cans is slow corrosion attack of the steel at microscopic pores in the organic coating (Collenteur, 1971). Hydrogen is produced during the corrosion process. The can eventually fails by hydrogen swell or pinhole corrosion after two or more years of storage at 77 °F. Unlike in plain tinplate cans, tin does not offer sacrificial protection to the steel. In enamelled cans, tin's protection is more mechanical than electrochemical.

Abnormal Corrosion

Corrosion in enamelled cans occurs at metal exposed areas in the organic coating wherever they occur in the can. Areas include the side seam, the body beads, the profile rings on the ends and the die code. There are four manifestations of corrosion in enamelled cans that lead to early failure.

- Pitting Corrosion
- Underenamel Corrosion and Enamel Flaking
- Sulfide Black Corrosion
- Stress Corrosion Cracking

Case History No. 4—Pitting Corrosion

Pitting corrosion involves rapid iron dissolution at fractures or pores in the organic coating. Early failure occurs by pinholing or hydrogen swell. Pitting corrosion in enamelled cans is the type of corrosion most frequently encountered in the food industry. Since 1980 almost 50% of all corrosion problems investigated by NFPA have been pitting corrosion in fruits, vegetables, fish and dairy products packed in enamelled cans. About 50% of these problems have been with green and wax beans. Some of the pitting corrosion problems occurred in products that are not traditionally known for pitting corrosion. For example, peas and tomatoes.

In Case History No. 4 excessive metal exposure explains an early failure problem in canned carrots by pitting corrosion.

Description of Problem. The packer experienced sporadic corrosion for a number of years especially No. 303 (454 g) and No. 10 (2.98 kg) canned carrots. The inside can bodies were 0.20 pounds/basis box (2.2 g/m²) tinplate coated with C-enamel containing zinc oxide. The ends were tin free steel. The welded side seam was striped. Failure was by hydrogen swell and pinhole corrosion in about one year. Corrosion was found to occur extensively at the weld area and along the beads.

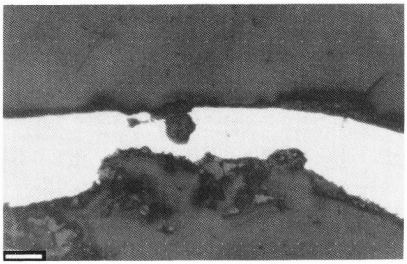

Figure 17. Cross section of a corroded section near the side seam weld of a can that contained carrots. Bar = 100 μm.

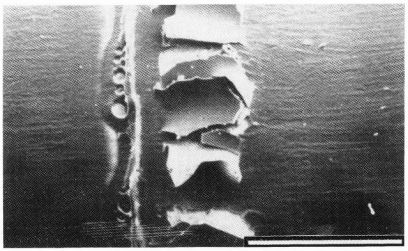

Figure 18. Fractured Enamel at a typical weld area. Bar = 1,000 μm.

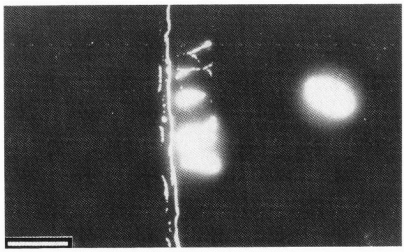

Figure 19. Backscattered electron image showing metal exposure at a typical weld area. Bar = 1,000 μm.

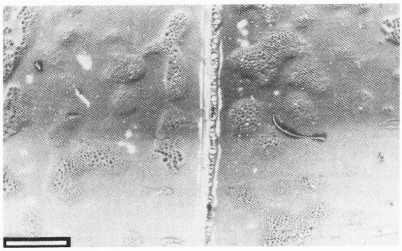

Figure 20. Backscattered electron image showing enamel blistering and metal exposure at a typical weld area. Bar = 1,000 μm.

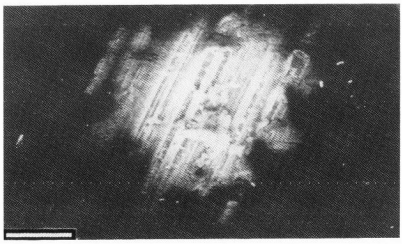

Figure 21. Backscattered electron image showing metal exposure at a typical area on the body. Bar = 100 μm.

Figure 17 shows a cross section of a corroded section near the weld. Figures 18–21 show the types of metal exposure present at the weld and along the beads on unused cans. Figure

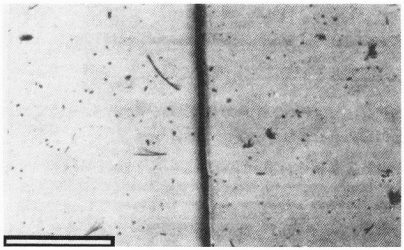

Figure 22. Backscattered electron image showing good metal coverage at a typical weld area. Bar=1,000 μm.

18 shows fractured enamel at the weld. Figure 19 is a backscattered electron image showing metal exposure at the weld. The backscatter detector is very useful for locating metal exposed areas. Figure 20 shows enamel blistering and metal exposure along the weld. Figure 21 shows metal exposure on the can body.

The cause of the premature corrosion failure in the canned carrots was excessive metal exposure. The packer worked with the can supplier to improve the coating integrity. Figure 22 shows the results of their effort. Almost no metal exposure is visible in the backscattered electron image at areas along the side seam weld and the problem was resolved.

Case History No. 5—
Underenamel Corrosion and Enamel Flaking

Underenamel corrosion is detinning or staining through the enamel film. Underenamel corrosion resulting in an overall etching of the tinplate is expected with some products and is acceptable. However, localized underenamel corrosion can lead to enamel lifting and flaking and to early failure by hydrogen swell. About 10% of the corrosion problems that NFPA has examined in the past decade were underenamel corrosion. The same corrosion accelerators in the product that promote detinning in plain tinplate cans will accelerate detinning at the weakened enamel areas. Figure 23 shows underenamel detinned areas on a can that contained a tomato product. This is the condition of the can after 92 days at 100 °F storage temperature. Figure 24 shows underenamel corrosion at the side seam of a can.

In Case History No. 5 the inadvertent use of black plate explains an early corrosion failure in canned pet food.

Description of Problem. In 1989 an enamel adhesion and corrosion problem developed on the food contact surface of can ends shortly after packing canned pet food. Tin free steel ends with organic coating protection on both sides were specified. The outside of the failed ends had a distinct brownish color compared to the gray color of the control ends. The organic coating on the ends was removed by soaking the ends in concentrated sulfuric acid. The problem ends oxidized quickly after the coating was removed. Oxides of various colors formed. The control lids did not oxidize.

Figure 25 shows an EDS spectrum of the control lids and

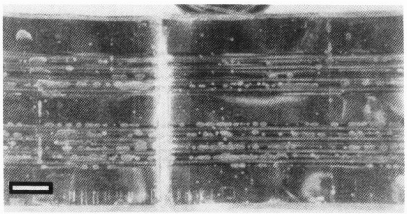

Figure 23. Underenamel detinned areas after 92 days at 100 °F on the inside of a No. 303 (8.1 cm in diameter) tinplate can that contained a tomato product. Bar=20 mm.

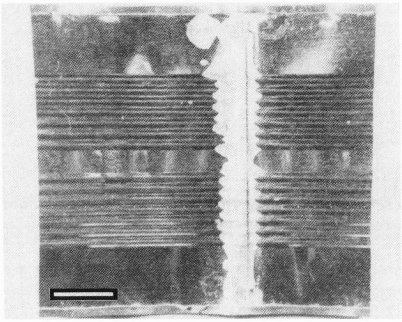

Figure 24. Enamel lifting and underenamel corrosion at the side seam of a No. 303 (8.1 cm in diameter) tinplate can that contained a vegetable product. Bar=20 mm.

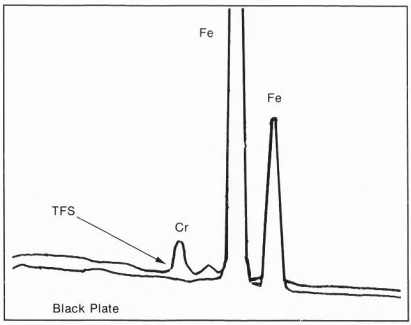

Figure 25. EDS spectrum of black plate (no chromium) lids that corroded in contact with canned pet food. TFS lids with chromium passivation gave good performance.

the defective lids. The chromium X-ray peak which is characteristic of chromium coated tin free steel is present in the control sample. The problem sample had no chromium. The failed lids are enamelled black plate which gives good performance with dry products but should not used with aqueous foods because of its borderline corrosion resistance. A brown appearance forms during enamel baking of this material.

Case History No.6.—Sulfide Black Corrosion
(Charbonneau, 1978)

Sulfide black formation is the result of rapid iron dissolution from the container. Black deposits may form as early as 24 hours after processing. Sulfide black is not a health hazard nor does it normally cause early corrosion failure, but similar to staining in plain tinplate cans, it may cause consumer complaints. Figure 26 shows a blackened lid from a No. 10 (2.98 kg) can that contained peas. In canned vegetables the problem is almost exclusively a headspace phenomenon usually confined to No. 10 ends (15.7 cm in diameter).

Figure 27 shows black deposits in a can that contained shrimp. Sulfide black sometimes occurs solely in the headspace of canned seafood but black deposits are generally found on interior surfaces throughout the container. All can sizes commercially used for packing seafood are susceptible to the problem.

During the 1980s, about 5% of the corrosion problems examined by the NFPA were sulfide black corrosion.

In Case History No. 6, metal exposure on the profile rings of the ends may explain a sulfide black problem in canned minced clams.

Description of Problem. In 1987 a sulfide black problem developed in canned minced clams. The cans were fabricated with welded tinplate bodies and tin free steel ends. The enamel on the inside surfaces contained aluminum. The black deposits were mainly present on the profile ring closest to the center of the lid. The deposits appeared to adhere tightly to the surface. No black deposits were found in the product.

Figure 28 shows the presence of black deposits at an area on the profile ring. The enamel was fractured at this point.

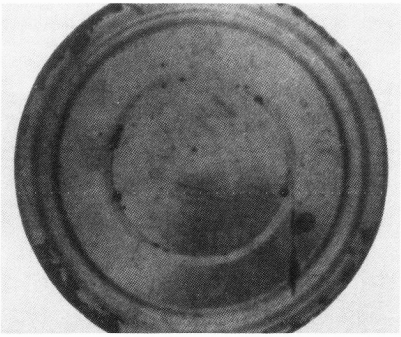

Figure 26. Sulfide black on a No. 10 tinplate lid (15.7 cm in diameter) from a can that contained peas.

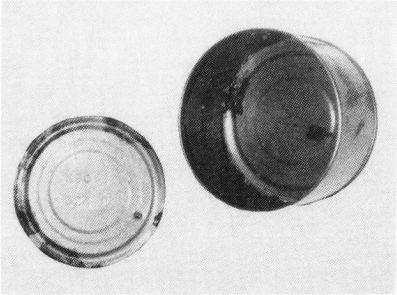

Figure 27. Sulfide black deposits in a 307×113 (8.7 cm in diameter) tinplate can that contained shrimp.

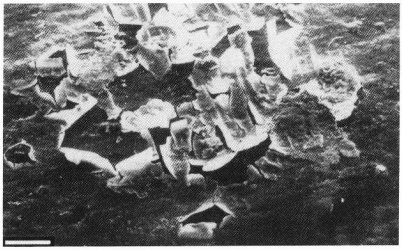

Figure 28. Sulfide black deposits at an area on the profile rings of a lid from a can that contained minced clams. Bar = 100 μm.

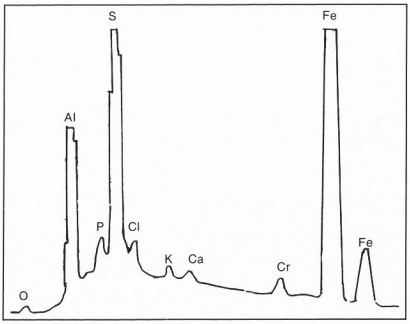

Figure 29. EDS spectrum of sulfide black deposits in canned minced clams.

Figure 29 is an EDS spectrum of the black deposits. The deposits contain mainly iron and sulfur and trace levels of oxygen, phosphorus, chloride, potassium and calcium and chromium. The iron and chromium are from the tin free steel lid. The aluminum is from the organic coating. The other elements are from the product. Sulfides, oxides and phosphates of iron have been identified in sulfide black deposits. The elemental profile of the deposits in the clam cans is consistent with this composition. Black deposits sometimes contain no sulfide. The name "sulfide black" is somewhat of a misnomer, but this type of corrosion has been around since the beginning of canning and this was name given at that time. The composition of the deposits appears to vary probably depending on what anions are available to iron when the corrosion starts during processing and cooling of the canned product.

Figure 30. Stress corrosion cracks at the weld on the inside of a can that contained pet food. Bar = 100 μm.

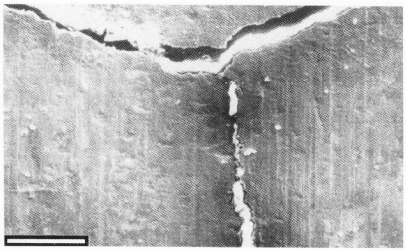

Figure 31. Stress corrosion crack near the weld on the outside of a can that contained pet food. Bar = 100 μm.

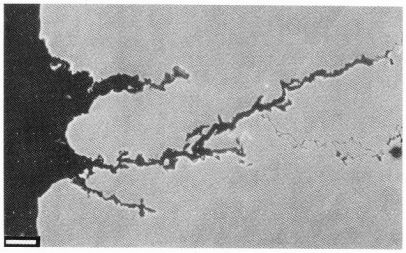

Figure 32. Branched stress corrosion crack in the cross section of a tin free steel lid from a can that contained potatoes. Bar = 10 μm.

Although the severity and incidence of the problem can be reduced by controlling headspace volume, can vacuum, and acidification of the product, the best preventative measure is to reduce metal exposure by proper choice of the sanitary enamel system. In Case History No. 6, it is possible that the enamel was susceptible to fracture at the profile ring but this diagnosis was not possible without examining unused lids and none was available.

Case History No. 7—Stress Corrosion Cracking (S.C.C.)

Stress Corrosion Cracking involves corrosion at stressed points in the container. Areas worked during fabrication (die codes, profile rings, body beads, and welded side seam) are key areas for S.C.C. to occur. S.C.C. may occur in as early as 3 months after packing or may not develop until after about 2 years of storage. Less than 5% of the corrosion problems investigated by NFPA during the last decade have involved S.C.C.

In Case History No. 7, copper probably from the product may have promoted S.C.C. Upgrading coverage appears to control a S.C.C. problem in canned pet food.

Description of Problem. In 1987 a S.C.C. problem developed in No. 300 (425 g) canned pet food. S.C.C. developed along the unrepaired (no side seam stripe) side seam. The cracks were mostly transverse to the weld, but some were longitudinal to the weld. Some cracking also occurred on the tin free steel ends. The problem developed in canned cat food but not in canned dog food. The can bodies were fabricated from tinplate. The can ends were enamelled tin free steel.

Figure 30 shows a S.C.C. at the weld viewed from the in-

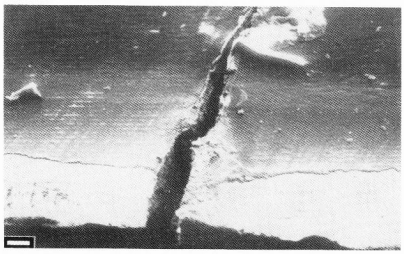

Figure 33. Stress corrosion crack on a tin free steel lid from a can that contained pet food. Bar = 100 μm.

side of the can. Figure 31 shows a part of the crack with corrosion deposits viewed from the outside of the can near the weld.

Figure 32 shows a S.C.C. in the cross section of an enamelled tin free steel lid from a can that contained potatoes. The crack has a branching pattern which may or may not be associated with S.C.C. Fractures in pet food cans only rarely have branched S.C.C.'s.

Tin, iron, calcium and potassium were major components in the EDS spectrum of the corrosion deposits. Smaller amounts of magnesium, silicon, sulfur, and copper were also present. Phosphorus varied from small to major depending on the area of the crack examined.

Figure 33 shows a crack in a tin free steel end. The same elements were present in the EDS spectrum of the end as in the weld cracks except no magnesium, silicon or copper were found. Corrosion deposits and product samples were analyzed to determine whether product ingredients influenced the corrosion.

The corrosion deposits along the weld from a can that contained cat food were dissolved using a cotton swab soaked in hydrochloric acid. Trace elements were analyzed using ICP Spectrometry. Al, Cr, Sn, P, Fe, Mn, Co, Ni, Ca, Cu, Zn, Na, K, and Mg were present. A non-corroded area at the weld from a can that contained dog food was analyzed as a control. The same elements were found. Only copper showed a significant difference. Copper was present at a level of 0.5 ppm in the corrosion deposits compared to 0.04 and 0.15 for control samples.

One dog food sample and a selection of cat food samples were analyzed for trace elements. The same 14 elements were found as in the corrosion deposits. Copper and iron were the only elements that appear to be different. Table 4 shows the iron and copper results. The level of copper generally is higher where the level of iron is higher. The source of the iron is likely from corrosion at the weld. The source of the copper is probably the product although the weld areas also contain copper residue from the wire welding during can making. These results may suggest that copper promotes S.C.C. but the mechanism is unknown. Chloride, phosphate, sulfide, sulfate and nitrates did not relate to S.C.C. The can specification was changed by adding a side seam stripe to the weld and by generally upgrading the organic coating.

Table 4. Iron and Copper Content of Canned Pet Food.

Sample	Fe (ppm)	Cu (ppm)
1	56	1.4
2	13	0.9
3	10	0.3
4	9	1.5
5	6	0.1
6	5*	0.1
7	2	N.D.

* Dog Food; N.D. = not detected

Concluding Remarks

Scanning Electron Microscopy together with X-ray Microanalysis, either by itself or in combination with food analytical procedures, is an excellent technique to investigate and diagnose the many causes of corrosion in plain and enamelled metal food containers.

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Discussion with Reviewers

E. J. Helwig: Comment concerning the reproducibility of the standard curve for tin coating weight and the applicability of the SEM method to analyze the lowest commercial tin coating weights of 0.05 lb/bb (0.6 g/m²) and 0.1 lb/bb (1.1 g/m²).
Author.: For commercial tin coating weights in the range 0.20–1.0 lb/bb (2.2–11.2 g/m²) the SEM method appears to be reproducible with the calibration line going through the origin. Samples of reflowed (alloyed) tinplate with tin coatings of 0.05 lb/bb (0.6 g/m²), 0.10 lb/bb (1.1 g/m²) and unreflowed 0.15 lb/bb (1.7 g/m²) were obtained from the tinplate industry and analyzed by SEM with the following results:

lb/bb	$(\text{Sn L}\alpha/\text{Fe K}\alpha)^{1/2}$
0.05	0.58
0.10	0.72
0.15	1.04

This data was reproducible. The calibration was linear except that it had an intercept on the Y axis, $(\text{Sn L}\alpha/\text{Fe K}\alpha)^{1/2}$, of approximately 0.2. It was necessary to subtract background from the Sn Lα and Fe Kα peak intensities. It appears that the SEM should be applicable to the full range of commercial tin coating weights.

E. J. Helwig: Case History No. 2—The role of nickel in pitting corrosion of tinplate cans has not, to my knowledge, been reported by other investigators. Has nickel played a similar role in other pack failures?
Author: I'm aware of one other instance where nickel was thought to promote pitting corrosion and this is unpublished. The pack failure was with canned green beans. Unlike the applesauce, where nickel ranged between 1–20 ppm, trace levels of nickel less than 1 part per million were involved in the green bean pack failure.

D. R. Hultberg: Case History No. 2—Were any headspace analyses conducted to determine levels of sulfur-bearing compounds in good or bad performing containers?
Author: No.

D. R. Hultberg: With regard to the black staining: Can you comment whether or not the nickel found in the stained areas was in the form of a nickel sulfide compound? What is your opinion about the potential effects of nickel sulfide (and, perhaps, a tin sulfide) compound on the corrosion observed on these samples?
Author: Note that in Figure 10 sulfur was present in the EDS spectrum of the nickel containing deposit. Nickel sulfide may be present, but we have not determined the form of nickel in the deposits. Assuming that nickel or tin is present as sulfides, the source of the sulfide would likely be the product including the sweetener. Small amounts of sulfur dioxide (SO_2) are sometimes present in corn sweeteners and when present in the canned product, SO_2 can react with tinplate, forming sulfides of tin and iron (Charbonneau, 1988). The presence of tin and nickel sulfide compounds on tinplate may passivate the tinplate surface and this may lead to localized pitting corrosion.

E. J. Helwig: Case History No. 7—The copper and iron data in Table 4 is intriguing, but not convincing. The high copper content in Sample 4 apparently didn't result in high iron pickup.
Author: I agree that the data don't show a strong trend. In analyzing commercial samples to determine the cause of a corrosion failure, one hopes that the samples examined are truly representative of the problem and that can to can variation is due to corrosion and not due to slight differences in product formulation. Pet food is a very complex food matrix with many nutrients added. It is conceivable that some of the variation in iron and copper may be due to can to can variation not related to corrosion.

Of the types of corrosion problems currently experienced in canned food, S.C.C. is considered by industry as the most worthy candidate for research. A joint industry program to investigate the causes of S.C.C. is being organized. Copper will be included in the list of product variables to examine under controlled test pack conditions.

P. Aubrun: Does "abnormal" corrosion in enamelled cans differ from "normal" corrosion by the size and origin of the metal exposed areas?
Author: Corrosion is "abnormal" when the shelf life of the canned product is significantly shorter than "normal" commercial expectations. Variations in product corrosivity, metal exposure wherever it occurs inside the can, and tinplate quality can lead to "abnormal" corrosion.

P. Aubrun: Figure 8 does not exhibit a pit but a cavern. The difference between a cavern and a pit is of significant importance for determining the mechanism of pitting corrosion. See my paper (Aubrun, 1990).
Author: In his paper, Aubrun proposes a very complex corrosion mechanism for the corrosion of tinplate cans containing pears. It was observed that the principles should be applicable to other light colored fruits. The formation of caverns and pits is part of the mechanism. They result from iron oxidation by carbon dioxide absorbed on tin. Figure 8 provides evidence that these caverns do exist. This particular cavern is not fully intact because the iron tin alloy shows only partial bridging over the cavern, *i.e.*, along the circumference of the hole. The transformation from a cavern into a pit, which is part of the proposed mechanism, is almost complete.