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Case Study – Analysis of Fractured Bottoms of Paint Cans

By Jozeti B. Gatti,* Silvia T. Dantas, Paula F. J. Bócoli and Murilo B. Masalskas

Packaging Technology Center – CETEA, Institute of Food Technology – ITAL, Campinas, Brazil

The purpose of this study was to determine the root cause of fracture in bottoms of rectangular 18 l cans of water-based acrylic paint used in the building industry and sold in retail. Following a change in the formulation of the inner coating of the cans, fractures developed in the double seams of the can bottoms, which were made of electrolytic chromium/chromium oxide-coated steel internally coated with pigmented varnish (epoxy melamine). Slight differences were detected in the infrared spectra of both the new and altered varnishes produced with the same base resin. The microanalysis of paint samples collected from both damaged and undamaged cans revealed presence of practically the same elements. The evaluation of the varnished surface of can bottoms revealed depressions in the varnish of all cracked bottoms, inclusive in the curved areas and bottom hook of the double seam, which did not get in direct contact with the paint. However, depressions were not detected in undamaged can bottoms. The metallographic analysis did not reveal significant differences between the microstructures of the metal of cracked or uncracked bottoms. The conclusion was that paint elements got in contact with the steel sheet in the defective spots of the varnished surface, thus starting punctual corrosion that evolved to stress corrosion with ensuing rupture. The stressing agent was the weight of the paint itself or else residual metal stress due to the change in its microstructure caused by the metal-forming process. Copyright © 2017 John Wiley & Sons, Ltd.

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KEY WORDS: stress corrosion cracking; steel can; fracture analysis; paint; electrolytic chromium/chromium oxide coated steel

INTRODUCTION

Product preservation is the key role of packaging; therefore, the concern about preserving goods is rising, partly owing to economic reasons (such as product recalls, damage to company reputation and lost sales) and partly owing to regulatory requirements to be met relating to distribution. Temperature and air humidity (pressure and speed), water (i.e. rain, moisture and other sources), radiation (sun and heat), chemicals and mechanically active substances such as dust and sand, the flora and fauna (microorganisms, rodents, insects, etc.), vibration (caused by traffic, handling, transportation, etc.), shock, fall, acceleration and electrostatic load, all of these, are possible effects caused by logistic processes that should be taken into account to preserve the goods.[1]

Besides the aforementioned issues, product loss may also be associated to defective primary packaging, which, in terms of savings, consumer confidence and environmental issues, may be detrimental to the industry as a whole. High added-value consumer products marketed in relatively large volumes, such as wall paints, have strong potential to damage other goods stored nearby in case of leakage and, as a consequence, make such goods improper to be marketed.

A common cause of failures in engineering materials, including packaging materials, is the phenomenon of stress corrosion cracking (SCC), which is a brittle fracture caused by the combined action of tensile stress and a corrosive environment.[2–5] According to Jones,[6] cracks extend as a result of the

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* Correspondence to: Jozeti B. Gatti, Institute of Food Technology – ITAL, Av. Brasil, 2880, 13070-178 Campinas, SP, Brazil.
E-mail: jozeti@ital.sp.gov.br

combined, synergistic interaction of mechanical stress and corrosion reactions. The combined simultaneous interaction of mechanical and chemical forces results in crack propagation where neither factor acting independently or alternately would produce the same effect.

Stress corrosion cracking does not require too much stress to occur. However, SCC does not occur if the stress lies below a critical value (threshold stress) that is usually below the tensile strength of the material. Stress can be either externally applied or else residual stress caused by cold work, induced by heating and cooling during heat treatment and welding, for example. However, compressive residual stresses (shot peening and burnishing) can be used to prevent this phenomenon. Static loading is usually considered responsible for SCC.[2,6]

Stress corrosion cracking in metal alloys is likely to take place in aqueous environments in the presence of specific chemical species. However, it depends on the material, temperature, pressure, degree of aeration and/or concentration of ionic species and activity, pH, electrochemical potential, viscosity solution, stirring or mixing.[7] In addition, an alloy may be immune in one heat treatment and susceptible in another treatment. SCC may develop in carbon steel when in contact with hot nitrate, hydroxide, carbonate/bicarbonate solutions and amine solutions, for example.[8] Amine cracking is predominantly intergranular and oxide filled.[9]

Stress corrosion cracking propagates along a specific path (active path) that can follow the grain boundaries or specific crystal planes within the grains. This way, stress corrosion-induced cracks may be intergranular, transgranular or mixed (combining intergranular and transgranular morphology). Anodic and cathodic mechanisms have been proposed to explain the synergistic stress–corrosion interaction that takes place at the crack tip and leads to crack propagation. According to these mechanisms, cracks initiate at the surface flaws of localized concentration of tensile strength (trenches, pits, accidental dents, notches and pre-existing cracks).[2,6] According to literature, after the formation of microcracks in the service time, the macroscopic crack will gradually appear.[7]

The purpose of this study was to determine the root cause of fracture in bottoms of 18 l cans of water-based acrylic paint used in the building industry and sold in retail. Information on normal conditions of the steel composition and mechanical characteristics were previously available. The bottoms of cans containing either white or colour wall paint developed cracks that caused the paint to leak approximately 7 months after canning. The cracks were located on the radius of the double seam countersink and always started in the rolling direction. The can bodies were made of tinplate, and the ends were made of electrolytic chromium/chromium oxide-coated steel (ECCS).

MATERIALS AND METHODOLOGY

Materials

The assessment included

- Can bottoms manufactured with electrolytic chromium/ECCS and coated inside with grey epoxy melamine varnish removed from 18 l cans containing acrylic paint used in the building industry. The can bottoms cracked approximately 7 months after canning. The chemical composition of the steel was

Maximum levels (%)									
C	Mn	P	S	Si	Cu	Ni	Cr	Al*	Others
0.13	0.60	0.03	0.03	0.03	0.20	0.15	0.10	0.08	0.02

- Undamaged can bottoms;
- White water-based acrylic paint packed in damaged and undamaged cans containing titanium dioxide, aluminium silicate, silicon dioxide, calcium carbonate, amines, dimethyl urea and ethylene glycol, pH range: 8.7–9.2.

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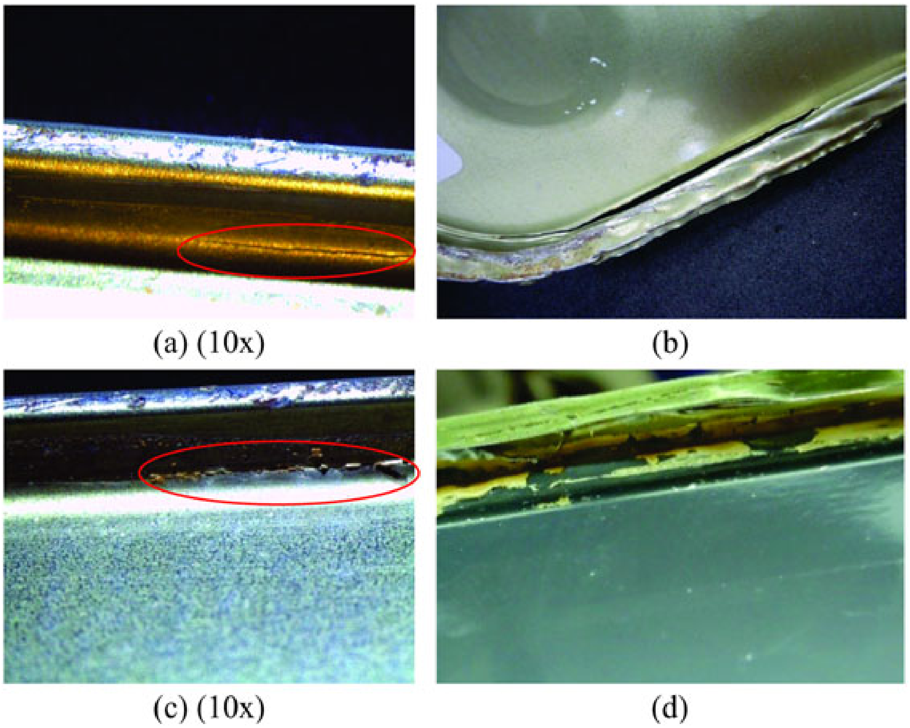

(a) (10x) (b)

(c) (10x) (d)

Figure 1. Photographs taken of an area of a cracked can bottom: (a and b) outside and (c and d) inside the damaged can.

Methods

A Spectrum 100 spectrometer Perkin Elmer (Waltham, Massachusetts, USA) was used to identify the varnishes applied to the inner side of can bottoms via infrared spectroscopy, employing the technique of attenuated total reflectance spectroscopy with direct analysis of the varnish coat of the metal sheet. Two determinations were performed with each sample of varnish.

The scanning electron microscopy (SEM) analyses and energy dispersive X-ray (EDX) microanalyses of the paints and of the specimens taken from can bottoms were conducted on Zeiss, model DSM 940A,

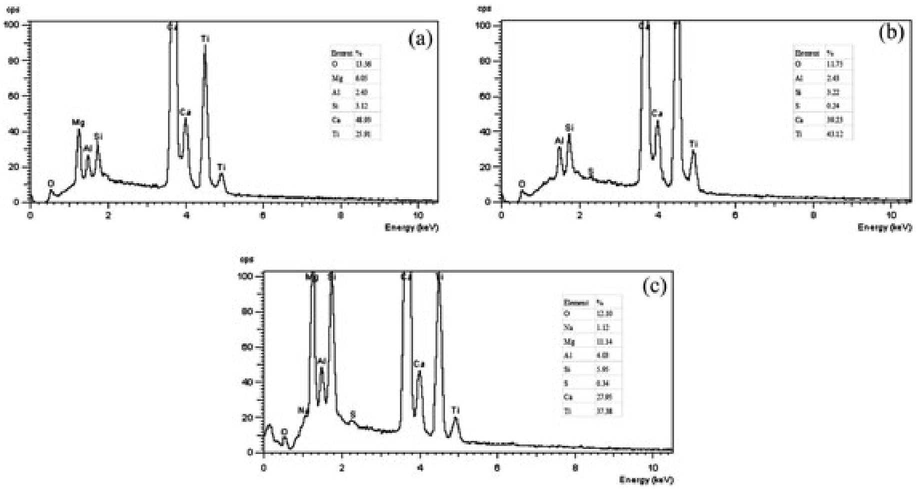

Figure 2. Microanalysis spectra representative of the two samples of paint: (a and b) paint from the undamaged can and (c) paint from the damaged can.

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and Oxford model Link Isis instruments using a beryllium window to identify the elements with atomic number (Z) equal to or above 11 and a light element window (SleW) to identify elements with atomic number (Z) below 11. The micrographs taken by means of SEM/EDX system were obtained via a secondary electron detector (relief contrast, image topography, secondary electron) and backscattered electron detector (atomic weight contrast, identification of similarity by colour shade, backscattered electron). All microanalyses were performed following the same parameters of X-ray data acquisition (25 mm working distance and 20 kV voltage). Before the analysis, the samples of paint were oven-dried at 140°C for 1 h, and all specimens were coated with either carbon or gold in a Balzers model SCD 050 metalizer.

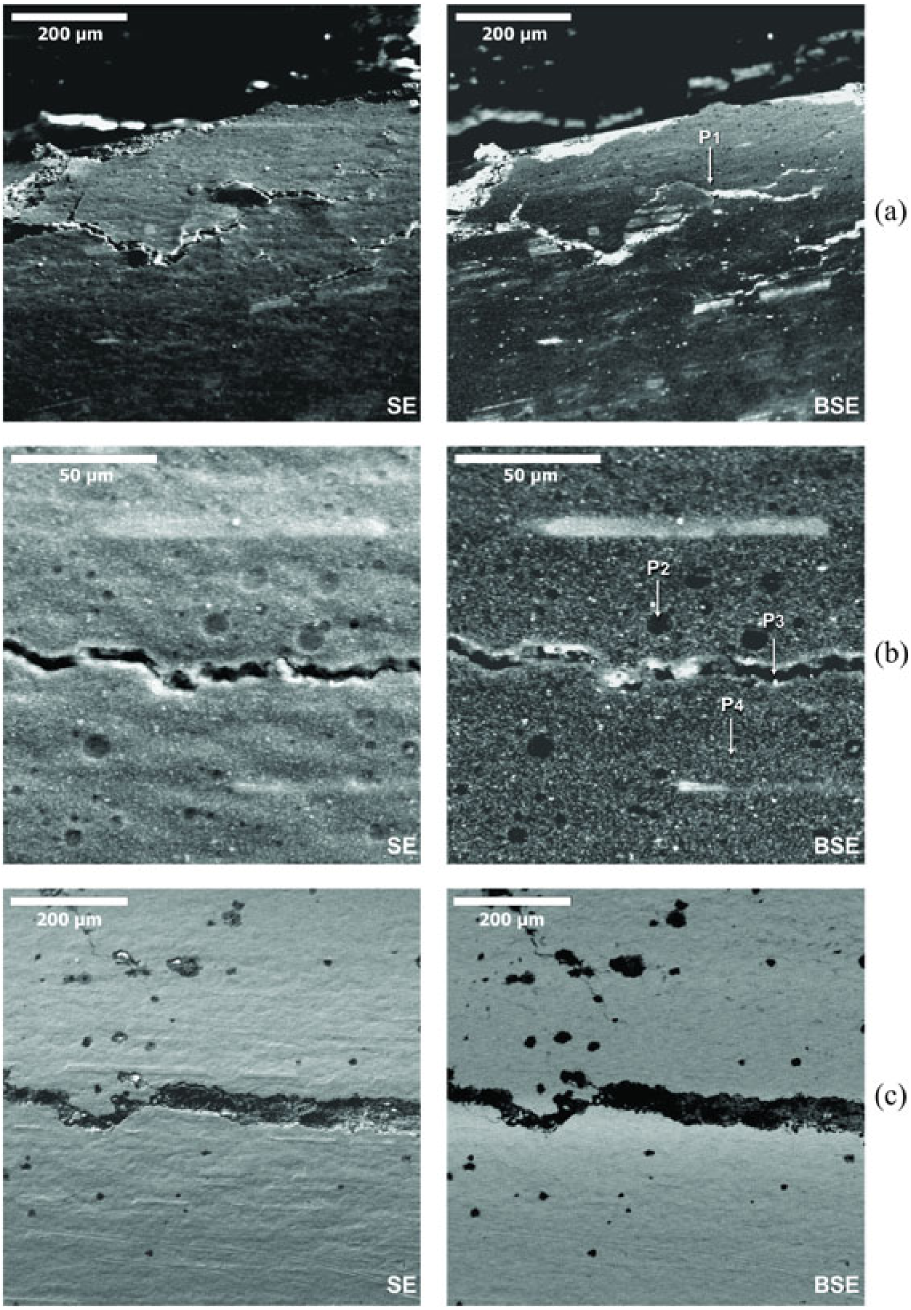

Figure 3. Microphotographs of the specimens collected from a cracked can bottom: (a) crack at the double seam bend, (b) surroundings of a fissure in the coating with defective spots and (c) area of Figure 3b after the coating was removed. BSE, backscattered electron; SE, secondary electron.

The metallographic analysis of can bottoms was conducted with the help of an LED optical microscope (Olympus Corporation, Tokyo, Japan) after the steps of cutting, mounting, grinding and etching with 2% Nital for 8 s.[10]

Table 1. Results of the microanalysis of the positions marked in Figure 3.

Element	Semi-quantitative analysis (%)			
	P1	P2	P3	P4
Al	1.75	1.69	2.52	1.01
Ca	4.13	0.40	1.92	0.16
Cl	5.15	0.42	0.35	0.40
Cr	0.15	3.89	5.79	3.92
Fe	78.04	20.68	30.41	35.67
K	0.28	–	–	–
Mg	0.60	–	–	–
Mn	0.25	–	–	–
Na	1.17	–	–	–
P	0.85	0.60	0.77	0.52
S	4.44	0.40	–	–
Si	3.20	0.65	2.33	0.63
Ti	–	71.27	54.87	57.7
Total	100	100	100	100

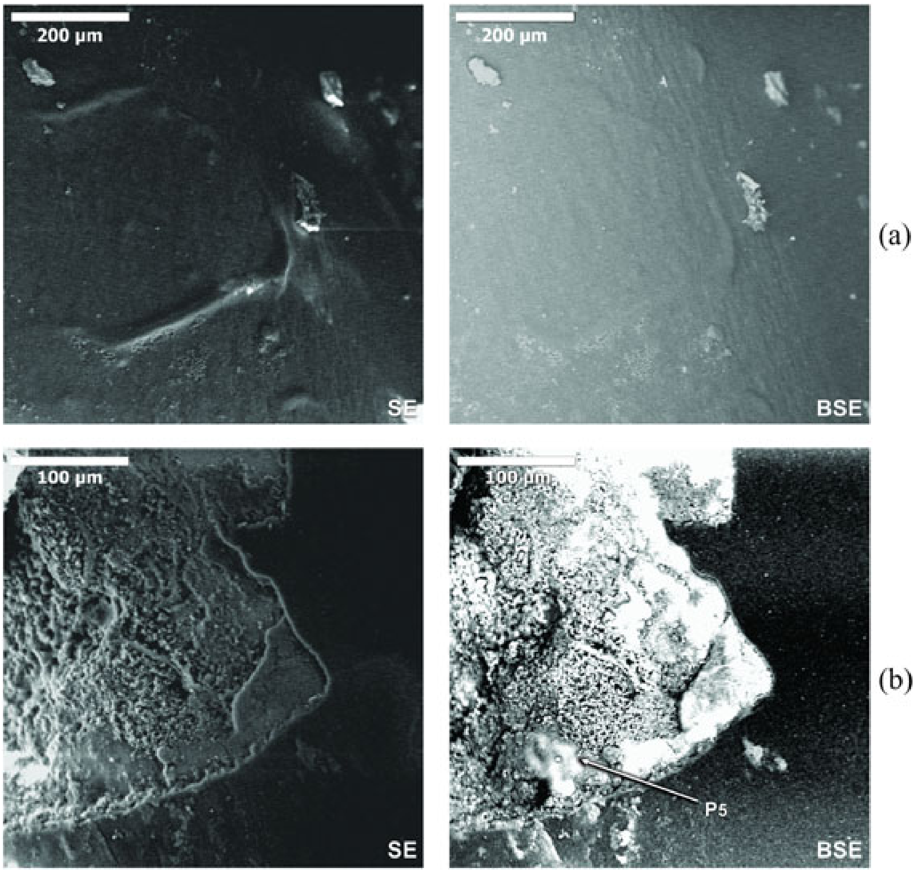

Figure 4. Microphotographs of the surface of the specimens collected from can bottoms with no cracking: (a) area of the double seam bend showing wrinkled varnish and (b) exposed steel in the double seam. BSE, backscattered electron; SE, secondary electron.

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RESULTS AND DISCUSSION

The comparison of the spectra obtained from the two varnishes via infrared spectrometry demonstrates that they are similar and that they have the same key absorbance peaks. The comparison of these spectra to the spectra from the literature showed the presence of epoxy-type resin and compounds containing amines/amides. Such differences were attributed to the presence of other components in the formulation.

Figure 1 shows photographs of cracks at the bend of the bottom double seam. Fracture/cracking is seen in a mechanical channel-shaped deformation at the bottom.

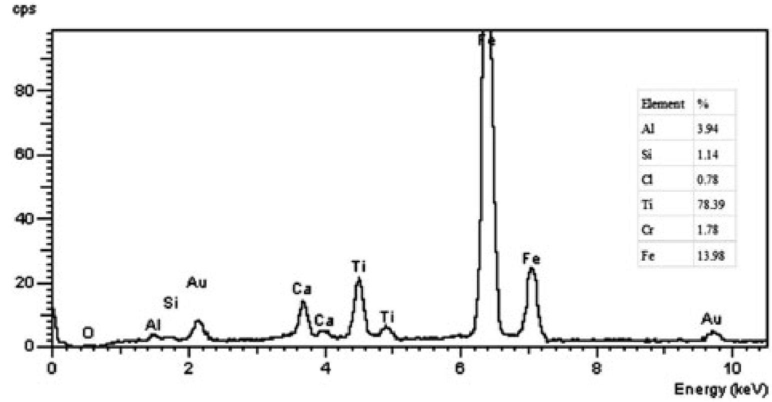
Fracturing occurred at the bottom of cans both with white base paint and with pigmented paint as well, suggesting that the pigment should not be related to the problem. Figure 2 shows the spectra representative of the white base paint collected from fractured cans and pigmented paint collected from undamaged cans after drying, taken via SEM/EDX system operating with 20 kV and 25 mm working distance and light element window.

According to the spectra shown in Figure 2, except for sodium, which was seen only in the paint from the damaged can, the same elements were detected in both samples of paint, including sulfur, but with different intensities. The intensities of the elements magnesium and silicon are higher in the paint from the damaged can.

Cracks that developed right in the double seam bend are shown in Figure 3a. Figure 3b, taken with larger magnification near a fissure in the coating close to another cracked area, shows uneven surface relief of the varnish film in the form of depressions. Figure 3c shows that, below the varnish film removed from the area around the fissure, the metal is intensely corroded, although it is not cracked yet. It can also be observed that corroded regions coincide with the depressions on the varnish film (Figure 3b and c).

The results of the microanalysis of the positions specified in Figure 3, shown in Table 1, reveal marked presence of iron at position P1 close to a cracked area. Sulfur and phosphorus were also noted at this position. Besides the metal and paint/varnish components, sulfur, phosphorus and chlorine were also detected at the positions P2, P3 and P4, taken from the varnish film in fissured and depressed spots. The source of sulfur can be either the steel or the wall paint, along with chlorine. Chlorine and sulfur are corrosion-accelerating agents on the steel sheet. Phosphorus concentrations above the specified maximum limit can affect steel ductility and toughness, thus increasing brittleness. Sulfur as a residual or alloying element above the specified maximum limit largely tends to segregate and occurs in steel particularly in sulfide inclusions.[11] While the microanalysis provides values for relative concentration, these elements appear in higher concentrations in the positions evaluated and may have weakened the steel, although the steel composition was in conformance with the specification.

The varnish in the radius of the double seam countersink of undamaged can bottoms was somewhat wrinkled (Figure 4a), with wrinkled spots extending to the inside part of the double seam (Figure 4b); however, no cracks were seen. The spectrum of Figure 5 confirms steel exposure in the spot, because iron element is detected more intensely than in the undamaged area, and chromium element is not detected.



Element	%
Al	3.94
Si	1.14
Cl	0.78
Ti	78.39
Cr	1.78
Fe	13.98

Figure 5. Microanalysis spectrum representative of the assessment conducted in the area shown in Figure 4b (P5), obtained through the light element window.

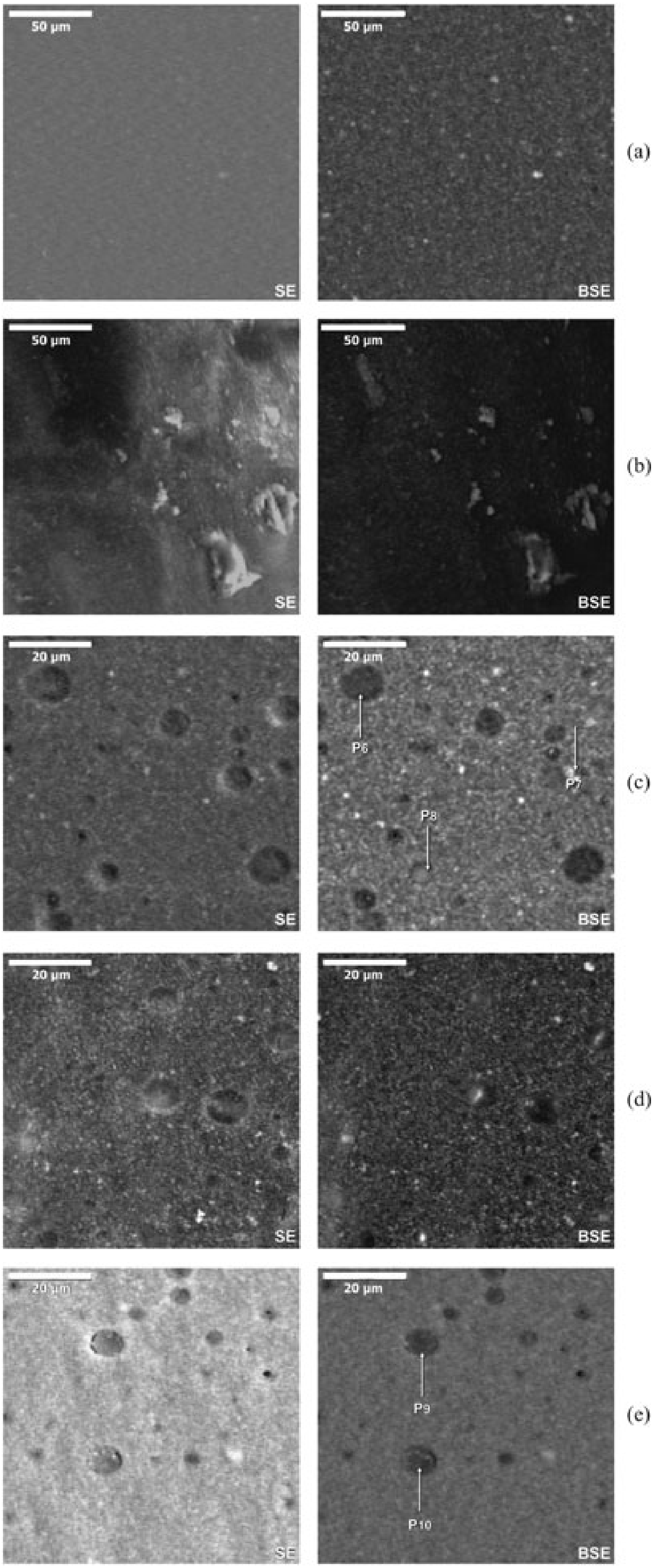


Figure 6. Microphotographs of the surface of a specimen collected from a can bottom: (a) flat area of a can bottom with no cracks, (b) area of double seam bend with no cracks, (c) flat area of a cracked can bottom, (d) area of the double seam bend of a cracked can bottom and (e) flat area of a cracked can bottom. BSE, backscattered electron; SE, secondary electron.

Table 2. Results of the microanalysis of the positions marked in Figure 6.

Element	Semi-quantitative analysis (%)				
	P6	P7	P8	P9	P10
Al	–	4.27	–	1.80	1.47
Ca	–	–	0.66	3.45	0.67
Cr	7.27	2.53	4.51	2.48	2.56
Fe	81.98	20.76	90.74	31.34	28.92
Si	–	1.78	0.50	3.05	1.25
Ti	10.75	70.68	3.59	57.87	65.13
Total	100	100	100	100	100

Many research studies have shown various possible causes of failure in cans of food or chemicals, such as double-seaming operations, can end construction, quality of protection layers of steel, chemical composition, residual stresses in can ends and the role of sulfites, sulfur dioxides and phosphates and pH.[12–15] According to Vågane *et al.*,[16] package integrity of canned products depends on recognized standards, which include defects with respect to the can profile, double seam, side seam, can end, can body, physical abuse and handling. However, defects of unknown origin may arise and compromise the integrity of the can when it is already in the consumer's hands, such as the example described in this paper.

Kim and Helwing[13,14] reported the occurrence of SCC in pet food can ends produced in ECCS in which the cracks were radially oriented and concentrated near the countersink radius, where the circumferential tension stresses were the highest. They observed that many of the cracks started at the base of corrosion pits, and there was no relationship between the cracks and the rolling direction of the steel. For the problem to be eliminated, the steel composition was changed as well as the lid profile. However, nothing was as effective as using a more appropriate coating system. These authors also reported cases of SCC in paint cans. In one of them, failures occurred in 5 gallon pails of road-marking paint, which was water-based with ethanol and ethyl silicate. Circumferential cracks developed near the bead of the pail body and at the corner of the hemmer bottom. The inner side of the pail was varnished with epoxy phenolic lacquer, but at the bead and at the crevice area of the hemmed part, there were sites with exposed steel. The cause of the failure was considered SCC, evidenced by intergranular branching cracks, probably related to alcohol in the paint composition.

In a similar situation involving internally unvarnished cans containing alcohol-based printing ink, the location and type of cracks were the same. Analysis of scrapings collected from the corroded area detected chloride and sulfate. Cracks in tinplate cans of tuna fish were also examined.[13] The problem started with punctual corrosion in defective spots of the varnish. The geometry of the pits changed the distribution of stress and chemical and electrochemical conditions in that specific spot, which became very different from the undamaged areas. The hydrogen produced by corrosion reactions in the area where the metal was exposed and the presence of hydrogen sulfide formed when the product was sterilized (which effectively accelerates hydrogen spreading in steel) must have contributed to one of the mechanisms of hydrogen embrittlement. The authors also examined the development of flaws in cans of meat soup, where rupture took place in a corroded area because of flaws in the varnish. Sulfur compounds were detected both in the headspace and in the soup.

Tsurumaru *et al.*[15] reviewed the same issue in food cans. They remarked that, at lower temperatures, when the inner vacuum of the packages is greater and the speed of corrosion reactions is slower, failures of this nature are reduced. The authors also noticed that stress corrosion is less frequent in tinplate sheets than in chromium-coated sheets and that the organic coating that works as a barrier between the metal and the product is critical. Moreover, the stress in several spots of round lids was determined as a function of internal pressure, to show that the development of stress corrosion is related to continuous stress applied to the lids and that the direction of the cracking is transverse to this stress. A different performance was observed in the cans under analysis, i.e. the fracture developed parallel to the rolling direction, confirming the conclusions of Kim and Helwing[12] that there is no relationship between the cracks and the steel rolling direction.

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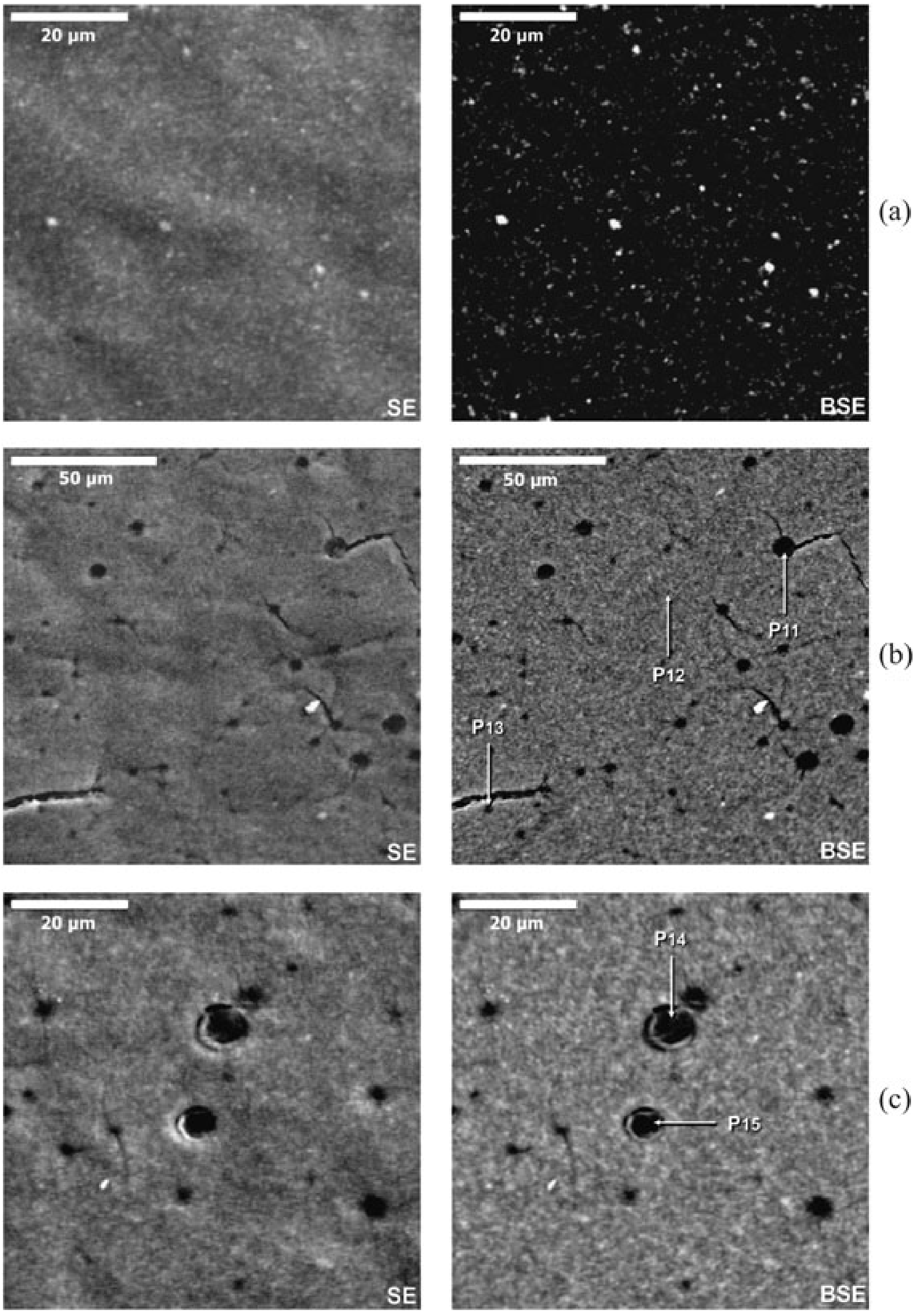

Figure 7. Microphotographs of the bottom hook collected from double seams of can bottoms that did not get in direct contact with the paint: (a) undamaged and (b and c) damaged. BSE, backscattered electron; SE, secondary electron.

As paints include a much greater number of ingredients, a specific study would be required to determine all compounds causing SCC.

Figure 6 shows microphotographs illustrating that there are no depressions in flat areas of the varnished surface of uncracked cans (Figure 6a) nor in the area of the double seam bend (Figure 6b). However, there are depressions in these two areas in cracked can bottoms (Figure 6c–e) that have a varnished surface with heterogeneous topography.

P6, P7 and P8 positions in areas with depressions shown in Figure 6c display large presence of iron, followed by titanium and chromium. This indicates that the metal was exposed in the spot, as shown

Table 3. Results of the microanalysis of the positions marked in Figure 7.

Element	Semi-quantitative analysis (%)				
	P11	P12	P13	P14	P15
Al	1.56	1.55	2.94	0.78	1.38
Ca	0.38	–	1.77	–	0.87
Cl	0.58	–	1.45	–	–
Cr	0.71	–	1.12	2.29	3.48
Fe	12.61	5.30	23.42	41.89	57.7
K	0.57	–	1.32	–	–
Si	0.90	0.74	2.80	0.72	1.71
Ti	82.68	92.42	65.18	54.32	34.87
Total	100	100	100	100	100

by the results of microanalysis in Table 2. In P9 and P10 positions shown in Figure 6e, also in depressions, the predominant element is titanium, followed by iron and by other elements belonging to the varnish, to the paint and to the metal sheet, such as chromium. The intense presence of titanium in the spot with depression may be related either to contamination of the area by the paint in the can or to uneven distribution of titanium in the can varnish.

Specimens collected from double seam hooks of can bottoms that at first had not contacted the paint were also assessed via MEX/EDX. There were no changes in the varnished surface of the undamaged sample (Figure 7a). However, depressions and fissures could be seen on the surface of the varnish collected from the damaged sample (Figure 7b and c). It must be noted that these failures cannot have

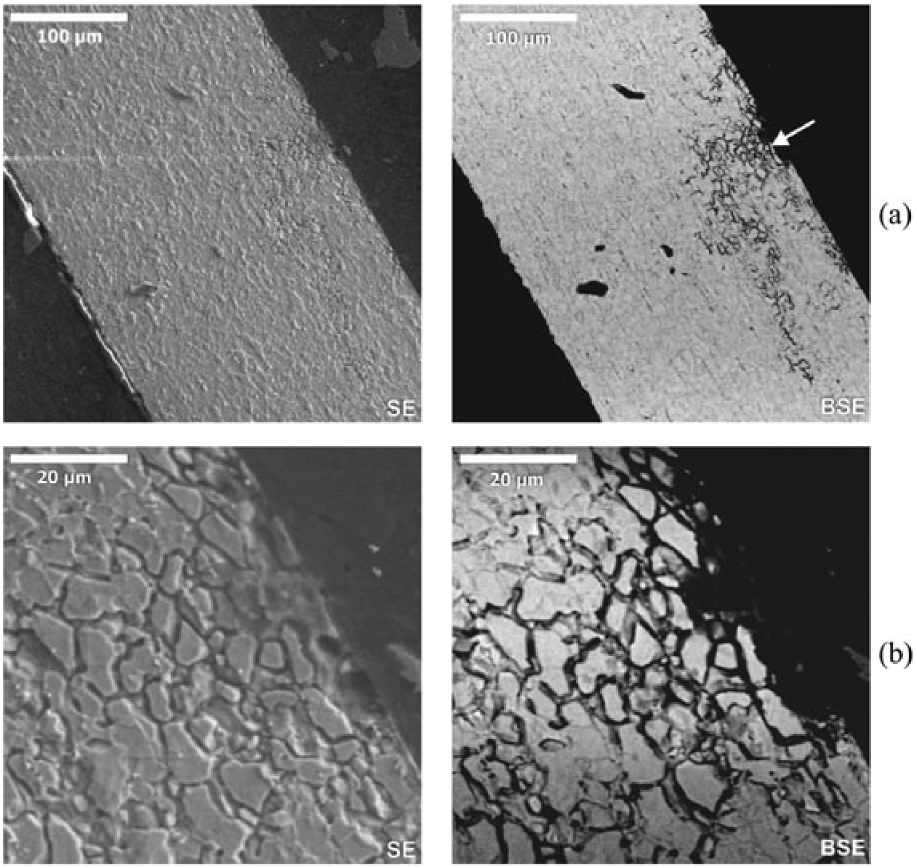

Figure 8. Microphotographs of the area of the radius of the double seam countersink of a cracked can bottom, in a spot with no full rupture of the material, illustrating (a) onset of intergranular corrosion and (b) detail of grain disaggregation. BSE, backscattered electron; SE, secondary electron.

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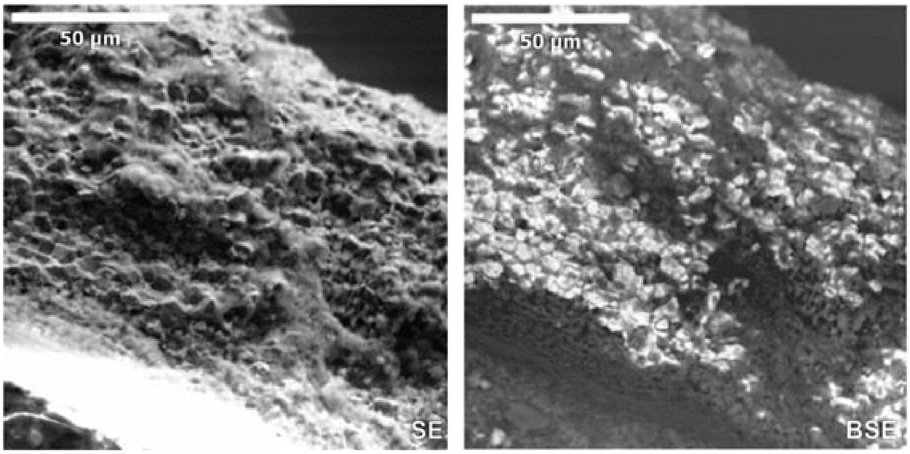

Figure 9. Microphotographs of the longitudinal section of a fracture. BSE, backscattered electron; SE, secondary electron.

been the consequence of direct contact of the varnish with the paint, because the area under analysis was located inside the double seam.

These defects can be associated to changes in coating composition, which formed these micropores during the curing process, because the bottoms failed during a specific period.

The results of the microanalysis shown in Table 3 reveal high relative concentrations of titanium (both in undamaged areas and in depressions and/or fissures) and iron. Such iron concentrations appear in different relative percentages in comparison with titanium, depending on the spot being analysed. They are lower in undamaged areas than inside the pits. This observation suggests either metal exposure or thinning of the varnish layer inside the depressions in the varnish film. This allows the beam of electrons to penetrate the metal sheet even deeper, resulting in higher intensity of iron. Detection of chromium only in defective spots of the varnish is also indicative of metal exposure or thinning of the varnish in that specific spot.

Punctual corrosion developed in these defective spots as a result of the contact of the exposed steel surface with the paint, which has components that develop corrosion (pH, carbonate, amine and sulfur). The pits on the steel surface, in combination with tensile stress in the double seam area caused by the weight of the paint (static loading) and by possible residual stress in the metal due to the metal forming process, led to fracturing of bottoms of paint cans as a result of development of SCC.

Figure 8 shows SEM microphotographs of the cross section of the double seam chuck wall radius in the inner side of a cracked can bottom in an area close to the crack but before rupture of the material. Figure 8a shows the onset of intergranular corrosion. Figure 8b shows grain disaggregation and development of SCC on the radius of the double seam countersink.

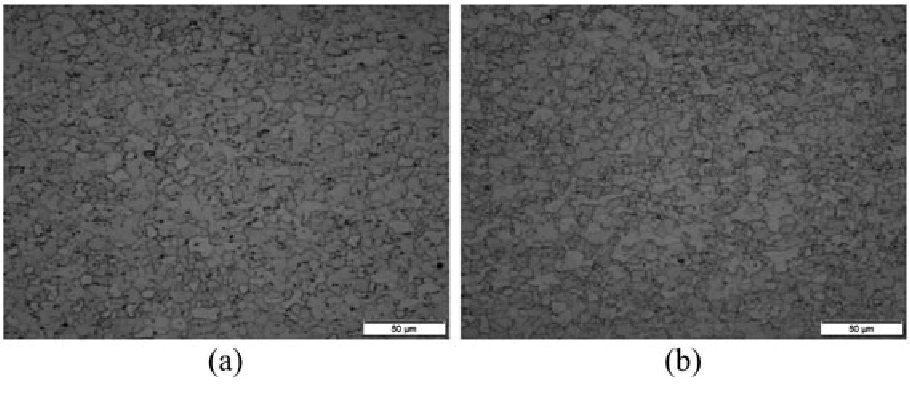

Figure 10. Micrographs taken with an optical microscope of the specimens collected from can bottoms: (a) cracked and (b) uncracked, after preparation of the surface.

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Figure 9 shows SEM microphotographs of the fractured/cracked surface displaying intergranular morphology.

Figure 10 shows microphotographs taken with an optical microscope of specimens collected from cracked and uncracked can bottoms during metallographic analysis. This analysis detected isolated carbides dispersed within the matrix of ferrite grains in both metallic materials. No significant differences from the microstructural point of view were found between them.

CONCLUSIONS

Depressions and microfissures in the varnish in the inner side of bottoms of paint cans led to punctual corrosion caused by the contact of paint with the steel surface. In addition, the tensile stress caused by the weight of the paint and possible residual stress in the metal bend in the double seam led to the development of SCC, resulting in the fracture of the can bottoms.

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