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Degradation of heritage cans: monitoring of museums' collections

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Abstract – This paper presents the outcomes of the CANS project (Conservation of cAns in collectioNS), an interdisciplinary research aiming at proposing conservation strategies for full cans, still retaining their original contents, in museums and collections. The paper includes the results of the condition report, measuring the state of conservation of 150 cans from 5 Swiss collections, the correlation between state of conservation, content and age of the can and the extensive characterization of the cans' materials for a better understanding of the corrosion mechanisms.

INTRODUCTION

Cultural heritage consists in artworks (painting, sculpture…) but also in usual and everyday objects (tools, machines…) sometimes unexpected, such as food preserves, like the ones illustrated in Figure 1. Cans are presented in several museum collections as witness to different time periods and significances.

Figure 1. Example of cans belonging to Swiss collections.

The CANS project, Conservation of cAns in collectioNS, has been an interdisciplinary research, involving 10 people from 4 different institutions. It was granted by the Swiss National Science Foundation and lasted 3 years. This project was conceived to answer to a precise request of help coming from museums having full cans in their collections and no guidelines or protocols to face the problems related to the conservation of these complex objects. In fact, the conservation of cans in collections is particularly problematic as severe corrosion phenomena occur due to interaction with environment as well as between the organic content and the metallic container.

The final goal of the CANS project was to define conservation solutions for heritage cans still retaining their original content. Secondary objectives, presented in this paper, included:

- The definition of a protocol for performing an appropriate condition report on heritage cans in order to collect significant data and information on state of conservation and degradation processes.

- The study of the long term corrosion mechanisms of tinplate in contact with food and the material characterization of tinplate.

Cans history and technology

A can is a composite object, composed by:

- an external label, which can be made of paper or directly printed or painted on the container
- the food content
- the metallic container that in turn is a composite material composed by a mild steel base covered on both sides by tin and often covered by a polymeric coating to isolate the metal from the food

As illustrated in the timeline reported in Figure 2, it is the Englishman Peter Durand who patented in 1810 the tin-plated iron canisters as a food containers. In 1812, Bryan Donkin and John Hall opened the first can factory in Great Britain. Tinplate is still used nowadays for the production of food cans even if the can industry underwent many important transformations since 1812 to nowadays. The most representative are the invention of the double seaming machine in 1898 allowing to close the cans by crimping the metals, without soldering, and the introduction of the electrolytic process for the tinning in the 1930's [1].

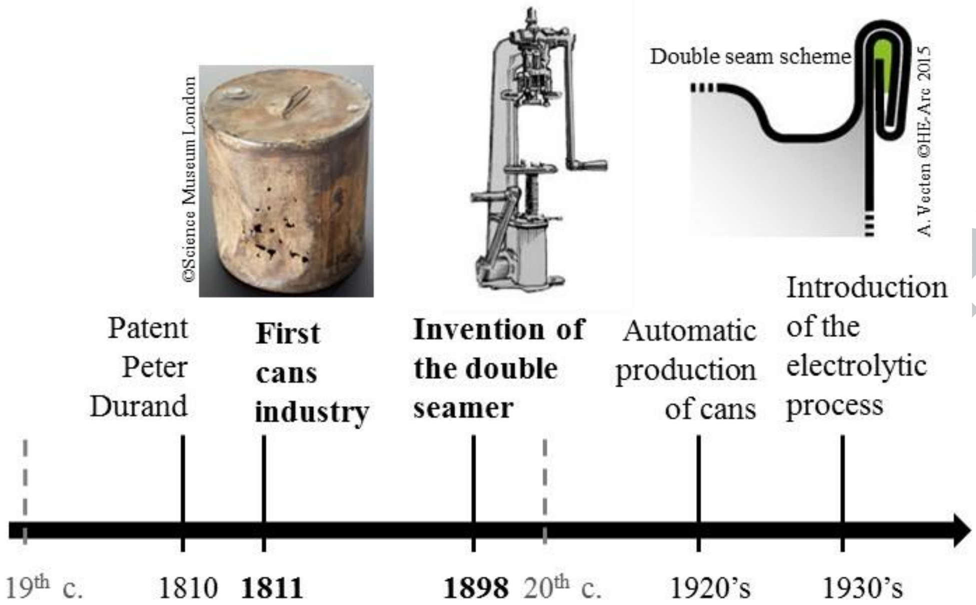


Figure 2. Timeline of cans technology evolution.

Cans in museums

In addition to their materiality, cans own important cultural values like, historical, social, artistic, symbolic and research value.

For this reason cans are present in different kind of museums:

- museums dedicated to food, nutrition or food industry
- museums dedicated to every day's life
- industrial heritage
- collections of objects coming from Arctic and Antarctic expeditions
- cans can be also used as tools, music instruments or toys (distorted cans)
- museums of contemporary art, where cans are often used as symbol

The difficulties of conserving cans in collections are linked to the fact that a can is produced to last from 1 to 5 years (shelf life for human consumption), while in collections there are cans that are up to 200 years old. The materials and in particular the food are not conceived to last for a so long period of time.

For that reason, cans in collections present several different problems like corrosion of the container due to the interaction with the content or non-adapted environmental conditions, swelling, bursting, mold development and biological risk like animal or insects attraction.

Before the CANS project no systematic studies were carried out on cans in collections and there were no adapted protocols or conservation methodologies for full cans in museums. The few articles in the literature concerning heritage cans refer to objects recovered in the poles, left from explorers expeditions of the 19^{th} and 20^{th} century [2, 3]. The study carried out on those cans are mainly dedicated to the food analysis to verify the presence of lead or botulism toxins or to the authenticity of the food. Some restoration works on cans have been carried out and published by the Antarctic Heritage Trust [4, 5]. Foods other than cans have been studied as part of museum collections, like chocolate [6] or fruit skins [7]. The industrial literature on food packaging widely studied the problem of cans corrosion and interaction with food [8, 9]. However, these studies are limited to the shelf life of the cans and never exceeds 15 years from cans production.

CONDITION REPORT

Materials and methods

The first goal of the CANS project was to determine the state of conservation of full cans in collections. The condition report, an evaluation of the objects aiming at describing their conditions at a certain date and time, is a common practice in the field of cultural heritage conservation for determining an object's stability and state of conservation [10]. In the case of heritage cans, no procedure existed for a proper evaluation of their state of conservation. For this reason a protocol was developed in order to observe and measure the most important parameter for heritage cans. This protocol includes:

- registration of the can's brand, content and year of production or expiration
- complete photographic documentation of all the sides of the cans. This documentation will be included in the archives of the museums and will allow to compare the state of conservation of the can during time.
- measurement of the cans: weight, height, diameter and height at the center of the can were recorded and reported in the condition report spreadsheet.
  In particular, the weight, measured by means of a balance, and the height at the center of the can, measured by means of an external caliper, allow detecting the presence of leakages or swelling due to internal corrosion
- observation and detailed description, supported by microscope images, of the surface of the can. This analysis allows detecting corrosion (external and internal) and consequently establishing the state of conservation of the can

The condition report and measurements were carried out on around 150 cans belonging to 5 different collections, with the aim of identifying the main degradation problems and correlate the observed degradations with the age of the can and its content [11].

Surveys were conducted on the following collections:

- The Alimentarium in Vevey (Canton of Vaud), opened in 1985. It is the first museum in the world exclusively dedicated to food and nutrition. The museum is managed by the Nestlé Foundation. In addition to permanent and temporary exhibitions about contemporary and ancient eating habits, activities such as workshops and tasting sessions are periodically organized. Cans, either full or empty, are part of both permanent and temporary exhibitions. Around 50 cans were analyzed in this collection dating from the 1890's to nowadays.
- The municipal Museum Burghalde in Lenzburg (Canton of Aargau) received in 2010 the archives of the Hero Company, including cans with and without their original content. Hero has been an important Swiss brand, founded in Lenzburg in 1886 and producing food goods. Some of the Hero archives were exhibited from 2011 to 2013 at the Museum Burghalde, during the exhibition entitled "Hero, seit

1886 in aller Munde" (Hero, from 1886 on everyone's lips). Around 65 cans were analyzed in this collection dating from the 1940's to nowadays, except one cans produced in 1886 (first day of cans' production by Hero in Lenzburg).

- The Ortsmuseum in Küsnacht (Canton of Zurich) is a small local museum where a historical store ("Tante Emma-Laden"), has been recreated. The store displays products commonly sold in the 1950's, including some concentrated milk cans. Around 15 cans were analyzed in this collection dating probably from the 1970s.
- The HAM foundation in Thun (Canton of Bern) is the museum of the Swiss Army. Within military equipment there are obviously also food ration, including cans. Around 5 cans were analyzed in this collection dating probably from the 1990's.
- The Historical Museum of Bern (Canton of Bern) is a museum dedicated to history. In the collection of this museum there is a lot of food and food packaging dating from the 1990's. There is no trace of information regarding the original exhibition for which these objects were acquired by the museum. Around 10 cans were analyzed in this collection dating probably from the 1990's.

Results and discussion

Storage environmental conditions are similar in all the five museums with no temperature and humidity control at the moment of the survey.

In Lenzburg and Küsnacht, cans are stored on wooden shelves. At the Alimentarium, BHM and HAM foundation they are kept in closed or open plastic boxes.

Some cans are permanently displayed in non-controlled closed showcases, often together with other objects.

The cans observed in this survey differ for age, content, shape and dimension.

Concerning the age, the cans date from the mid of the 19th century to nowadays. In fact, many museums are still collecting cans and new or really recent cans are part of the collection.

The measurements of the dimensions showed that the cans of the Swiss collections are situated in these ranges [11]:

- Volume: from 0.12 dm^3 to 3.3 dm^3
- Weight: from 76 g to 3 kg
- Height: from 28 mm to 253 mm
- Diameter: from 52 mm to 156.5 mm

Most of the cans have the classic cylindrical shape, however, rectangular or oval shapes can be found, in particular for fish or meat products (pilchards, corned beef, …). Since cans have been produced by hand for decades, it is not unusual to find cans in collections with really peculiar shapes like truncated cone.

The contents of the 150 cans considered for this study are listed in Table 1.

Table 1. Content of the 150 cans observed during the condition report.

Content	Quantity (approximate number of cans)

Vegetables of different kind	35
Fruits of different kind	25
Meat or meat based products	< 10
Fish	< 10
Prepared food (pasta, soups, …)	30
Desserts	5
Milk based product	20
Other (coffee, …)	15

Most of the cans contain fruit, vegetables or prepared dishes. The really high number of milk-based products is linked to the production of typical Swiss products. For the same reason, the number of cans containing fish is really low.

The main degradation phenomena observed on cans in collections are the following [11]:

- Corrosion (external and/or internal)
- Swelling (verified by measuring the height at the center of the can)
- Bursting
- Perforation with or without leakages

The amounts of cans presenting each kind of different degradation phenomena are reported in Table 2.

Table 2. Degradations observed on cans during the condition report

Main form of degradation	**Detailed form of degradation**	**Quantity (%)**
Corrosion	No signs of corrosion	7%
	Corrosion of the top, of the bottom or both	75%
	Corrosion of at least one of the double seams	80%
	Corrosion of the cylinder	30%
	Perforation	30%
	Filiform corrosion	10%
Leakage	Leakage	45%
Swelling	Swelling	45%

The 7% of cans presenting no sign of corrosion are mainly represented by new cans, recently included in the collections.

Even if the number of cans presenting corrosion on the double seam is extremely high (85%), this form of corrosion is not particularly problematic because it is due to a combination of environmental conditions and to the fact that the tin layer may be thinner in this point of the container due to the seaming process.

The number of cans presenting severe internal corrosion phenomena is quite high, as can be deduced by the number of cans presenting:

- swelling (45%), as a consequence of gas (H_2) development inside the can due to the interaction between the container and the organic content
- perforation (30%) due an advance degree of internal corrosion, as can be observed in Figure 3
- leakages (45%), due to perforation or excessive internal pressure of the gas developed inside the can

Figure 3. Can presenting perforations due to internal corrosion (Alimentarium, Musée de l'alimentation, une fondation Nestlé, Vevey)

When the gas inside the can cannot be evacuated, the container could arrive to burst, with damaging consequences for the can itself and for the other objects stored or exposed nearby (Figure 4).

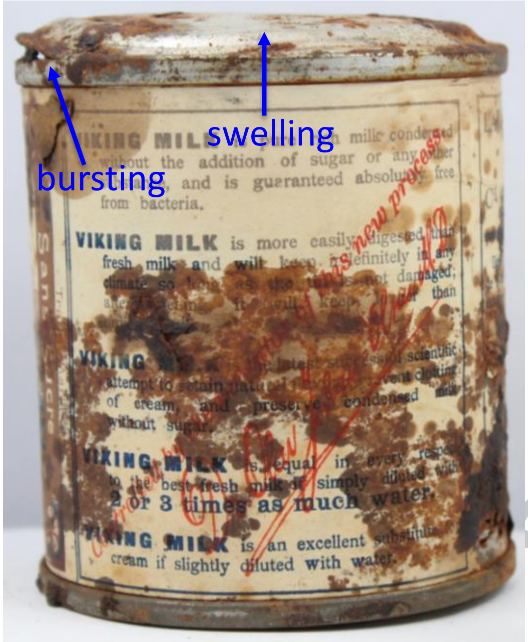


Figure 4. Can presenting signs of swelling and bursting (Alimentarium, Musée de l'alimentation, une fondation Nestlé, Vevey)

Perforations and leakages can also damage the labels of the cans, not only due to unaesthetic stains of spilled content, but also because of the embrittlement of the paper or mold growth.

During the condition report, it was observed that the degree of degradation of the can does not always correspond to its age. In fact, there are cans in the collections that are still in good state of conservation even after few decades from their production and others that are completely degraded just few years after the expiring date. This phenomenon is linked to different factors including:

- Environmental conditions during the cans storage. In fact, the higher is the temperature, the faster is the kinetic of the corrosion reactions [12].
- Nature of the content. Some foods are particularly aggressive for the tinplate and can accelerate the corrosion rate. Between them the most critical for the tinplate are nitrates, anthocyanins, both acting as oxidants and sulfur-containing compounds (animal proteins that are degraded during sterilization releasing free sulfide or hydrosulfide ions and evolving hydrogen sulfide gas into the headspace) [13]. The pH below 5, and specifically between 3 and 4.5, and the presence of complexing organic acids, like citric, tartaric, malic and oxalic acid, forming complexes with Sn^{2+}, also play a role in the corrosion of the container [12].
- The quality of the materials composing the can.

Concerning the last point, it is worth mentioning that the thickness of both tinplate and tin coating decreases considerably respect to the 19th century. The analysis in the 1930's of a can produced in 1824 revealed a thickness of the base steel of 0.47 mm and a thickness of the tin coating of 11.55 µm [14]. Nowadays, the base steel of commercial cans can vary from 0.15 to 0.50 mm and the tin coating thickness lies between a minimum of 0.4 µm and a maximum of 2.5 µm [13].

With a tin coating layer that is 10 times thinner respect to 200 years ago it is easily explained the shorter lifetime of the cans produced in the recent years.

Since the quality, stratigraphy and composition of the tinplate seems to play a key role for determining the lifespan of the heritage cans, a thorough characterization of commercially available tinplate materials was carried out.

MATERIALS CHARACTERIZATION

Food cans are complex systems which corrosion behavior depends on the interaction between the food and the tinplate. Figure 5 shows the classical vision of tinplate structure, which consists of an external tin layer (possibly covered by a very thin superficial passivation layer), an interfacial alloy layer composed by the $FeSn_2$ phase and finally the steel substrate. The intermetallic phase tin-iron alloy ($FeSn_2$) is formed at the tin-iron interface during the flow-melting step applied after tin electroplating.

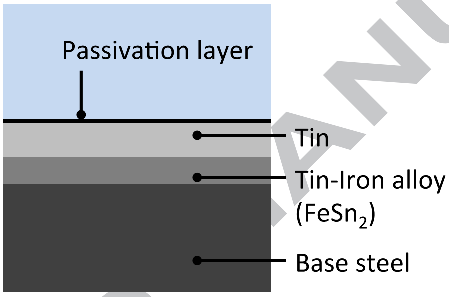


Figure 5. Classical representation of the structure of tinplate [13]

According to this structure, the lifetime of a collection can is determined by the sequential corrosion of the different layers composing the tinplate and leading to its perforation. Equation 1 describes mathematically this concept.

$$t_{total} = \frac{d_{Sn}}{v_{corr,Sn}} + \frac{d_{FeSn_2}}{v_{corr,FeSn_2}} + \frac{d_{Fe}}{v_{corr,Fe}} \quad (1)$$

Where t_{total} is the time needed for perforation, d_x is the thickness of each layer and $v_{corr,x}$ is the corrosion rate (corroded thickness by unit time) of the metal constituting each layer due to the interaction with the contained food.

Within the CANS project, the lifetime of tinplate cans was evaluated using ad hoc prepared tinplate cans containing pH 4.2 (stabilized using citric acid) tomato sauce. The cans were stored at 3 different temperatures: 4°C, 22°C (room temperature) and 40°C. The wall thickness of the steel was measured as 200 µm while the tin layer and the alloy layer thicknesses were 0.4 µm and 0.15 µm, respectively. Average corrosion rates reported in the literature [15-17] for this type of food were 130 µm/year, maximum 14 µm/year and 0.4 µm/year for iron, $FeSn_2$ phase and tin, respectively. Introducing these values into Equation 1 yield a lifetime before perforation of 2.5 years. However, it was observed that perforation occurred already within 9-12 months from canning date. Clearly, the model underlying

Equation 1 presents some limitations. One of these is probably related to the fact that the alloy structure is not as ideal as depicted in Figure 5. Indeed, technical materials are likely to contain defects such as porosity, scratches and variations in layer thicknesses.

In order to get a picture of the tinplate structure closer to reality, an extensive characterization of the tinplate was therefore carried out using a multi-analytical approach with the aim of understanding the influence of the materials characteristics on the corrosion mechanisms [18].

Materials and methods

Commercially available tinplate samples of different type were used for this characterization: E1.4/1.4, E2.8/2.8, D5.6/2.8, D8.4/2.8, D11.2/2.8.
This denomination follows the current standards for canning industry and tinplate production [19].

Surface analysis and electrochemical techniques were used for characterizing the samples. For detailing the tinplate composition and the surface characteristics, the following techniques were used:

- SEM-EDX (Zeiss GEMINI 300)
- Scanning Auger Microscope (PHI680)
- 3D White Light Interferometry with a 10x objective (Smart WLI GBS)
- XRF (Thermo Niton XL3t GOLDD+)

Results and discussion

From the analyses performed, 4 parameters resulted to be especially critic for the determination of the lifetime of the can:

- local variations in tin coating thickness
- roughness of the surface (both base steel and tinplate surface)
- porosity of the tin layer
- coverage of the tin-iron alloy ($FeSn_2$) formed at the interface between the tin coating and the base steel

The tin coating thickness can be determined by means of electrochemical techniques, as defined by the standards [19, 20], or using Auger Electron Spectroscopy depth profiling. The two methods were compared during this study and the results obtained are in good agreement [18].

In addition to these two techniques, having the disadvantage of being destructive for the sample, portable XRF has also been used to measure the tin thickness. In fact, this technique may potentially be used directly on historical cans that, due to their unicity, cannot be destroyed for characterization purposes. The results of the XRF analysis has been then compared with the ones obtained by electrochemical techniques and AES. As it can be observed in Figure 6, there is a good correspondence between the results obtained by destructive techniques and portable XRF, for the 5 samples analyzed. Therefore the portable XRF has high potentiality for the characterization of heritage cans.

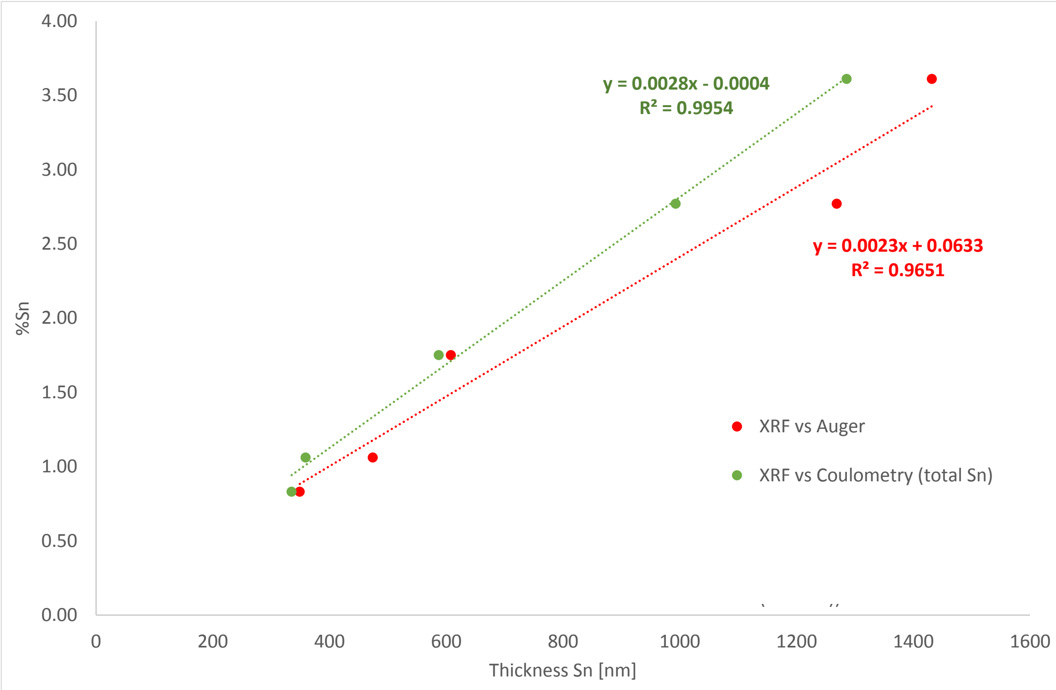


Figure 6. Calibration curves obtained by plotting the Sn amount (%) measured by XRF vs the thickness of Sn measured by Auger (red) and coulometry (green) respectively

Concerning the roughness, in Figure 7 it is possible to observe the surface of the tinplate sample D8.4/2.8 as received ad after the ions etching. It can be noticed that the striae of the base steel are still partially visible through the tin coating. Furthermore, this technique allows to identify defects of the tin layer such as scratches and porosities. The effect of the roughness of the base steel is also observable in Figure 7a, showing the image obtained at the SEM of a tinplate sample with a thin layer of tin (E1.4/1.4). Figure 7b shows that, the typical acicular structure of the $FeSn_2$ alloy is clearly visible at the top of the striae below the tin layer. Furthermore, in these areas the tin coating is not homogenous and porous.

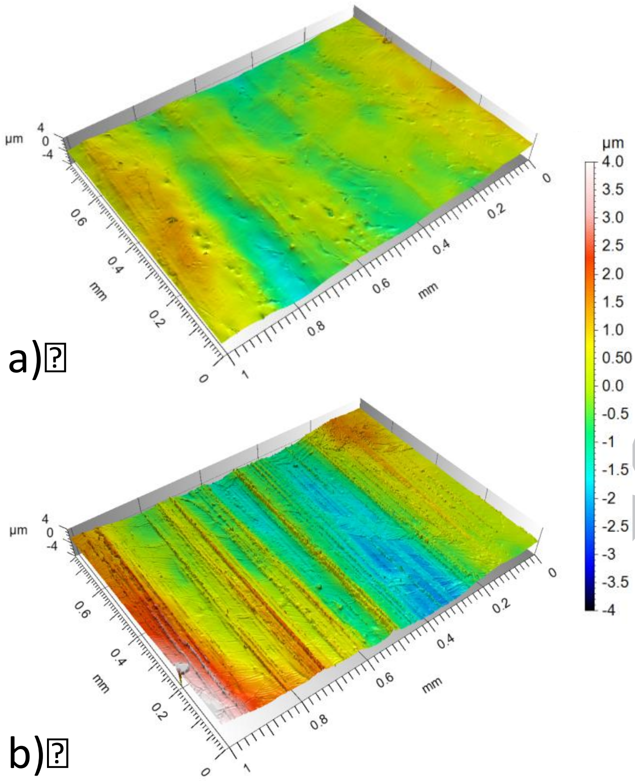
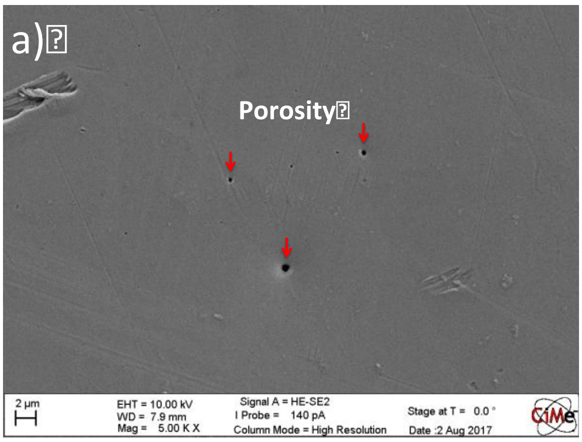


Figure 7. 3D white light interferometry of the surface of the tinplate (D8.4/2.8) before (a) and after (b) the removal of the tin coating

Porosity of the tin layer was observed by means of SEM for all types of tinplate (Figure 8). The porosity is limited for tinplate coated with thick layer of tin (Figure 8a) while is much more extended for samples coated with thin layers of tin (Figure 8b). Porosity was measured using the electrochemical method (chronoamperometry) called Iron Exposed Value (IEV) [21]. Chronoamperometry is performed on a tinplate coupon of 0.7854 cm^2 at 1.3 V vs SCE in a solution at pH 10 of Na_2CO_3 [0.2] $NaHCO_3$ [0.2] NaCl [0.005]. The current value after 3 minutes of polarization give the value of the exposed iron.



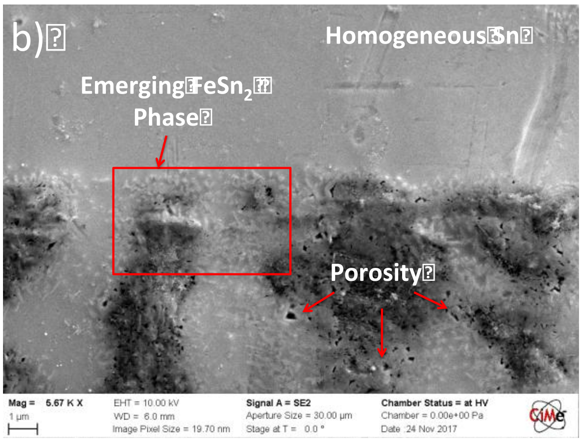


Figure 8. SEM image surface of the tinplate as received: D11.2/2.8 (a) and E1.4/1.4 (b)

According to the production process, period and geographical location, the tinplate can present few isolated pores or an extended porosity that can, like in Figure 9, in the worst cases, exposes also the underlying tin-iron alloy and base steel and consequently accelerate the corrosion rate.

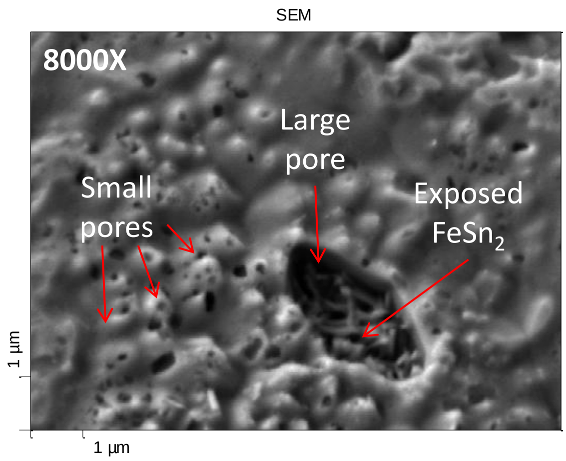


Figure 9. SEM image of a commercial tinplate sample showing extended porosity

The tin-iron alloy, which composition is $FeSn_2$, is an interfacial layer formed between the tin coating and the base steel by heat treatment after the electrolytic tinning. It ensures the good adhesion of the tin layer on the steel substrate and it is also supposed to be chemically inert and thus to impart further corrosion protection [17].

SEM analysis of the alloy layer exposed after electrochemical dissolution of the tin layer (Figure 10) showed that the coverage of this phase can be very poor and that the base steel can be directly exposed, between the needle-like structure of the $FeSn_2$, to the aggressive food environment.

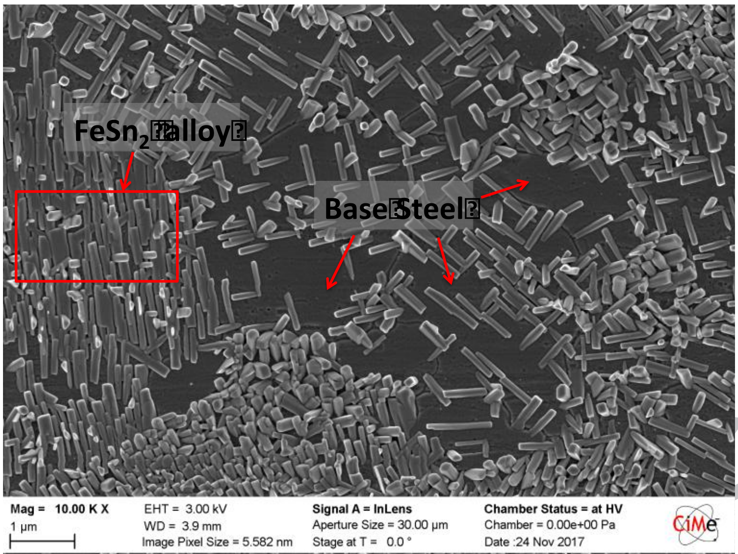


Figure 10. SEM image of the $FeSn_2$ alloy observed on the sample D 8.4/2.8

This study clearly shows that the tinplate structure is more complex than the simple version represented in Figure 5. The realistic representation of the tinplate structure, obtained after this investigation, is shown in Figure 11 [18]. In order to predict cans lifetime and corrosion resistance, it is therefore necessary to consider the real structure of the tinplate and this, in turn, requires an extensive material characterization. Since most of the analysis techniques are destructive, this characterization can hardly be carried out on unique collection pieces but requires the availability of cans that can be sacrificed.

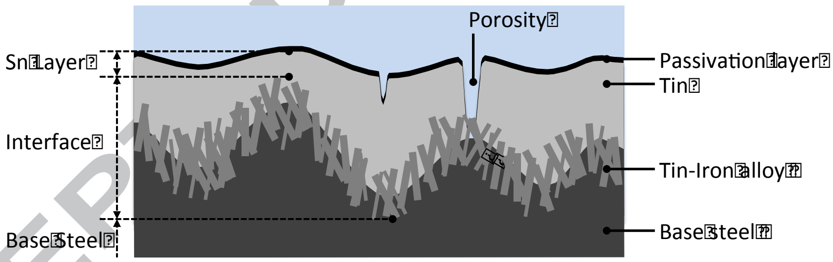


Figure 11. Realistic representation of the structure of tinplate [18]

CANS WITH LACQUER COATINGS

Most of the cans produced nowadays are internally protected by a lacquer or a polymeric coating. This layer allows to further separate the food and the container using an organic barrier instead of a thick layer of pure tin.

On the short term (shelf life), this protective layer is really efficient, but on the long term (decades), it reveals to be clearly less efficient than a thick tin coating. An example can be observed in Figure 12, where it is shown how the failure of the polymeric coating, in particular the one protecting the soldering can have devastating consequences on the label due to a massive leakage of the content. Failures of this type were observed on several cans in museums and it would be worth further investigating the degradation of internal coatings.

Figure 12. Can presenting failure of the polymeric coating and consequent staining of the label (Museum Burghalde, Lenzburg)

CONCLUSIONS

The condition report carried out during the CANS project on 150 cans belonging to 5 Swiss collections showed that the degradation of cans in museums' collections depends on many different factors:

- Environmental conditions
- Content
- Can's materials characteristics

The last parameter resulted to be the most critical, because corrosion of cans is highly dependent on real tinplate structure (Sn thickness, porosity, …).

The tinplate material quality and structure is extremely variable. For heritage cans, that have been produced over 200 years, this variability is due to different technology production methods and age. For cans produced nowadays, entering in the collections at the present time or in the future, a certain variability, even limited by the highly standardized production methods, is still present and is linked to geographical origin and costs of the materials. It is therefore not always possible to define the structure of the tinplate in a univocal way. For this reason, a precise characterization of tinplate material structure is necessary for the prediction of cans lifetime.

The use of non-destructive techniques, like portable XRF, has high potentiality for the non-invasive characterization of historical cans, and they deserve further developments.

To propose adapted conservation solutions for cans in collections, the knowledge of all the above mentioned factors is necessary.

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- Tinplate cans are included in museums' collections as part of the cultural heritage
- Heritage cans in museums present severe corrosion and degradation phenomena
- Corrosion of cans is highly dependent on real tinplate structure
- Characterization of the tinplate material is fundamental to model corrosion