

The shelf life of foods in the metallic cans

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Abstract

The paper presents the canning of heat preserved foods; this is a method of food preservation that relies upon the hermetic sealing of foods inside a metallic container and the sterilisation or pasteurisation of the food by heat treatment.

Keywords: metallic cans, preserved foods, sterilisation or pasteurisation

1. Introduction

Canning of heat preserved foods is a method of food preservation that relies upon the hermetic sealing of foods inside a metallic container and the sterilisation or pasteurisation of the food by heat treatment. No preservatives are therefore necessary to prevent the food spoiling due to the growth of microorganisms. Some chemical reactions can, however, continue to take place inside the can, albeit slowly; these include breakdown of colour, flavour and other natural food components. In addition, the food interacts with the container.

The **shelf life of canned foods** is determined by a variety of factors but all relate to deteriorative reactions of some form or another, either those introduced during production or processing activities or those occurring during storage. In order to understand these processes better it is important to be able to define shelf life more exactly. Shelf life can be defined in two ways: minimum durability and technical shelf life.

- Minimum durability is defined as the period of time under normal storage conditions during which a product will remain fully marketable and will retain any specific qualities for which express claims have been made.

However, beyond this point the food may still be satisfactory for consumption.

- Technical shelf life is defined as the period of time under normal storage conditions after which the product will not be fit to eat.
- For example:
- A canned fruit product is being sold with the claim 'contains 10 mg/100 g of vitamin C. On production, the product contained more than 10 mg/100 g but after 18 months storage, the vitamin C content has been reduced to only 7.5 mg/100 g. The minimum durability has therefore been exceeded but this loss of vitamin does not make the food unfit to eat. The technical shelf life has therefore not been reached.
- A second product is found after two years to contain 250 mg/kg of tin. This level is above the maximum EU legal level of 200 mg/kg tin (Regulation No 1881/2006/CE) and so the technical shelf life has been exceeded. Three main factors affect the shelf life of canned foods and are implicated in deteriorative reactions:
- sensory quality of the foodstuff, including colour, flavour (plus taints) and texture;
- nutritional stability;

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- interactions with the container.

The first two of these are outside the scope of this paper, the remainder of which will concentrate on container interactions, both with the can contents and with the external environment.

Aspects of interactions between the can and foods

Regarding the interactions between the can and its contents, all foods interact with the internal surface of the can in which they are packed. The most common form of this interaction is corrosion. In plain tinplate containers, this takes the form of etching or pitting corrosion, and staining of the surface may also occur. However, internal lacquers are available which reduce this effect by providing a barrier between the food and the metal can wall. This also allows the use of other forms of metal container (e.g. tin-free steel or aluminium) which would otherwise be corroded very quickly.

In the unlacquered form, only tinplate has any corrosion resistance to the acids found in foods; all the other metals must be lacquered. Even tinplate must be lacquered where particularly aggressive products are packed, such as tomato purée, or where there is danger of pitting corrosion or surface staining (for example, in meat products).

According to: "Guidelines on metals and alloys used as food contact materials" (Technical Document, 2001), those metallic materials which are covered by a layer of surface coatings able to constitute a "functional barrier" to the migration of the metals into the foodstuffs thereby reducing the potential risk of migration of the metal.

Conventional food cans are composed primarily of steel with a thin layer of tin applied to the internal and external surfaces. The tin coating is an essential component of the can construction and plays an active role in determining shelf life. The most significant aspect of the role of the tin coating is that it protects the steel base-plate which is the structural component of the can. Without a coating of tin, the exposed iron would be attacked by the product and

this would cause serious discoloration and off-flavours in the product and swelling of the cans; in extreme cases the iron could be perforated and the cans would lose their integrity.

The second role of tin is that it provides a chemically reducing environment, any oxygen in the can at the time of sealing being rapidly consumed by the dissolution of tin. This minimises product oxidation and prevents colour loss and flavour loss in certain products. It is this positive aspect of tin that makes it appropriate for particular product types to be packed in tinplate containers with internally plain (i.e. unlacquered) can component(s) – body and/or ends.

Several attempts to replicate this effect of quality preservation with certain products – for example, by introducing tin into lacquers and adding permitted tin salts – have been made, but none are as effective as the normal tinplate can. The increasing use of fully lacquered cans for some of these products in recent years, in order to reduce the tin content of the product, is generally believed by the food manufacturers to have resulted in some loss of quality in the food product. In order to confer these positive attributes the tin must dissolve into the product.

These accelerators are used up as tin is dissolved and therefore primarily influence the earlier stages of corrosion (phase 1). This means that as storage continues and the tin concentration increases, the rate at which tin is dissolved normally falls and the level of tin tends to plateau off (phase 2). This reduced level of de-tinning continues until most of the tin is dissolved and significant iron exposure occurs, when the rate at which tin is dissolved accelerates again (phase 3).

The rate of dissolution is normally relatively slow and shelf life is specified such that the level of tin remains below the EU legal limit of 200 mg/kg within the anticipated shelf life. Container and product specifications are defined to ensure that this is achieved. Tin corrodes preferentially off tinplate surfaces due to the ability of tin to

act as a sacrificial anode in the corrosion process.

The corrosion of tin is however; relatively slow due to the large hydrogen over-potential which exists on its surface. This protects the steel from corrosion and explains why a relatively thin layer of tin is able to provide such good corrosion protection (Figure 1).

Most food materials contain very low levels of tin (< 10 mg/kg), although foods packed in containers which have internally exposed tin may, under certain conditions, contain much higher levels.

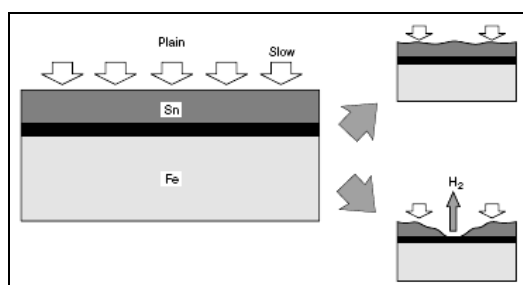


Figure 1. Corrosion processes in plain, unlacquered tinplate can. Normally the tin dissolves evenly. If localised detinning occurs, however, the underlying iron is attacked and hydrogen is evolved.

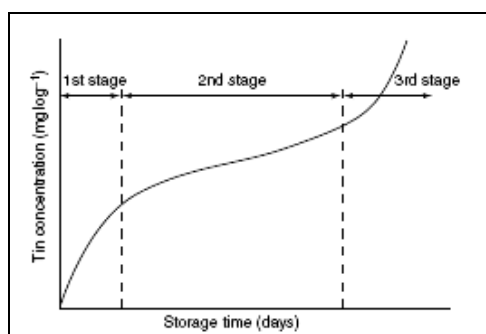


Figure 2. Tin dissolution in acidic foods, schematic rate curve.

The dissolution of tin from the can surface

Tin in canned food is derived from the tin coating which dissolved into the product during storage. This time dependence, together with the many other factors that control tin content, make the concept of mean tin levels difficult to deal with, even for a single product. One of the few generalisations that can be made is that tin levels in products packed in fully lacquered

cans are very low. In cans with an unlacquered component, however, corrosion is essential in that it confers electrochemical protection to the iron which makes up the structural component of the can. Tin pick-up is normally relatively slow – typically, 3–4 mg/kg per month for a 73 × 111 mm plain-bodied can of peach slices in syrup – and should not give rise to excessive tin levels within the expected storage life of a product. Under certain and unusual circumstances, however, dissolution often tin is more rapid than it should be and high tin levels can be reached.

Many factors interact in a complex way to affect the rate at which tin concentration increases in the food. It is because of these complex interactions that the only way of reliably predicting the rate of tin pick-up, and therefore shelf life, is through packing trials and previous experience of the product.

There are numerous factors that influence the rate of tin pick-up and these factors are well established:

- Time and temperature. Tin is dissolved over time at a rate influenced by storage temperature, initially at a higher rate than later in storage.
- Exposure of the tinplate. The area of exposure of tin is less important than the presence or absence of exposed metal. Containers with no exposed tin will give low tin levels, whereas products where there is even partial exposure, e.g. asparagus cans with one plain end or a tin fillet will dissolve tin at significant levels.
- Tin-coating weight. Although the thickness of the tin coating will ultimately limit the maximum possible level of tin, the rate of tin pick-up is increased when thinner tin coatings are used. Many other aspects of container specification are also important, e.g. tin crystal size, passivation treatment etc.
- Type and composition of the product. Several factors such as acidity/pH have a direct influence on the rate of tin dissolution. Certain compounds such as

specific organic acids and natural pigments may complex metals to alter the corrosivity of the product in respect of tin and iron.

- Presence of certain ions. Certain ions such as nitrates can greatly increase the rate of corrosion. These can arise from the product itself, from ingredients such as water and sugar, or from contaminants such as certain fertiliser residues.
- Vacuum level. Two chemical factors that increase the rate of tin pick-up are residual oxygen and the presence of chemical compounds such as nitrates (sometimes referred to as cathode depolarisers) as in Figure 2.

This third phase of the plot is normally outside the normal shelf life and is therefore seldom of any significance until high tin levels are reached as most of the tin coating has been removed and significant iron exposure occurs.

The iron

There is no recommended maximum level or legal limit for the iron content of foods. Iron is an essential element in the diet, and so this aspect plays no part in limiting the legally permitted shelf life of food products. However, high levels of iron in the food will make it unpalatable.

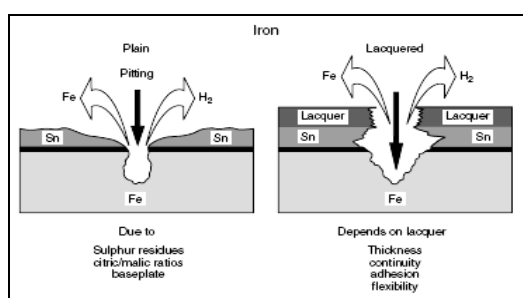


Figure 3. Comparison of pitting process in unlaacquered (left) and lacquered (right) tinplate food cans.

Dissolution of iron does occur from tinplate and from TFS containers although its rate is limited by physical factors such as the amount of steel base plate which is exposed through the tin layer or through the lacquer. All tinplate containers have microscopic pores in the tin layer exposing the steel

beneath. Normally these corrode at a slow rate but under certain situations pitting corrosion may occur, leading to preferential attack on the steel with deep craters or pits being produced which could lead to perforation and product spoilage (Figure 3).

High iron corrosion usually only occurs towards the end of tin corrosion when significant areas of steel become exposed. Once the base steel is exposed, components of the product (e.g. fruit acids) may corrode the iron and yield hydrogen gas which causes cans to swell.

The role of lacquer

The lacquer applied either on one or on both sides of tin plate for cans is done in order to protect the metallic surfaces from both the atmospheric corrosion and the can content reaction the lacquer protecting as well the food from metal contamination. Unfortunately in practice due to the lacquer coating impermeability imperfection the corrosion phenomena is not completely stopped. On the contrary it seems that in this situation there is no more inversion regarding the tin potential in ratio with the iron fact that very well explains the frequent cases of pitting corrosion of the varnished tin cans, especially those for fruits whose pH is between 4.0 - 4.5 (Bugajski, J. 1991). In Figure 3 there is schematically presented the tin corrosion through the imperfections of the lacquer coating. The lacquer's nature for internal protection can be acid resistant or sulfur resistant, according to the aggressive action of the components of the canned product.

The interior lacquers can be colored for esthetic reasons (white for sanitarium appearance) or to cover the staining effect on the metal surface due to the sulfur from certain meat products or vegetables, effect generated during the can sterilization. The shelf-life of polyester lacquer-based packages is often smaller than that of epoxy-phenolic lacquer based packages.

Experiments

The lab experiments surveyed the interaction between product and package during the time of storage (2 years). There

were used two types of food products packed in metallic cans made of tin plate, three pieces drawn with 2 lacquering systems:

- white sulphur resistant lacquer (epoxy-phenolic, pigmented aluminium);
- yellow acido resistant lacquer (epoxy-phenolic).

The verification was lead on single lots obtained from the production of a vegetable can manufacturer (peas and tomato pasta). From each lot there was taken a sample in accordance with the STAS 3730-92 requests. The cans were stored in the conditions mentioned in the product requirements. In order to study the interaction between the product and metallic package/ can, the canned foodstuff was periodically analyzed, during the storage time for the organoleptic, physico-chemical (heavy metals content) and microbiological characteristics.

The determination of the heavy metals content

The samples mineralization (dehydrated peas and tomato pasta) was lead according to the STAS 5954/1-86: the organic

substance is destroyed through carbonization and then incineration in the electric oven at 450 - 500 °C, and the resulting ash is conveyed in a solution by dissolving it in diluted hydrochloric acid (dry type of mineralization).

The measurement of the metal content was performed by AAS spectroscopy the results being given by the equipment soft and expressed in ppm (mg metal/kg product). For the iron analyze it was used an atomic absorption spectrophotometer „Analyst 400” with air- acetylene flame, background absorption correction (D₂ lamp). The tin content was analyzed with an ICP-AES spectrophotometer. The heavy metals content values for the products: „Rehydrated canned peas” and „Tomato pasta” are displayed in the table below (Table 1 and Table 2).

Results and discussions

After the 12 and 24 months of storage the heavy metals content of the rehydrated peas canned in metallic cans protected by lacquer coating white or yellow didn't vary significantly. The values obtained for tin were under the detection limit (≤0.20 ppm).

Table 1. The analysis of the heavy metals content for the product „Rehydrated canned peas”

Heavy metals content	Results (ppm)											
	Initial			After 6 months of storage			After 12 months of storage			After 24 months of storage		
	Rec.1	Rec.2	M*	Rec.1	Rec.2	M*	Rec.1	Rec.2	M*	Rec.1	Rec.2	Sum
White lacquer												
Iron	12.50	13.50	13.00	13.00	13.18	13.09	14.16	14.56	14.36	14.72	14.73	14.73
Tin	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20
Yellow lacquer												
Iron	12.50	13.50	13.00	12.36	12.42	12.39	14.50	14.40	14.45	14.2	13.9	14.0
Tin	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	≤0.20	0.32	0.32	0.32

Table 2. The analysis of the heavy metals content for the product „Tomato pasta”

Heavy metals content	Results (ppm)											
	Initial			After 6 months of storage			After 12 months of storage			After 24 months of storage		
	Rec.1	Rec.2	M*	Rec.1	Rec.2	M*	Rec.1	Rec.2	M*	Rec.1	Rec.2	Sum
White lacquer												
Iron	13.58	15.28	14.43	16.08	15.84	15.96	18.76	18.08	18.42	21.31	19.30	20.30
Tin	≤0.20	≤0.20	≤0.20	2.52	2.06	2.29	7.95	7.75	7.85	35.34	35.60	35.47
Yellow lacquer												
Iron	13.58	15.28	14.43	15.29	15.50	15.39	16.00	15.92	15.96	17.42	17.02	17.22
Tin	≤0.20	≤0.20	≤0.20	2.26	2.32	2.29	18.12	17.98	18.05	56.26	55.90	56.08

M* - the arithmetic sum of the values obtained after the analysis of two cans with products

In the case of the tomato pasta it was observed a slightly increment of the iron and tin content for the two lacquer systems during the storage from 12 to 24 months the difference being made by the high tin values in the case of the yellow lacquer and for the iron in the case of the white lacquer. In the case of both lacquers there were no values detected to surpass the imposed limits of 200 mg/kg (Regulation No 1881/2006/CE) the iron content not being regulated.

However in the case of the yellow lacquer for the product Tomato pasta canned in metallic cans there have been some exfoliations of the protective lacquer the product presenting as well a reddish color but the taste and flavor remaining the same for the tomatoes sauces characteristics. From the microbiological point of view all the cans analyzed presented a good shelf life.

Conclusions

Taking on account the risks that can rise for the package identity from using the lacquers there is a need for extensive tests in order to establish the package shelf-life required for the different foods that is canned.

When it comes to talk about the way the shelf life of a product is influenced by the material of the metal packaging it can be said that the tin dissolution influences it

more than the iron. Besides the fact that the higher concentrations of tin in foodstuff influence their shelf life these concentrations also influence (even though not dramatically) the human health. When it comes to iron's influence, the high levels of it only influence the shelf life of the products when they affect their flavour or colour otherwise bringing benefice to human health.

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