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Review Paper

TIN-PLATE CORROSION IN CANNED FOODS

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Abstract
For a hundred years ago, man by test, experince and error screened steel for produce food containers, tin is a kind of steel use to make tinplate cans. However, tin have great problem, corrosion. Corrosion abounds in nature, it is a phenomenon appeared in tin cans, and that mean happened to large amounts of food cans. More attention will be give to corrosion happens in large quantities of canned foods packs under various headings. The tin-plate corrosion occur in two sides, either in the interior of cans containing food products; due to electro-chemical reaction; or exterior of cans; due to metal itself and environment conditions. In human health, internal reaction corrosion may be changing the organoleptic properties of food stuff and could be giving some toxicological problems. To protection of tinplates against corrosion there are many methods are frequently used in the food canning industry.
Key words: Coat; lacquer; food stuff; toxicity limit, dissolution.

INTRODUCTION

The color of tin is silvery-white with high ability to corrosion, tin cans are made of tinplaate, steel sheet or strip; in some locations cans made of aluminum; coated on both sides with commercially pure tin and has been used for well over a hundred years as a robust form of food packaging. The tinplate cans are fabricated from low carbon mild steel sheet with a thin coat of electrodeposited tin [1] (**Calderón and Buitrago, 2007**).

A tin can, tin, steel can, or a can, is a sealed containre for the distribution or storage of goods, composed of thin metal. Many cans require opening by cutting the "end" open; others have removable covers. Cans hold diverse contents: foods, beverages, oil, chemicals, etc. (**Murphy, 2000).**

The tin can was patented in 1813 by the English inventor Peter Durand, based on experimental work by the Frenchman Nicolas Appert **(Cavendish, 2003**). He did not produce any food cans himself, but sold his patent to two other Englishmen, who set up a commercial canning factory and by 1813, were producing their first canned goods (**Robertson, 2006**).

Tinplate is widely used by the packaging industry. About one third of the world tin production goes to manufacture of tin cans that mean food containers recorded the largest varied applications. More than 2.5 million of tin cans are consumed every year in the United Kingdom. As well as, 25 % of worldwide production of steel used to produce beverage tinplate cans (**Cyclopaedia, 2013**). Frequently, these applications are employed to make cans for packing food, beverages and aerosol products and which used to preserved food for long time and safe according to the food composition and internal coated. **Fabech (1998**) recorded that, food producer are used lacquered cans for various category of foods, which including water, beverage, soft drinks and some alcohol drinks (beers and wine). In addition, fruit juices, nectars, tomato and tomato products. The steel of cans may be concentrated in above products and change the organolptic attributes and self-life of food, in case somewhere of lacquer coated lay as scratch. Consequently, that bare inside the container lead to oxidation reactions of tin with food substances (**Blunden and Wallace, 2003**). The reaction happened among food and tin type called stannic (divalent type, Sn^{+4}, tin IV), the last one have a toxic effects. There are differences between toxicity according to some properties of food. The pH-value played a major effect, at pH above two the tin found in form Sn $(OH)_2$ with low solubility. In another side, there are complex forms of tin appears with some chemicals (alcohols, esters, fatty acids) and constant with some organic acids (**Weber, 1987; Lemanceau, 1963**).

Tin is considered to be a priority contaminant by the Codex Alimentarius Commission (**CODEX, 2010**). Tin can enter foods either from natural sources, environmental pollution, packaging material or pesticides. Higher concentrations are found in processed food and canned foods. Dissolution of the tinplate depends on the of food matrix, acidity, presence of oxidizing reagents (anthocyanin, nitrate, iron and copper) presence of air (oxygen) in the headspace, time and storage temperature **(Perring and Basic-Dvorzak, 2002).**

Inorganic tin salts are poorly absorbed by gastrointestinal tract rapidly extracted. Nevertheless, there are several case reports of gastric irritation and vomiting in humans consuming canned foods or beverages, particularly sour fruit products packaged in tinplate cans especially containing high levels of tin. Food and especially canned food represent the main source of human exposure to tin **(Knápek et al., 2006)**.

Corrosion occurs in different metals after a certain amount of time. Corrosion usually is caused by air particles getting into a small pore of the metal, and tin plates have a variety of corrosion that happens to them. It is a typical process that is not always preventable (**Leah, 2012**). This review aim to take general overview to corrosion; determination methods, types of corrosion and a risk to consumer health.

DETERMINATION OF TIN IN CANNED FOODS

Internal corrosion in food cans is characterized by metallic dissolution which is an electrochemical reaction. Techniques that are most commonly used for determining tin are UV/VIS spectrophotometry (**Huang et al., 1997**) who found that the complex of tin (IV) with bromopyrogallol red (BPR) in the presence of nonyl phenoxy polyethoxyethanol (OP) and cetyltrimethylammonium bromide (CTAB) has a sensitive absorption peak at 304 nm. Also, the electrochemical methods are measuring the corrosion rate of tinplate under the conditions that occur in the interior of cans containing food products. **Scully (2000**) recorded that a variety of methods such as electrical resistance, gravimetric-based mass loss, quartz crystal microbalance-based mass loss, electrochemical, and solution analysis methods enable the determination of corrosion rates of metals. The polarization resistance method, based on electrochemical concepts, enables determination of instantaneous interfacial reaction rates such as corrosion rates and exchange current densities from a single experiment. There are a variety of methods capable of experimentally determining instantaneous polarization resistances such as potential step or sweep, current step or sweep, impedance spectroscopy, as well as statistical and spectral noise methods. All of these methods utilize two-, three-, or four-electrode electrochemical cells.

Calderón and Buitrago (2007) were used Cyclic polarisation (CP) and electrochemical impedance spectroscopy (EIS) were carried out in a three electrode cylindrical cell, This kind of electrodes can be used due to high corrosion potential stability in the test solutions (**Kok, et al., 2005**). The use of additives in products that will be packed in tinplate containers has to be carefully considered, with knowledge of their performance and the reactions that will take place between chemicals and metal surfaces. The use of an additive in electrolyte solution (SE) was detrimental to the anti-corrosion performance of tinplate. In the SE a reversal of cathodic/anodic behaviour was observed in the galvanic couple between low-carbon steel and tin. This means that the tin coating no longer acts as a sacrificial anode, and consequently rapid corrosion of the tinplate occurs

Mino (**2006**) determined the tin in canned foods by X-Ray fluorescence spectrometry, X-Ray measurements were performed on pellet samples with a wavelength-disperive X-Ray fluorescence spectrometer equipped with a rhodium anode X-Ray tube. Concentrations of tin and other elements were analyzed using the fundamental parameter method with several standard samples.

Inductively coupled plasma atomic emission spectrometry (**Rončević et al., 2012; Perring and Basic-Dvorzak, 2002**), electrothermal atomic absorption spectrometry (**Chiba, 1987**) and flame atomic absorption spectrometry (**Knápek et al., 2006**) in this method, the samples nebulised by a high sensitivity nebuliser to nitrous oxide and acetylene flame.

Lambrev et al. (1997) used the neutron activation for studying corrosion processes and protective ability of paint coatings. The method involves the neutron activation of specimens in a reactor followed by radioactive migrant detection with gamma-ray spectrometry of high resolution. The method is shown as appropriate for determining the partial rates of the components of tin and chrome plate protected with various coating or presented as bare metal in model media as well as real preserves.

DISSOLUTION OF THE TIN INTO THE FOOD

There are many factors affected on dissolute of tin into foods. Firstly, chemical factors (inside tin) include oxidizing agent (from food or head space) and nitrates (might be from fertilizing ingredients), (**Palmieri et al., 2002**), as well as anthocyanin. Secondly, environmental factor (outside tin) include temperatures. Thirdly, other factors such as: type of steel, volume of containers and volume of head space. **FSA (2002**) studied that the fully lacquered cans for acidic foods decreased of 99.5 % of 1200 tested cans below the United kingdom limit of 200mg/ kg of tin.

Poisoning of the tin into the food

Since 1980, systematic efforts have been made by the Joint UNEP/FAO/WHO Food Contamination Monitoring Programme to collect information on dietary intake of various contaminants. Tin poisoning refers to the toxic effects of tin and its compounds. Cases of poisoning from tin metal, its oxides, and salts are "almost unknown" on the other hand certain organic compounds are almost as toxic as cyanide (**Graf, 2005**). Maximum level of tin in canned foods is 200 mg/kg for canned foods other than beverages and 100mg/kg for canned beverages, Including fruit and vegetable juices (**CR, 2006)**. **MAFF (1992**) reported that the recommended maximum permissible levels are 250 mg/kg body weight for solid foods and 150 mg/kg (200 mg/kg in United Kingdom) for beverages (**CODEX, 2005; WHO, 2004**). **Blunden and Wallace (2003**) found in their review some evidence suggesting that the contents of almost 4% of plain internal tinplate food cans contain over 150 mg/kg of tin. Adverse gastrointestinal effects were observed in limited clinical studies at concentrations of 700 ppm.

Although tin is corrosion resistant, acidic food like fruits and vegetables can cause corrosion of the tin layer. The acute toxicity of inorganic tin is manifested as gastric irritation, nausea, vomiting, diarrhea and abdominal discomfort have been reported after ingesting canned food containing 200 mg/kg of tin (**Knápek et al., 2006**).) The maximum levels for tin established by European Union legislation vary from 50 mg/ kg in canned baby foods and infant foods up to 200 mg kg^{-1} in canned food (**Boutakhrit et al., 2011**). **Blunden and Wallace (2003**) mentioned that the limit of tin for chronic exposure of 2 mg/ kg body/ day, and in the worst case from 8 to 16 mg/ day (0.13 – 0.30 mg/ kg body weight) for adults with weight 60 kg. A 2002 study showed that 99.5% of 1200 tested cans contained below the UK regulatory limit of 200 mg/kg of tin, an improvement over most previous studies largely attributed to the increased use of fully lacquered cans for acidic foods, and concluded that the results do not raise any long term food safety concerns for consumers. The 2 non-compliant products were voluntarily recalled (**FSA, 2002**).

TYPES OF CORROSION

Leah (2012) recorded three types of corrosion appears in tin-plate cans, (1) Filiform Corrosion: this type happens under the thin coatings of tin. It distributes throughout the tin plate like little threadlike filaments. The directions the corrosion takes are never similar. They usually bulge and crack the coating. (2) Pitting Corrosion: happens in a specific area of the surface, it usually occurs because of dirt particles sticking on the tin plate. There are also water-line attacks, crevice corrosion and concentration-cell corrosion. (3) Erosion Corrosion: happens slowly and over time. It occurs after a tin plate has been exposed to something, such as water or air, for too long. Erosion begins with a small air bubble and continues on the path of corrosion.

INTERNAL CORROSION

Internal corrosion in food cans is an electrochemical reaction, and the levels of it depending largely on the type and acidity of food, the presence of oxidants, the duration and temperature of storage and presence of air in the can headspace (**JECFA, 2000**). These reactions may cause organoleptic changes in the product, loss of vacuum, swelling, and leaking in extreme cases. In some instances the metal dissolution may give rise to toxicological problems. Therefore, these phenomena are often the limiting factor in the shelf life of canned products and affects in color, texture, and sensoric properties of the foods (**Mannheim and Passy, 1982**).

Internal corrosion in some canned food

The dissolution of iron and tin from tinplate cans filled with some foods are studied by many researchers, **Madegowda et al. (2006)** suggested that among different fractions of mango pulp, only organic acid fractions were responsible for corrosion. Corrosion was more in pulp and nectar prepared from unpeeled mangoes. The peel contains gallic acid and ellagic acid of which the former acts as accelerator of corrosion. **Grassino et al. (2009)** studied the corrosion behaviour of tinplate cans in contact with tomato purée (pH 4.34), who found the maximum values in cans were up to 284 mgkg (-1) for tin and 513 mg kg(-1) for iron at elevated storage temperature. **Tošković et al. (2002)** noted that the brine composition of legumes packed in tinplate was changed during stored at 25ºC.

EXTERNAL CORROSION

External corrosion of tin cans is depend on a metal itself, it's hydrogen over-voltage and surface homogeneity, the formation of galvanic microcells in the heat processing metallic equipment due to non-homogeneity of its metal surface and due to contact of one metal with another. The external corrosion may be attributed to the environment, such as food residues, quality of process water or steam, corrosive glues or labels and poor handling (**Mannheim et al, 1983**).

ANTI-CORROSION

There are variable methods used to protect the tin from corrosion, such as stainless steel, electrogalvanized cold-rolled steel (a type of zinc-plated steel), enclosure design fully sealed enclosures to damp places, and painting treatments or powder coating on the surface of metal.

In food cans, the surface of the tinplate is normally coated with a lacquer to improve the corrosion resistance of the container. The anti-corrosion performance of lacquered tinplate cans depends on the barrier properties of the lacquer and on the nature of the canned products (**Armstrong and Wright, 1992**). When the lacquer used does not produce an effective barrier action, the corrosion of tinplate depends on the electrochemical interaction between tin and canned products. The high hydrogen over-voltage of tin leads to very low corrosion rates of the metal when exposed to a reasonable pH range (**Murphy, 2000**). In natural environments, the tin metal is protect from further corrosion because which is protect by very stable oxides and hydroxides. While, tin has the ability to form soluble complexes with certain anions, when this occurs the corrosion of tin is accelerated. Organic acids contained in the products may pass into brine and effect the corrosion, addition of very small amount of nitrates (up to 0.01g) leads to acceleration of corrosion in storage of foodstuff with $pH<7$ (**Tošković et al., 2002**).

Radojčić et al., (2008) studied the influence of natural honey (chestnut and acacia) and natural honey with black radish juice, on corrosion of tin in aqueous and sodium chloride solutions using weight loss and polarization techniques. The inhibition efficiency of acacia honey was

lower than that of chestnut honey, while the addition of black radish juice increased the inhibition efficiency of both honey varieties. The process of inhibition was attributed to the formation of multilayer adsorbed film on the tin surface. The adsorption of natural honey and honey with black radish on tin was found to follow the Langmuir adsorption isotherm.
During food and beverage packaging in tinplate cans the dissolution of tin and chromium into food content may occur. Therefore, the use of essential onion oil (EOO) improves the protection of tinplate compared with dioctyl sebacate oil (DOS) oil, and is almost as effective as epoxy phenolic lacquer, the addition of EOO can be recommended due to lower cost of canned food production and enhanced organoleptic properties, but the storage temperature has to be lower than 36 °C (**Grassino et al., 2010; Grassino et al., 2009a).** Moreover, **Grassino et al. (2009b)** reported that the addition of potassium nitrate to tomato purée prevents the corrosion process in the case of tin, dissolution of tin started after 30 (36°C) and 60 (20°C) days of storage as a consequence of nitrate action.

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