INORGANIC TIN CONTAMINATION IN CANNED FOODS

CXC 60-2005

INTRODUCTION

History of use of tin

1. Tin is a soft, white, lustrous metal with an atomic weight of 118.7 and the chemical symbol Sn after its Latin name, *Stannum*. It has a relatively low melting point (231.9 °C) and is highly resistant to corrosion, which makes it an ideal element for the protective coating of metals. Over 50% of the world's tin production is used for plating steel or other metals.

2. Today some 15 million tonnes of tinplate are produced each year using rapid and highly sophisticated production methods. These methods are able to control steel thicknesses and tin coating masses to within the extremely fine tolerances required for modern can making processes such as high speed welding.

Tin as packaging for canned food

3. Tin is used to protect the steel base from corrosion both externally (aerobic conditions) and internally when in contact with foods (anaerobic). Under the anaerobic conditions expected inside an internally plain processed food can, tin will normally behave as the sacrificial anode, dissolving very slowly whilst protecting the steel base from corrosion and creating a reducing environment in the can. It is this mechanism that has enabled the plain tinplate can to maintain its long history and proven track record of providing wholesome food on a year round basis and safe storage for long periods of time.

4. The later development of can linings (lacquers) enabled different types of food products to be satisfactorily packed. For example, some highly pigmented foods (beetroot, berry fruits) have their colours bleached by tin dissolution and are best protected from contact with tin by use of linings. A small number of food products (e.g. sauerkraut) have a different corrosion mechanism, in which the tin does not behave sacrificially and direct corrosion of the steel base can occur. These products should also have the additional protection of an internal lacquer system.

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5. The uses of tin have changed considerably over the years. Humans have, however, been exposed to tin for centuries, through the food they eat, with no known negative long term effects. Only limited data is available on the toxicological effects of inorganic tin as present in canned foods, resultant from dissolution of the tin coating. The main potential hazard from acute ingestion seems to be gastric irritation in some individuals from exposure to high levels.

6. Hence the canning industry worldwide and government regulators consider it both desirable and in accordance with good manufacturing practice that measures be adopted to minimise the levels of tin in canned foods, whilst continuing to allow for the functional use of plain tinplate cans.

Technological and commercial implications

7. Metal packaging faces strong competition from glass and plastics. Even with innovations such as easy opening tear top cans, metal containers are below the average growth of market share for packaging products.

8. The best solution to prevent or reduce detinning of cans by aggressive foods is internal lacquering. The use of lacquers has permitted the extension of the use of cans to additional products, including highly aggressive ones.

9. The coating thickness greatly affects the performance of the lacquered food can. Non-aggressive products such as apricots and beans require a thickness of 4-6 µm while tomato concentrate needs layers of 8-12 µm to prevent interaction between the can and its contents.

10. Adhesion is required to prevent reactions between the can and its contents. Currently adhesion is tested by measuring the force required to lift a dry lacquer coating from the metal in a peel test. While this test readily identifies films which are unsuitable there is no guarantee that those which pass would give satisfactory long term results when in contact with specific foods.

11. Toxicologically significant contamination of canned food from tin dissolution may arise as a result of poor manufacturing practices or prolonged/incorrect storage or both.

12. Although lacquering of cans significantly reduces the risk of tinplate corrosion, the use of lacquer coatings is not always practicable or cost effective.
13. It could be argued that "since lined cans are readily available, then why not use them for all canned foods and thus prevent any tin uptake?" There are, however, very valid technical and marketing reasons why some products require to be packed into plain cans.

Flavour and colour

14. The need for tin dissolution to maintain the desired colour and flavour attributes of products such as asparagus, light coloured fruits and juices and tomato based products has long been established. It is believed that the presence of tin creates a reducing atmosphere in the can preventing undesirable oxidative changes in these products, which would otherwise develop brown discolourations and unacceptable flavours. Such quality loss would severely affect their marketability and sales with significant implications for the canning industry and their suppliers.

15. It is interesting to note that this concept also works in reverse – some highly pigmented foods, such as acidified beetroot and berry fruits, must always be packed into fully lined cans because, apart from their aggressive behaviour towards tin, colour bleaching via tin dissolution can be a significant problem.

Corrosion factors

16. Most of the products normally packed into plain cans are relatively high acid products. In addition to the organoleptic considerations, should these products be packed into lined cans a change of corrosion mechanism would result. For the more aggressive products this would result in a greater tendency for underfilm corrosion/delamination (particularly for tomato products) and to pitting corrosion of the steel base and subsequent implications of potential for perforation failure.

17. The tin level is dependent on a large number of factors, many of which relate to natural variations or occur after the can has left the control of the manufacturer:

Corrosion mechanisms

18. With respect to the internal tinplate surface of cans, there are four main corrosion mechanisms:
    - i) Normal detinning;
    - ii) Rapid detinning;
    - iii) Partial detinning; and,
    - iv) Pitting.

19. **Normal detinning** is the slow corrosion of the tin coating, and is an essential process in plain cans to provide electrochemical protection to any exposed areas of base steel. This process leads initially to etching of the tinplate and much later to detinning of the surface. Normally, etching should occur evenly over the wetted internal surface of the can; in the first month or so the mirror surface should change to one in which the shape of the individual tin crystals may be seen with the eye. Grey detinned areas should not be evident in cans stored for less than 1.5–2 years. Under normal detinning conditions

tin is anodic to steel and offers complete cathodic protection. Dissolved tin enters into unobtrusive complexes with product constituents. The hydrogen is oxidised by depolarisers or diffuses through the steel wall. This corrosion situation is characteristic of some citric products, stone fruit products and most low-acid products.

20. **Rapid detinning** is caused by the use of plate with a tin coating mass that is too light, or by a product that is intrinsically too corrosive or contains corrosive accelerators. Whilst the tin is sufficiently anodic to protect steel, the electrochemical rate is high, often resulting in hydrogen evolution and early product failure. Nitrate in products with pH less than 6 has been implicated in incidents of rapid detinning. This is one type of mechanism for rapid detinning. The other is 'direct attack on the tin'. During detinning no hydrogen forms, can vacuum remains unchanged. Examples are depolarisers like nitrate, oxygen, and sulphite. Certain azo dyes, anthocyanins, phosphates and dehydroascorbic acid have also been implicated in rapid detinning.

21. **Partial detinning** together with pitting is a rare form of corrosion. Tin is anodic to steel but localised anodes develop on exposed steel causing iron dissolution (pitting). Early failure takes place due to hydrogen swelling or to perforation at the sites of pitting. This mode of corrosion occurs with tinplate with poor corrosion resistance, or in certain products that have high corrosivity, such as prunes and pear nectar.

22. **Pitting** corrosion occurs when the normal tinplate tin/iron couple is reversed and iron becomes anodic to tin. Tinplates containing high arsenic levels can promote pitting corrosion in can products containing corrosion accelerators. Preferential absorption of protective substance onto the tin surface, such as can occur in sauerkraut, leads to pitting. Products formulated with acetic or phosphoric acids have also suffered spoilage losses due to pitting. Perforation and hydrogen swells occur within a year in such products. Products containing copper and nickel residues can promote pitting corrosion. Products containing proteins and associated amino acids can produce sulphur compounds during heating, including mercaptans, sulphide ions and hydrosulphide ions which readily react with tin to cover the metal surface with thin layers of tin sulphides. Tin sulphides films reduce the passivity of the tinplate surface and may promote pitting corrosion of the base steel.

Corrosion inhibitors

23. **Passivation** refers to the chemical treatment applied after tin deposition which stabilises the surface characteristics of tinplate by controlling tin oxide formation and growth; two levels of passivation are usually available – cathodic dichromate (CDC) is the higher level and the treatment usually applied.

24. The most obvious influence on internal corrosion in plain tinplate cans is the chemistry of the food product. It should be noted that fruits, vegetables and tomatoes will have significant natural variation in, for example, pH and acid type and concentration, dependent on variety, maturity, time/place/ conditions of harvest, soil chemistry and agricultural practices. These are difficult for the canner to control and may ultimately impact on the level of tin uptake by the product.

Corrosion accelerators

25. The presence of a chemical species with the ability to accept electrons will increase the rate of corrosion. Some products may contain such 'depolarisers' which will accelerate tin dissolution. Good process control by the canners helps to minimize the presence of headspace oxygen and the presence of oxidizing agents like nitrates and sulfites which can accelerate tin dissolution.

Storage temperature

26. A further significant factor influencing tin levels is the length and temperature of storage subsequent to canning. Tin uptake will increase with time and most products exhibit first order reaction rates where the rate of dissolution doubles for every 10 °C rise in temperature.

1. SCOPE

27. Whilst there are other sources of tin exposure in humans, the most common route is via ingestion of inorganic tin from canned foods.
28. This code of practice relates solely to the migration of inorganic tin into foods from the internally plain (i.e. not lacquered) tin coating of tinplate cans.

29. This code of practice is not intended to apply to tin exposure from any other source and is specific to inorganic tin.

30. This code of practice relates to thermally processed canned human foods (including fruit and vegetable juices) which are packed into plain tinplate cans. It is considered that this description covers both:
    i) Hot fill and hold products; and,
    ii) Hot or cold fill and retort products.

31. Dry goods and 100% oil products are not included, because they do not experience tin migration.

2. RECOMMENDED PRACTICES TO MINIMISE TIN UPTAKE BY FOODS PACKED INTO PLAIN TINPLATE CANS

32. There are many factors which may influence the level of product tin uptake in plain tinplate cans. Some are very minor and others, usually specific to the chemistry of the processed food, may have a significant effect on internal can corrosion and product tin dissolution. The recommendations contained below are based on an attempt to identify all of these factors, no matter how minor, and to suggest specific areas where monitoring or other controls would be beneficial.

33. In summary the factors which have been identified can be grouped as follows:
    i) Choice of tin coating mass and passivation level;
    ii) Damage to tin coating or passivation;
    iii) Type of food product, pH and acid content;
    iv) Presence of corrosion accelerators, such as nitrates, in the raw food ingredients;
    v) Presence of sulphur compounds in the food;
    vi) Presence of oxygen within the sealed can;
    vii) Process times and temperatures;
    viii) Storage times and temperatures; and,
    ix) Storage humidity.

2.1 Packaging manufacturer

2.1.1 Tinplate supplier

34. Tinplate customers should state the end use when ordering tinplate. The tinplate supplier should have sufficient expertise to ensure that specifications for the tinplate are appropriate to the stated end use and notify the customer should there be any concerns (e.g. with regard to the passivation level or the requested tin coating mass).

35. The tinplate manufacturer should have quality procedures in place to ensure that every tinplate order conforms to the required standard (e.g. ASTM; ISO etc.). Incorrect tin coating masses or passivation levels could result in abnormal corrosion and increased product tin levels. Low oil levels may lead to abrasive damage to the tin coating during transport and can manufacture.

2.1.2 Can maker

36. Can makers should approve tinplate suppliers on the basis that each supplier has demonstrated compliance to agreed standards and ordering requirements.

37. The can maker should have sufficient expertise to ensure that the customer’s ordering requirements (i.e. passivation and tin coating mass) are appropriate for the end use and should notify the customer of any concerns.

38. The can maker should assist the customer in determining the correct can specification for any new food product or recipe change. Such changes should be tested to ensure that product tin uptakes are not excessive.

39. Machine settings for processes where metal working occurs (e.g. beading) should be such as to minimise damage to the tin coating.

40. If a sidestripe is applied to 3 piece cans then excessive heat should be avoided when curing the stripe.

2.2 The canner

2.2.1 Raw Materials

41. The canner should work closely with the can supplier to ensure an appropriately specified can is supplied for any given application. Procedures should be in place to ensure that cans are supplied to specification.

42. The canner should consult with the can maker to determine the correct specification can for any new product or any recipe change of an existing product. It is extremely important that sufficient pack testing is conducted to gain a thorough knowledge of the corrosion mechanism, likely product tin uptakes and overall suitability of the can specification for the product.

43. Canners should be knowledgeable about the shelf life of all their products with respect to likely tin uptakes. It should be noted that fruits and vegetables in particular may have a significant variation in their chemistry, dependent on variety, maturity, time/place/conditions of harvest, soil chemistry and agricultural practices. These are difficult for the canner to control and may ultimately impact on the level of tin uptake by the product.

44. Quality procedures should be in place to ensure that product batches conform to recipe specification.

45. Particular attention should be paid to the pH of the food and the addition of food acids. It should be recognised that corrosion is pH dependent and that too large a drop in pH may give a significant change in corrosive behaviour and tin uptake. Different food acids (e.g. citric, malic fumaric and acetic) behave in different ways with respect to internal corrosion and any ingredient change from one type of acid to another should be thoroughly tested. Acetic acid is particularly aggressive towards tin.

46. The presence of a chemical species with the ability to accept electrons will increase the rate of the corrosion reaction. Nitrate is a corrosion accelerator and its presence, even at low levels (1mg of NO_3^- will yield nearly 8mg of Sn^{2+}) causes rapid de-tinning. In a 400g can, 10mg of NO_3^- will rapidly react to give approximately 80mg of Sn^{2+} or, in other words, a product tin concentration of 200 ppm. In about one year 100 ppm of nitrate will completely de-tin a No. 303 can with an inside coating weight of 11.2 g/m^2. Nitrates originate from over zealous use of fertilizers and some fruits and vegetables can accumulate high levels (e.g. tomatoes and pineapples). It is essential, when nitrates are likely to be a problem that the canned food manufacturer and his suppliers have a system in place to ensure fruits, vegetables and other ingredients are acceptable for use in canning.

47. Sulphur residues have also been known to cause corrosion problems in plain tinplate cans. These residues can be of agricultural origin or may have resulted from bleaching or preserving agents used in some ingredients. The canned food manufacturer and his suppliers should again carry out any necessary testing and make sure that the raw materials are fit for purpose.

48. Some foods, especially protein rich meat and fish and, to a lesser extent, vegetables (e.g. peas, beans, corn etc.) contain naturally occurring sulphur compounds. These can react with a plain tinplate surface to give a purple-black stain of tin sulphide. Although the stain is harmless, it may serve to change the passivation of the tinplate surface, which, in turn, could alter the rate of tin uptake. The areas of staining may also be localised – stressed areas such as can beads; contact points with a solid product in a liquid medium; headspace/product line interface. Whilst an overall increase in passivation is more likely to slow tin uptake, localised areas of staining can have a detrimental effect, especially if a corrosion accelerator such as oxygen is also present. Degree of sulphide staining is also influenced by pH, process time and temperature and the presence of certain cations. Al^{3+} and Fe^{3+}, Fe^{2+} ions, found in some treated potable water, act as catalysts for the breakdown of naturally occurring sulphur compounds. Subsequently the presence of these ions increases the rate and severity of sulphide staining. Clearly the canner must have an intimate knowledge of his product; the likely variations that could occur in raw materials and process; and the range of effects that these variations could produce within the can. That knowledge should be used to set controls where necessary and to determine consistent supply.

49. All raw materials from all suppliers should be well documented especially when a supplier is changed or a raw material is obtained from another source or location. In the unlikely event that unexpectedly high product tin levels occur, documentation makes it easier to track back to any specific changes and to take appropriate action.

50. Water quality should be monitored as some water supplies may contain corrosion accelerators such as nitrates.

2.2.2 Processing

51. The canned food manufacturer should take all necessary steps to eliminate oxygen from within the can prior to closing and to ensure an adequate can vacuum. Oxygen is a corrosion accelerator and its presence in a can after closing can lead to early tin dissolution, especially from the headspace area. Oxygen can be present in the interstices of the product and steam exhausting plus a high fill temperature will help its removal. Minimising headspace, whilst still allowing for product expansion, also helps eliminate oxygen. Another control method is closing under vacuum. Steam injection to the headspace must be consistent and controlled. Line stops and delays between filler and closer should be avoided.

52. The primary method used for removing oxygen is closing under vacuum. Steam exhausting is not used as much.

53. Chemical reactions, such as corrosion, are accelerated by increasing temperature. Canners should be aware that excessive processing times at high temperatures may have an effect on advancing tin uptake.

54. Inadequate cooling and drying should be avoided because this means, for a large mass of cans, that they will remain at an elevated temperature for a considerable period of time. Cans should be cooled to 35–40 °C. Cans cooled to a lower temperature may not dry adequately leading to external rusting. Cans that are not adequately cooled can be subject to spoilage by thermophilic bacteria or products may suffer a loss in quality.

2.2.3 Finished goods storage

55. Internal can corrosion, like any chemical reaction, is temperature dependent. In general for every 10 °C rise in temperature the reaction rate will double. The expected level of tin uptake from a can stored at high temperature (i.e. 40 °C) would be significantly higher than from a can stored at lower temperature (i.e. 10 °C) for the same period of time. Canned food manufacturers should consider the location of their finished goods storage areas when determining maximum storage times. For example: - what is the likely maximum temperature; are some areas heated more by the sun; how many days per annum at relatively high temperatures etc.?

56. Stock control is required to ensure finished canned goods from earlier production dates are used first.

57. Warehousing be done under conditions where the temperature can be controlled. Large swings in temperature can lead to condensation of moisture on the exterior of cans which can lead to rusting.

2.2.4 Other considerations

58. Can damage should be minimised as this can lead to local areas of de-tinning. For this reason it is preferable to use ink jet coding rather than embossing.

2.3 Transport and warehousing

59. Please refer to paragraphs 56 and 57 in Section 2.2.3 Finished Goods Storage.

60. Temperatures encountered during Transport need to be considered if the canned goods are likely to remain at these temperatures for any length of time (i.e. during shipping). If possible, it is preferable to export stock from a more recent production date if high temperatures are likely to be encountered during shipping or at the final destination.

2.4 Retailer

61. The retailer should maintain correct stock rotation to ensure that shelves are stocked with cans in production date sequence.

2.5 Consumer

62. The consumer should choose a storage location for canned foods that is not subject to excessive heat. Cupboards should not be close to ovens or heaters and should preferably not be in direct sunlight.

63. Unused food or juice left in plain tinplate cans may rapidly accumulate tin in the presence of air. It should be transferred immediately to a clean plastic or glass container and stored in the refrigerator.

GLOSSARY OF TERMS

64. This glossary defines the main technical terms used in the preceding code and relates specifically to the tinplate, can making and canning industries.

Aerobic	presence of oxygen.
Anaerobic	absence of oxygen.
Annealing	heating process used in tinplate manufacture to soften the steel strip after cold rolling and to impart the required hardness; the process can either be continuous (continuous annealing or CA) or in batches (batch annealing or BA).
BA	see ***Annealing.***
Beads, Beading	corrugations rolled into can walls to give added strength to the can body.
CA	see ***Annealing.***
Can linings	see ***Lacquers.***
Closer	machine used to seal an end onto a can.
Closing under vacuum	applying a vacuum to the closing chamber of the can closer, whilst sealing the end.
Corrosion	chemical action of dissolving the surface of a metal (eg. tin in food medium).
Corrosion accelerator	chemical species with the ability to accept electrons, which will increase the rate of a corrosion reaction.
Corrosion mechanism	specific chemistry of any corrosion reaction; especially for tinplate when 2 metals (tin and iron) are coupled and where one or both has the potential to dissolve.
Detinning	descriptive of the corrosion process where the internally plain tin coating is slowly dissolved by the food medium; rapid detinning refers to abnormally fast tin dissolution, caused by the presence of corrosion accelerators.
DR Tinplate	'double reduced' tinplate where a second rolling is used to reduce steel thickness in order to produce a thinner but stronger product.
Electrolyte	substance which dissociates into ions when dissolved in a suitable medium; hence a tin rich electrolyte is used in tinplate manufacture (see ***Electro-Tinning***); the food in

	contact with an internally plain can may also be described as an electrolyte.
Electrolyte Tinplate	low carbon mild steel strip coated on both top and bottom surfaces with an electrolytic deposition of tin; the deposited tin exists as an alloyed and free tin and has a passivated surface as well as a coating of oil.
Electro-Tinning	act of plating tin from a tin rich electrolyte onto a continuous steel strip to produce electrolytic tinplate.
Electro-Plating	see ***Electro-Tinning.***
Embossing	use of a die to stamp a product code or manufacturing date into a can end
Environment	see ***Reducing Environment*****.**
Filler	machine used to automatically fill a can with the desired weight or volume of food.
Fill Temperature	temperature at which the food is filled into the can.
Food Acids	organic acids, naturally occurring in foods, especially in fruits and vegetables; also used to impart flavour and to modify the pH of foods.
Headspace	space left in the top of the can after filling and end sealing, in order to allow for product expansion during thermal processing.
Hot Fill and Hold	process where a high acid food product (usually juice or liquid) is filled at high temperature, the end sealed and cans held for a period of time before cooling; commercial sterility is achieved without retort processing.
Inject Coding	use of an ink jet to print a product code or manufacturing date on the can end
Internal Corrosion	corrosion occurring within a food can (see ***Corrosion***).

Ion	electrically charged (positive or negative) atom or molecule formed by the loss or gain of one or more electrons or by dissolving an electrolyte in a solvent.
Lacquered Tinplate	see ***Lacquers*****.**
Lacquers	inert organic coatings used to give additional protection to tinplate; usually applied in liquid form and 'cured' at high temperatures.
Linings	see ***Lacquers*****.**
Pack Testing	storage and regular sampling of canned foods under controlled temperature conditions to determine internal corrosion characteristics and potential shelf life.
pH	measure of acidity.
Plain Cans	cans made from plain tinplate.
Plain Tinplate	bright tinplate without any additional lacquer coating.
Process Temperature	see ***Process Tim*****.**
Process Time	the calculated time at a particular temperature (process temperature) for which a specific can size and food product need to be heated in order to achieve commercial sterility.
Product Line	maximum level or height of the product in the can; the headspace is above the product line.
Rapid Detinning	see ***Detinning*****.**
Reducing Environment	conditions expected inside a plain processed food can, whereby the contents are protected from oxidative reactions such as colour change.
Retorting	method of heating cans, usually under steam pressure, to create internal can temperatures well in excess of 100 ^{o}C in order to achieve commercial sterility in a shortened period of time; retorts are, in effect, very large pressure cookers.
Retort Processing	see ***Retorting*****.**

Sacrificial Anode	refers to a metal which slowly dissolves in a corrosion reaction and, in so doing, protects a second metal from corrosion (eg. tin behaving as the sacrificial anode to protect the coupled steel base); see also ***Corrosion mechanis*** **.**
Shelf Life	the expected acceptable commercial life of any canned food.
Shelf Life Testing	see ***Pack Testing*****.**
Sidestripe	thin band of lacquer designed to protect the weld of a can body from corrosion.
Steam Exhausting	passing filled cans through a tunnel of steam, prior to sealing, to assist in oxygen removal from the product and headspace.
Steel Base	low carbon mild steel strip to which the tin coating is electrolytically applied.
Stock Rotation	method of ensuring the oldest canned products are identified, removed first from warehouse storage and are first onto the retailers shelf.
Sulphide Staining	where naturally occurring sulphur compounds in foods react with a plain tinplate surface to form a purple-black stain of tin sulphide.
Thermal Processing	use of any heat process to ensure the commercial sterility of filled cans (see also ***Hot Fill and Hold*** and ***Retorting*****).**
Tin Coating	See ***Electrolyte Tinplate*****.**
Tin Coating Mass	mass of tin, expressed in g/m^2, which is applied to each side of the steel base; standard coating masses generally range from 2.8 to $11.2 g/m^2$ in increments of $2.8 g/m^2$; the internal tin coating mass of plain cans is usually either 8.4 or $11.2 g/m^2$.
Tin Migration	see ***Corrosion*** and ***Detinning*****.**
Tinplate	see ***Electrolyte Tinplate*****.**