# A CASE STUDY OF RESEARCH AND DEVELOPMENT AT THE GOLDEN CIRCLE CANNERY

by

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EXTRACT

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# CHAPTER 3

# THREE DEVELOPMENT PROJECTS

## 1. NITRATE IN PAPAWS

### (a) Introduction.

Processing of papaws has had an eventful history at Golden Circle. Originally, papaw was processed into two products - papaw tidbits consisting of papaw cubes in syrup, and fruit salad which contained papaw as well as other tropical fruits.

Papaw tidbits have always been packed in internally lacquered cans but the fruit salad, initially canned in unlacquered c no was later processed into lacquered and unlacquered cans depending on the nitrate content of the papaw. Events leading up to this are described later when the effects of nitrate on tinplate are considered.

On the basis of a routine spot test, papaws were graded into two categories - high nitrate and low nitrate. The former was placed in unlacquered cans while the latter, the low nitrate papaw, was canned in plain steel as corrosion was minimal.

In spite of this, papaw has now been removed from fruit salad and replaced by peaches, which present no problem.

Commercial users who require papaw fruit salad in large A10 cans receive the product in unlacquered cans - their attention being, drawn to the fact that it has a short shelf life, perhaps no more than 2 to 3 months. Generally it is used immediately it presents no problem.

### (b) The Problem.

In 1965 the cannery came across canned papaw products which appeared to be normal externally, but in which some cans had lost the entire tin lining from the inside of the can.

At first the problem was thought to be due to the change from using hot dipped tinplate to electrolytic plate, despite very satisfactory performance in test samples. Further analyses and evaluation of a full day's run located in warehouse stocks showed a severe corrosion problem. The cans involved were both hot dipped and electroplated and whilst there were minor differences in average content of tin around 20 ppm in favour of the hot dipped product this was considered insignificant when levels of around 200 ppm of tin were being encountered. Other causal factors were obviously involved.

Such amounts of tin may not sound significant and in fact are under the maximum set by Queensland laws, but when more than 150 ppm of tin have passed into solution the product is approaching an area of marginal consumer acceptance, and levels higher than the 250 ppm maximum are certain to cause complaints.[1]

**(c) Locating the cause.**

Process variables such as cooking temperatures and times were studied without profit. The first clue proved to be the behavior of individual papaws which showed marked variations in the corrosion rate, unrelated to maturity, variety or district. Chief Chemist at Golden Circle Peter Seale described their approach to the problem:

> Among the list of causal factors, some 30 in number, which we had compiled, was nitrate content, which had been under some suspicion as a likely cause of rapid detinining of tomato paste in South Africa. Following this lead and using a spot-test procedure, we commenced checking fruits and found levels varying up to 300 ppm of nitrate. We rapidly obtained highly significant correlations between the nitrate content, rate of corrosion and tin content after extended storage. Our first eight trials were positively correlated and then commenced searching for reasons and for counter measures.[2]

**(d) The Quick Response.**

The first hope of a solution was when a molybdenum deficiency in the tissue was suspected. Sprays and injections of this trace element produced no change during the latter part of the 1966 season.

**(e) Further Investigations.**

Investigations proceeded in two directions: cultural checks and technological checks.

(1) Cultural checks.

A full survey of cultural practices employed by some 200 growers had shown broad correlation between the usage of nitrogenous fertilizer and accumulation within the fruit. In 1961, Department of Primary Industry trials showed that yield per tree could be increased from 13 to 26 kg by an annual application of 1 kg of sulfate of ammonia.

Applications of 0 to 180 kg of nitrogen per acre per year were made by growers and one local grower had 100 ppm nitrate in his irrigation water. However, there were also anomalous cases where no fertilizer has been added and high levels of nitrate were detected. Agronomists noted the tendency for older patches to be substantially free of nitrate while younger ones had a high nitrate content. This suggested the presence of an enzyme which could reduce the nitrate to a less corrosive form in the larger root systems of the older plantings.

(2) Technological Leads.

The nitrate-tin reaction was at this time receiving considerable international attention. A group of seven U.S Universities were co-operating in a study of spinach packs.[3] Researchers, were also active in South Africa, Italy and France.

Golden Circle researchers sought possible solutions to their problem by investigating the nature of the detinning reaction as discussed below.

## CHEMISTRY OF CORROSION

The structure and dimensions of tinplate are shown schematically, in cross-section in Figure 3:[4]

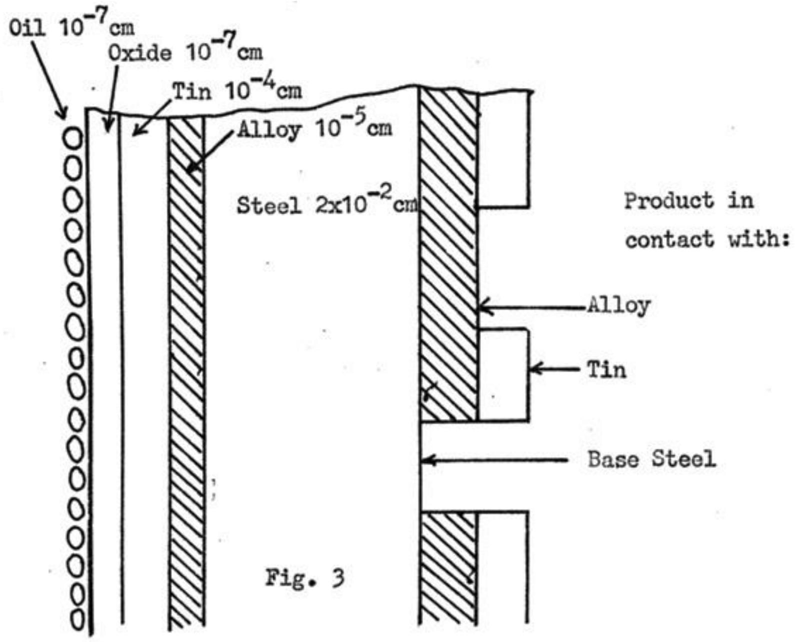
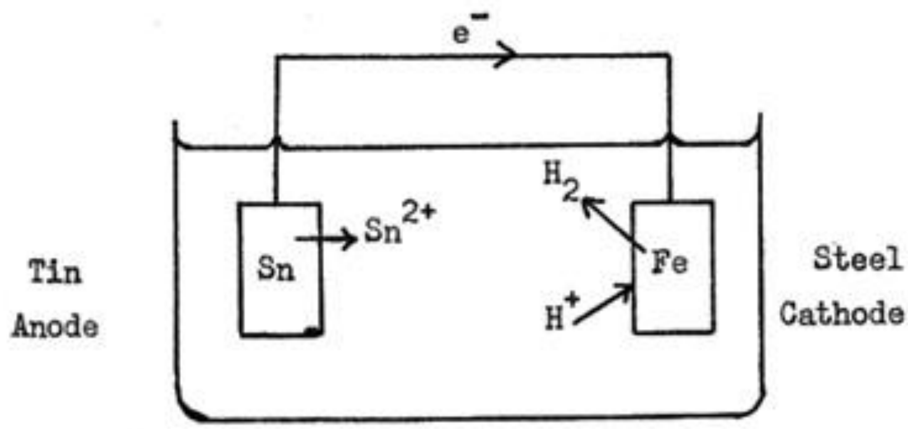



Fig. 3

The tin-coating is so thin and soft, that even under the best conditions of manufacture and handling the coating will contain minute imperfections which will allow the product to contact the iron-tin alloy and the base steel.

Heat processing of the product destroys the oil layer and the oxide film, on the surface of the tinplate and so remaining are two dissimilar metals in contact with an electrolyte, the fruit juice or syrup. This constitutes an electro chemical cell. Its components are a large tin electrode and a small steel electrode connected electrically by the alloy, all of which is immersed in an acidic electrolyte

This cell can be represented by the following diagram:




In canned food the tin acts as an anode and corrodes to produce stannous (tin) ions and electrons. The electrons move to the steel cathode which accepts the electrons to give hydrogen gas. In a corroding can some of this gas accumulates in the head-space while some enters the steel and diffuses out of the can. The overall reactions are:

| | | | |
|---|---|---|---|
| $Sn$ | $\rightarrow$ | $Sn^{2+} + 2e^-$ | at anode |
| $2e^- + 2H^+$ | $\rightarrow$ | $H_2$ | at cathode |

The steel does not corrode and is said to be cathodically protected by the tin in the same way as a zinc coating protects the iron in galvanized iron. Since only a minute area of steel is involved compared to the large area of tin, the reaction at the steel cathode is slower and thus determines the overall rate of corrosion. Corrosion is said to be under cathodic control.

Since nitrates cause rapid detinning in canned foods it is likely that it affects the cathodic part of the process, which is rate determining.

The reaction of nitrate and tin are shown in the following equations:

$$4\,Sn \rightarrow 4\,Sn^{2+} + 8\,e^-$$

$$NO_3^- + 2e^- + 2H^+ \xrightarrow{\text{slow}} NO_2^- + 4\,H_20$$

$$NO_2^- + 6e^- + 8H^+ \xrightarrow{\text{fast}} NH_4^+ + 2\,H_20$$

Thus for every 1 atom of nitrogen that reacts 4 atoms of tin are involved.

In terms of mass, nitrate reacts with eight times its own mass of tin.

Because hydrogen gas is not produced when nitrate is present, (it is oxidized to water), the can vacuum does not change appreciably during nitrate detinning and thus no external changes are noticeable.

CSIRO research[5] revealed that the rate of detinning in the presence of nitrates is not determined by the usual electron - hydrogen ion reaction but by two main factors (a) concentration of nitrate and (b) the A of the electrolyte. In fact, in solutions of pH 6 corrosion is negligible, which explains why canned meat products can tolerate high nitrate levels.

In response to French research which suggests that ferrous ion is the catalyst for the reaction Golden Circle researchers tried and failed to substantiate this claim, even after repeated trials.[6] Pursuing this idea further they tried a series of trials incorporating a variety of sequestering agents capable of complexing ferrous ions and effectively removing them from solution but again without the hoped-for result.

By the end of the 60s Golden Circle had achieved only partial success with nitrate corrosion in that the source and mechanism but not the solution had been found. The Managing Director of Golden Circle commented that they had only shown the problem occurred and would earn few plaudits until a satisfactory solution was demonstrated.[7]

**(f) Partial Solutions to the Problem:**

The problem was to some extent overcome by using cans internally lacquered. This achieved success with the problem of corrosion as the tin was separated from the electrolyte by a plastic film.

From 1966 onwards all papaw deliveries were screened with a spot test for nitrate. Low nitrate papaw was bought at a $16 per ton premium compared to high nitrate papaw. High nitrate papaw went into lacquered cans, low nitrate into unlacquered cans. The effort associated with this arrangement was such that it was eventually scrapped in 1968 and lacquered cans were used for all papaw products.

### (g) Future Research.

Golden Circle Chief Chemist Peter Seale summed up their position by indicating what answers or innovations were needed on both the cultural and technological side. In terms of cultural control:

> "The most satisfactory answer is undoubtedly to produce raw materials with acceptable low nitrate levels."

On the technical side:-

> Lest we be accused of adopting a placid attitude as food technologists and pass the problem on, unreasonably, to the farmer, what are our options in technical sense? As I see this situation we can - either prevent product contact with tin by using an inert barrier such as lacquer; accept a shorter shelf life and loss of some quality factors, or look for some technical innovation that (1) will remove nitrate in an acceptable side reactions or (2) introduce a blocking mechanism that will prevent the reduction of nitrates or (3) in pretreatment of the problem material before canning, devise a process that will reduce nitrates to an oxidation level lower than nitrate and preferably through to the ammonium stage.[8]

ENDNOTES


1. Food and Drug Regulations, 1977. Brisbane: Queensland Government Printer.
2. Peter Seale. 1968. Pineapples and Progress. *Proceedings of the Royal Australian Chemical Institute*, 35, p. 145.
3. R.P. Farrow, et. al., 1969. The Tinplate Producers Research program on Internal Can Corrosion. National Canners Association Research Foundation, Washington.
4. P.W. Board. 1973. The Chemistry of Nitrate Induced Corrosion of Tinplate. *Food Technology in Australia*, Jan. 1973, pp. 15-16.
5. Research done by P.W. Board, a research chemist with the Division of Food Research, North Ryde, Sydney. Refer P.W. Board. 1973.
6. Peter Seale. 1968. op cit., p. 146.
7. Peter Seale. 1973. Nitrates in Canned Foods - The Scope of the Problem. *Food Technology in Australia,* Jan., pp. 10-11.
8. ibid., p. 11.