



Symposium – Nitrates in canned Foods

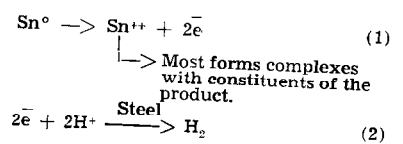
THE CHEMISTRY OF NITRATE-INDUCED CORROSION OF TINPLATE

P. W. BOARD

CSIRO Division of Food Research, North Ryde, NSW, 2113

Rapid detinning has been reported in a number of canned foods in recent years and subsequent investigations have shown that, in many instances, nitrate in the product was responsible for accelerating the corrosion processes. This paper describes the chemical reactions involved in the common form of slow detinning that occurs in most plain cans of food and then discusses how nitrate alters these reactions to cause abnormally rapid corrosion.

space while some enters the steel and diffuses out of the can. The overall reactions are as follows:—



The steel does not corrode and is said to be cathodically protected, or sacrificially protected, by the tin.

Since discharge of the electrons produced by corrosion of the large area of tin is concentrated at a minute area of steel the cathodic reaction becomes rate limiting and

Tinplate

The structure and dimensions of tinplate are shown schematically in cross-section in Fig. 1. The tin-coating is so thin and soft that even under the best conditions of manufacture and handling the coating

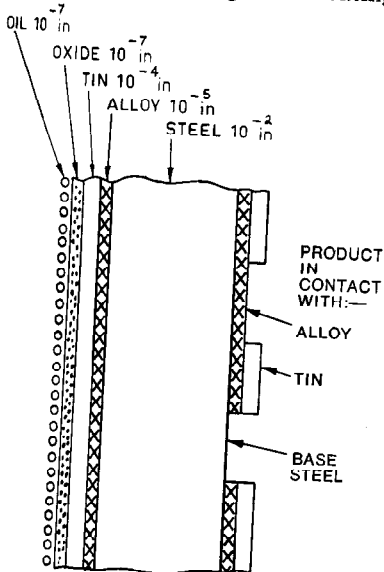


Fig. 1 Schematic cross-section of a sheet of tinplate showing approximate thickness of the various components of the plate. Commonly the oil film and oxide layer are destroyed when they come in contact with the product; the product then has access to the tin coating or to the alloy or base steel at imperfections in the tin coating.

Based on the 1972 AIFST/NZIFST paper.

will contain minute imperfections which will allow the product to contact the FeSn₃ alloy and the base steel. For the purposes of this discussion the tinplate will be considered to consist of a large area of tin connected electrically to a minute area of base steel in a corrosion cell filled with the product which acts as the electrolyte. The oil and oxide films on the surface of the tinplate are usually destroyed during the heat processing operation or soon after, and the alloy may be regarded as an inert barrier between the product and the base steel. In this case, therefore, the corrosion of tinplate may be considered in terms of the cell shown in Fig. 2.

Usual corrosion process

This cell has a large tin electrode and a small steel electrode which are connected electrically and the electrolyte is deoxygenated because oxygen disappears from plain cans within a few days of processing. In almost every food under these conditions tin acts as an anode and corrodes to produce stannous ions and electrons. The electrons move through the connecting lead to the steel electrode which acts as a cathode, *i.e.*, the electrons react with hydrogen ions in the electrolyte in a multistep process to give hydrogen gas. In a corroding can some of this gas accumulates in the head-

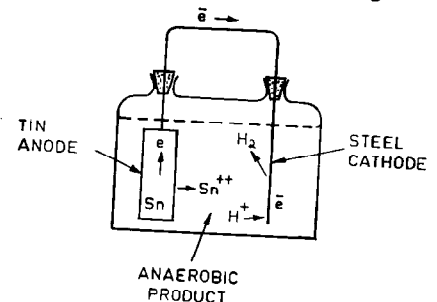


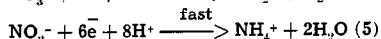
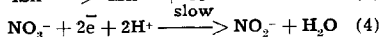
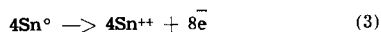
Fig. 2 Corrosion cell simulating conditions pertaining to corrosion of tinplate in the absence of nitrate.

the detinning process is said to be under cathodic control. It should be noted that the cathodic process takes place to only a negligible extent on the tin surface because tin has a high overvoltage. This means that there is a high energy barrier to the reaction of electrons and hydrogen ions and the discharge of hydrogen gas on a tin surface. The hydrogen evolution reaction occurs almost exclusively at the steel surface where the overvoltage is smaller. It should be emphasized that slow detinning is desirable in cans of food to provide cathodic

protection to the exposed areas of base steel and so prevent pitting corrosion, perforation of the tinplate, discoloration of the product, and other undesirable reactions.

Rapid corrosion

Since nitrate causes accelerated detinning in many canned foods it is likely that it affects the cathodic part of the corrosion process, which is normally rate determining. The main reactions of nitrate are shown in the following equations.



Nitrate acts as an electron acceptor or depolarizer, so a new pathway is available for removing the electrons produced when the tin dissolves. The high hydrogen overpotential is no longer a barrier to the discharge of electrons at the tin surface because the hydrogen evolution reaction is replaced by the electron-nitrate reaction which can readily take place on the large tin electrode. Note that hydrogen is not produced in these reactions so the can vacuum does not change appreciably during nitrate detinning.

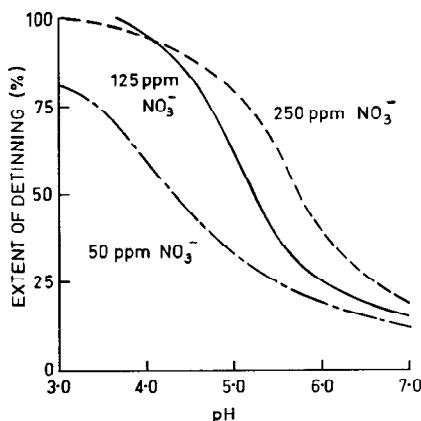


Fig. 3

Influence of pH and concentration of nitrate on the extent of detinning of 1 lb electrolytic tinplate. The plate was held in contact with the solutions for 2 months at ambient temperature.

Equations (4) and (5) suggest that the rate of detinning depends on the concentration of nitrate, and the concentration of hydrogen ions or pH. These points are demonstrated by the curves in Fig. 3 which are based on data published by Farrow *et al.* (1970). The curves show the percentage of detinning that occurred

with 1 lb electrolytic tinplate that was in contact with citrate-buffered solutions of nitrate for 2 months at ambient temperatures. At pH between 6 and 7 nitrate had little or no accelerating effect on the rate of corrosion of tin. At more acid pH the rate of detinning increased with increase in concentration of nitrate. At pH < 4 and with 125 and 250 ppm NO₃⁻ the plate was virtually completely detinned in 2 months.

Other reactions

Equation 5 shows that NH₄⁺ is the only nitrogen end-product of the reduction of nitrate, but in fact other products which may include nitric oxide, nitrous oxide, nitrogen, and hydroxylamine might also be produced. Farrow *et al.* (1970) found that in citrate-buffered systems at pH < 5 about 80 per cent conversion to ammonia occurred, but at higher pH the amount of ammonia formed accounted for only a small part of the nitrate lost (Fig. 4). They also obtained evidence that nitrogen was a product of the reduction of nitrate at pH 5, but experimental difficulties obscured the results at pH 4. Nitrous oxide was readily detected by gas chromatography in the headspace gases of cans containing model electrolyte systems. The concentration of nitrous oxide varied during storage because this gas also accelerated detinning and in the process was probably converted to nitrogen. It was suggested that some of the nitrous oxide was produced by reduction of nitrate by stannous ions. Nitric oxide was not detected because of the analytical techniques used by Farrow *et al.* (1970) and perhaps because nitric oxide would have only a transient existence in a corroding can.

Horio *et al.* (1968) found that nitrate detinning was triggered by the oxygen that was present in the can at the time of processing. They suggested that oxygen increased the initial rate of formation of stannous ions by corrosion of the tin coating; these stannous ions reduced nitrate to nitrite which readily attacked the metallic tin to form more stannous ions and so establish a chain reaction.

The chemistry of the role of nitrate in accelerating corrosion of tinplate is now well understood. Nitrate causes rapid detinning by acting as a depolarizer or electron acceptor so that the usual rate determining step in the corrosion of tinplate, the

electron-hydrogen ion reaction, is bypassed. The main products of the action of tin and nitrate are stan-

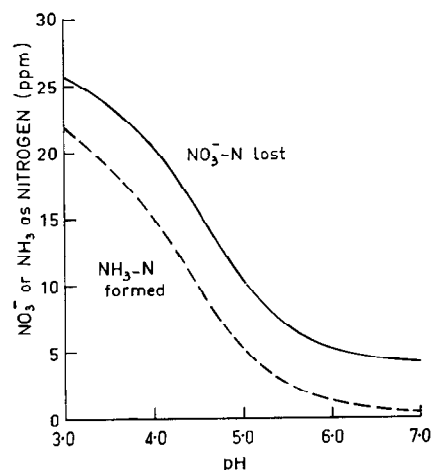


Fig. 4

Nitrate nitrogen lost and ammonia nitrogen formed during reaction of citrate buffered solutions of nitrate (125 ppm nitrate = 27 ppm nitrogen) with 1 lb electrolytic tinplate for 2 months.

nous ions and NH₄⁺, but other nitrogen compounds are also formed. One nitrate ion accepts 8 electrons during its reduction to NH₄⁺ and causes 4 tin atoms to go into solution. The action of nitrate is highly pH-dependent and is negligible at pH > 6.

REFERENCES

- FARROW, R. P., LAO, N. T. and KIM, E. S. (1970). *J. Fd Sci.*, **35**, 818.
 HORIO, T., IWAMOTO, Y. and KOMURA, S. (1968). *Rep. Toyo College of Fd Technol. and Toyo Inst. Fd Technol.* 1966-1967, Serial No. 8, 22.
 THOMAS, G., MERGEY, C., LEBLANC, C., HANUSSE, H., MONVOISIN, J. and CHEFTEL, H. (1966). *Tech. Meet., Com. Int. Permanent de la Conserve*, Paris, 15-18 November. Rep. C.S.10.

TECHNICAL LITERATURE

"EGG PASTEURIZATION MANUAL"
 80 pages. ARS, USDA, Western Utilization Research and Development Div., Albany, Calif. 94710, 1967.

"LAYOUTS AND OPERATING CRITERIA FOR AUTOMATION OF DAIRY PLANTS PROCESSING CHEDDAR CHEESE"

Marketing Research Report No. 891, 42 pages. ARS, USDA, available from U.S. Govt. Printing Office, Washington, D.C., 20402, 1971. Price: 70c.