Liberation of Tin from a Tinplate Cans by Trimethylamine Oxide

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To clarify the internal corrosion mechanism in food cans, the effect of trimethylamine oxide (TMAO) on the liberation of tin from tinplate was examined. In the range of pH 2.8-8.0, tin liberation by TMAO was maximum around pH 4, at which there was also marked decomposition of TMAO. Around that pH, the amount of tin liberated was proportional to that of TMAO added. Tin liberation by TMAO increased both at higher temperatures and with the lapse of time at 37°C. Generally, the amount of tin liberated almost paralleled that of TMAO decomposed. Both tin liberation and TMAO decomposition were to a certain extent depressed by phytic acid and inositol. From these results, it was concluded that tin liberation from tinplate cans is caused by TMAO.

In canned foods, much attention is paid to the internal corrosion of food can, since this usually results in the metallic contamination of the contents. Though there have been published many reports on the corrosion processes of metals,¹⁻³⁾ the mechanism involved in the internal detinning of food can remains for the most part to be elucidated.

It is well known by experience that the internal tin layer of food can is rapidly attacked by trimethylamine oxide (TMAO) at high levels.⁴⁾ The present study was carried out to obtain the fundamental information of the liberation process of tin in tinplate can, using a model system containing TMAO.

Experimental

Buffered TMAO solutions In the distilled water previously boiled to minimize the dissolved oxygen, was dissolved TMAO at 5-50 mM. After addition of citric acid to a final concentration of 1/10 M, the solutions were adjusted with 1/5 M phosphate to various pH values between 2.8 and 8.0.

Canning procedures The buffered TMAO solutions thus prepared were canned in plain tinplate cans (74.1 mm in diameter; 59.0 mm in height) by over-filling to avoid the headspace. After heating in a boiling water bath for 60 min unless otherwise stated, the cans were cooled immediately in cold water and stored at 37°C. At suitable intervals the TMAO solution was taken from each can and analyzed for the amounts of tin liberated and the remaining TMAO.

Analytical methods Tin was determined polarographically employing 1 N HCl-1 N NH₄Cl as the supporting electrolyte. TMAO was determined according to DYER *et*

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*al.*⁵⁾ The remaining amount of TMAO was expressed as percent of the initial amount of TMAO.

Results and Discussion

Effect of pH on tin liberation The corrosive action of a detinner in electrolytic solutions is greatly dependent on the pH of media. The cans containing 10 mM TMAO at seven different pH values were heated at 100°C for 60 min and stored at 37°C for 2 days. As shown in Fig. 1, the tin liberated was highest around pH 4 in the range of 2.8–8.0. The amount of remaining TMAO was minimum approximately at this pH. In the absence of TMAO, the tin liberation was much smaller over this pH range.

Effect of TMAO concentration on tin liberation The effect of TMAO concentration on the tin liberation was examined at pH 4.0. As given in Fig. 2, the tin liberation was almost proportional to the amount of TMAO added. In addition, a slight increase of pH of the buffered TMAO solution by heating was observed. This pH increase is probably due to the formation of amines and/or ammonia from TMAO.

Effect of heating on tin liberation A 10 mM TMAO solution (pH 3.8) was canned and heated at 100°C, and the time course of tin liberation was examined. As shown in Fig. 3, the amount of tin liberated was increased hyperbolically with the time of heating.

The effect of temperature on the tin liberation was also examined. In the preliminary experiments, a significant temperature effect on the tin liberation was found in the presence of large amounts of TMAO. Hence, the cans packed with the solution containing 50 mM TMAO at pH 3.7 were incubated at various temperatures for 60 min and analyzed. As

Fig. 1. Effect of pH on the liberation of tin by TMAO. The cans containing 10 mM TMAO were heated at 100°C for 60 min.
○: Liberated tin in the presence of TMAO
□: Liberated tin in the absence of TMAO
●: Remaining TMAO

Fig. 2. Effect of TMAO on the liberation of tin. The cans containing TMAO and 0.0615 M citric acid-0.0771 M phosphate buffer (pH 4.0) were heated at 100°C for 60 min.
○: Liberated tin
□: pH after heating

Fig. 3. Time course of tin liberation by TMAO. The cans containing 10 mM TMAO and the same buffer as in Fig. 2 were heated at 100°C.

can be seen in Fig. 4, the rate of tin liberation sharply increased near 50°C under these conditions. These results suggest that the tin liberation proceeds according to ARRHENIUS formula below 50°C, beyond which the liberation is to some degree depressed by a weak ionization of oxygen.⁶⁾

Tin liberation during storage The cans containing the buffered 10 mM TMAO solution at pH 4.0 were heated at 100°C for 30 min. The cans containing the buffer solution alone were also prepared as the control. These cans were kept for 25 days at 37°C. As shown in Fig. 5, the amount of tin liberated increased rather hyperbolically with the storage time, while the amount of TMAO decreased almost correspondingly. The concentration of tin liberated in the control cans remained unchanged throughout the period of storage.

Depression of tin liberation Some attempts were made to depress the tin liberation caused by TMAO. Since the corrosion of metals is depressed by a organic colloidal solution,⁷⁾ phytic acid and inositol were tested here. Phytic acid and inositol were added at

Fig. 4. Effect of temperature on the tin liberation by TMAO.

Fig. 5. Tin liberation by TMAO during storage at 37°C. The cans were stored at 37°C after heating at 100°C.

- : Liberated tin in the presence of TMAO
- : Liberated tin in the absence of TMAO
- : Remaining TMAO

Table 1. Depression by phytic acid and inositol of the tin liberation by TMAO. The cans containing 0.5 mM phytic acid and 2 mM inositol to 5 mM TMAO-20 mM citric acid were stored at 37°C for 3 days after heating at 100°C for 15 min.

	Liberated tin (ppm)	Depression (%)	Remaining TMAO (%)
Control	77.3		10.0
Phytic acid (0.5 mM)	52.0	32.7	39.8
Inositol (2 mM)	62.8	18.7	23.5
Phytic acid (0.5 mM)+inositol (2 mM)	44.5	42.4	44.0

the final concentrations of 0.5 and 2 mM, respectively, to the buffered TMAO solution, and heated at 100°C for 15 min. After storage at 37°C for 3 days, the amount of tin liberated was assayed. As seen in Table 1, the tin liberation as well as the decomposition of TMAO were fairly effectively depressed by phytic acid and inositol, especially by the former.

From these results, it is reasonably concluded that the tin liberation from a tinplate can is caused by TMAO. Further studies on the depression of tin liberation by these agents are now in progress.

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