NOTE

缶詰食品中におけるトリメチルアミン・オキシドの変化

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FATE OF TRIMETHYLAMINE OXIDE IN CANNED PRODUCTS

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Trimethylamine oxide(TMAO) is known to be extremely corrosive against the internal surface of the can when contained in canned marine products (1, 2), and this has been mainly attributed to the oxidation of metals by TMAO, which, in return, is reduced to trimethylamine(3). TMAO, in virtue of its N-methyl structure, is expected to undergo decomposition after the intramolecular rearrangement into 1- and 2-carbon fragments, and it was found in this laboratory that dimethylamine(DMA) is formed during the storage of canned marine products containing appreciable amount of TMAO. The purpose of this note is to describe the fate of TMAO contained in the canned carp in tomato sauce and the possible mechanism of its action on the metals. The choice of carp was because it is known not to contain endogeneous TMAO.

Varying amounts of TMAO(9, 45 and 90 mmole per kg product (67.5, 335 and 670 mg%, respectively)) were added to the tomato sauce for the manufacture. The cans were packed and sterilized conventionally, and stored at 37°C. After storage for 1, 3 and 6 months, the contents were subjected to the analyses of:

TMAO by means of the rapid procedure developed in this laboratory (5),

TMA by means of the Dyer's procedure (6-8),

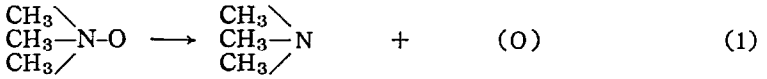
DMA by the Dyer's thiocarbamate method for secondary amines (9,10),

Formaldehyde (*FA*) by colorimetry after distillation and condensation with chromotropic acid (11),

Tin with polarograpgy, and

Iron by the A.O.A.C.' s *o*-phenanthroline method.

1. When the initial concentration of TMAO is low, TMA is the major product, but no appreciable level of metal dissolving due to the action of TMAO was observed, indicating that only simple reduction of TMAO proceeds in the presence of food material (Fig. 1-B, 2-B).



The amine formation stops after 1-month storage.

2. From TMAO of higher concentration (45 mmole/kg), TMA formation is again predominant (Fig. 1-C) accompanying dissolving of both tin and iron (Fig. 2-C), indicating that TMAO attacks the alloy layer through tin layer.

$$(CH_3)_3N\text{-}O + Sn \longrightarrow (CH_3)_3N + Sn(II, IV) \quad (2)$$

$$(CH_3)_3N\text{-}O + Fe \longrightarrow (CH_3)_3N + Fe(II, III) \quad (3)$$

DMA is also formed to certain extent. This will be discussed below.

Both the amines were found to remain unchanged when once formed during 3-month storage. Metal dissolving also stops when the TMAO added has been consumed.

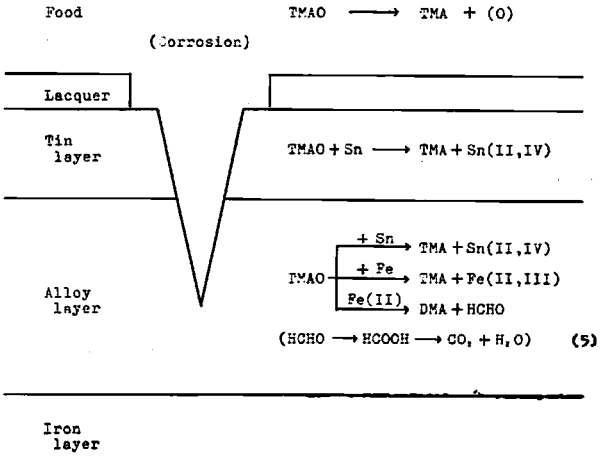
3. When the TMAO content is extremely high (90 mmole/kg), the TMA formation and detinning stops after 3-months of storage, whereas a marked increase in the DMA formation and iron-dissolving can be observed. These facts strongly indicate that in the cans containing excess amount of TMAO, iron is preferably attacked in the alloy layer, and the bivalent iron thus formed accelerates the decomposition of TMAO to DMA and FA (Fig. 1-D, 2-D).

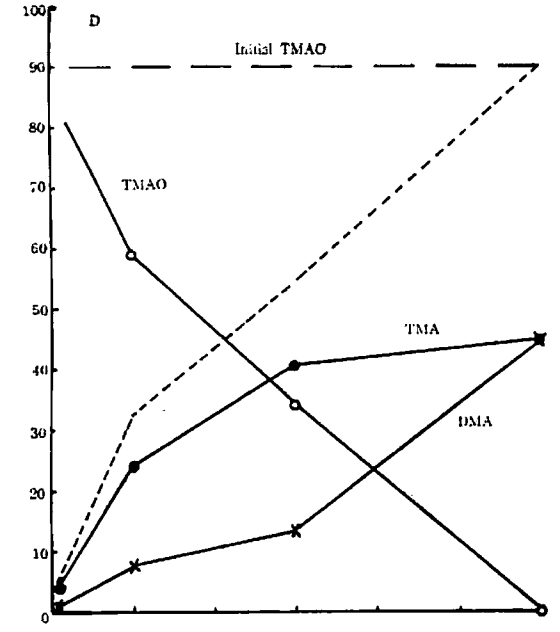
$$(CH_3)_3N\text{-}O \xrightarrow{Fe(II)} (CH_3)_2NH + HCHO \quad (4)$$

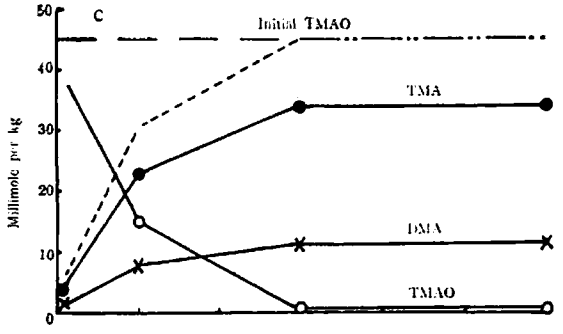
However, attempts to detect FA failed probably due to its decomposition in the canned product.

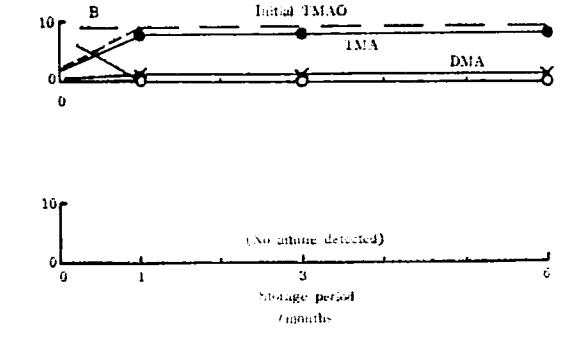
4. The common feature of the amine formation is that the sums of the amines formed are equivalent to the amount of TMAO disappeared irrespective of initial concentrations of TMAO and storage periods, indicating that no other amines (or other nitrogen-compound) are formed from TMAO during storage (Fig. 1 and 2).

5. A postulated mechanism of the reaction of TMAO in canned marine produts is shown in the following scheme.



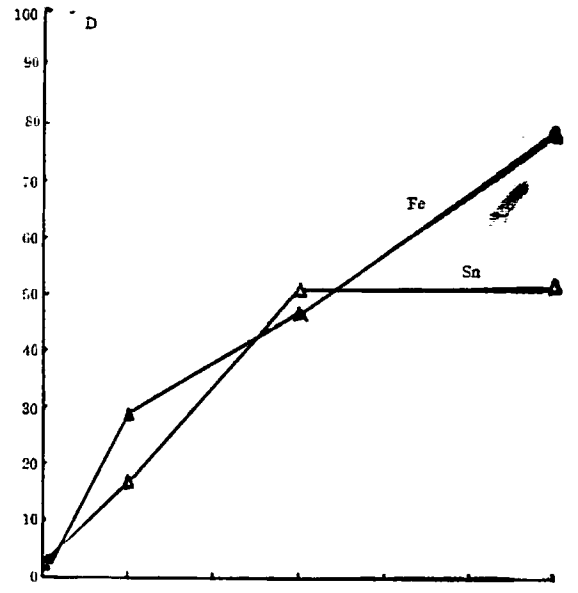


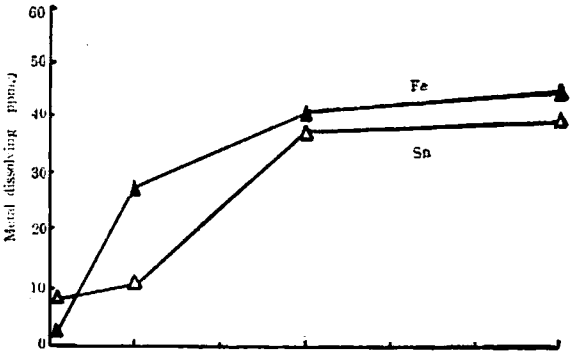


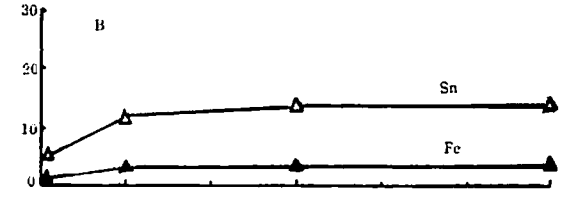


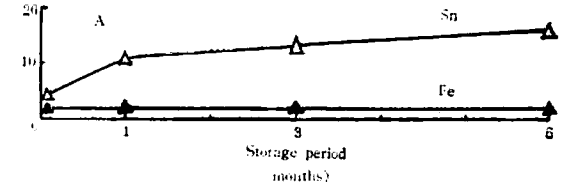
Storage period (months)

Fig. 1 Formations of amines during storage of canned carp in tomato sauce.
····· TMA + DMA









Storage period (months)

Fig. 2 Dissolving of metals during storage of canned carp in tomato sauce.

要　　旨

缶内面に対していちじるしく腐蝕性であることが知られているトリメチルアミン・オキシドの缶詰食品内における変化と金属溶出との関係を明らかにするため，天然には TMAO を含まないことが知られているフナを用い，種々の濃度の TMAO を含有せしめたトマト漬フナ缶詰を試作し，貯蔵期間中のアミン類の生成量と金属溶出量の関係を追跡した（缶はラッカー塗装缶を用いた．）

1．TMAO 低濃度の場合：主として TMA が生成し，TMAO による金属溶出はみられない (Fig. 1-B, 2-B)．食品中において TMAO が単純に還元されるものと考えられる．（(1)式）

2．TMAO 中濃度（45mM）の場合：やはり TMA 生成が優勢であり，このときスズ，鉄両方のかなりの溶出がみられることから，TMAO の作用は合金面まで及んだものと考えられる（2，3式）(Fig. 1-C, 2-C)．

一度生成した TMA，DMA はいずれも貯蔵中変化せず，また TMAO が完全に消費されたあとは，金属類のいちじるしい溶出はみられない (Fig. 1-C, 2-C)．

3．TMAO 濃度が高い場合(90mM)：TMA 生成は3カ月貯蔵でほとんど停止するのに比し，DMA の生成がはげしく進む．また，スズの溶出もほとんど止り，代って鉄の溶出のみがいちじるしい．このことから合金層では TMAO は優先的に鉄に作用し，溶出した鉄イオンによる TMAO の DMA＋FA への分解反応が進んでいると考えられる（4式，Fig. 1-D, 2-D)．

4．全 TMAO 濃度，全貯蔵期間を通じて，TMA と DMA の生成量の和は TMAO の消失量に等しいことから，TMAO の TMA, DMA 以外のアミンへの変化は考えられない(Fig. 1，2)．

5．トマト漬フナ缶詰中における TMAO の変化と金属溶出との関係は模式のようになると考えられる．

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