Influence of certain factors on the appearance of yellow-brown discolorations on the surface of cured canned pork

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The appearance of yellow-brwon discolorations on the surface of cured canned meat, a problem which has existed for some decades, remains even to-day an interesting subject for research. The surface parts on which the yellow-brown discolorations most frequently appear, have been exactly described in numerous works dealing with this phenomenon (5, 6, 8). We also have data concerning the size of the surface of damaged tin coating as the cause of this phenomenon (5, 8). The effect of certain compounds of curing mixture (apart from $NaNO_2$) and complete mixture on the appearance of yellow-brown discolorations have been examined, too.

To-day, it is a generally accepted theory that discolorations of this kind that appear on the content surface are caused by the oxidation of cured meat pigments. This means that NO_2 (formed during curing) catalized by iron, oxidizes nitrosomyoglobin to metmyoglobin (5).

In the literature that we have had access to, we have not found any data concerning the dependence of yellow-brown discolorations on the quantity of formed nitrosopigments, namely concerning the influence of the duration of curing.

For these reasons, we wanted to attempt to throw some light on this problem from the already stated aspect. That is why we have made it our task to examine the following:

— whether the duration of curing, that is, the quantity of formed nitrosopigments in relation to the quantity of added $NaNO_2$, and the surface of damaged tin coating effect the phenomenon of discoloration and to what extent, and

— whether there exist a topmost limit, i.e. that quantity of added nitrites above which discoloration of this kind does not appear, besides the lowest limit of the quantity of added $NaNO_2$ which leads to yellow-brown discolorations.

MATERIALS AND METHODS

Preparation of meat substrates For our experiments we used chilled hams (+4 °C/24 hours) well trimmed of any visible fatty and connective tissue and minced in a grinder through a 8 millimeters plate. Minced meat was divided into 2 parts; 2.8 % of NaCl and 0.5 % of Polital M5 polyphosphate preparation were added to one part. The same quantities of NaCl and polyphosphate were added to the second half, plus 0.01 % of $NaNO_3$. Both parts of meat were divided into 12 parts each. 10 % of $NaNO_2$ solution of different concentration (according to meat weight) was added to each of these parts. The concentrations of $NaNO_2$ solution were so made up that the initial concentrations of nitrites in meat (with and without added $NaNO_3$) were the following:

I — 1200 ppm	VII — 18,75 ppm
II — 600 ppm	VIII — 9,37 ppm
III — 300 ppm	IX — 4,69 ppm
IV — 150 ppm	X — 2,34 ppm
V — 75 ppm	XI — 1,17 ppm
VI — 37,50 ppm	XII — 0,58 ppm

Preparation of small plates of tinplate Small plates of tinplate (35,0 × 3,5 mm, width 0,28 mm) were obtained by cutting large plates of hot dipped tinplate into small plates and these were then prepared in three ways:

a) the first group of small plates was additionally completely tinned in melted tin so that all the edges and possible later damages on tin coating were protected. Plates prepared in this way were pierced with a needle of Ø 0.7 mm.

b) the second group of small plates of tinplate was prepared in the same way as the preceding one. The only difference was that the plates were pierced twice in the same way.

c) the third group included small plates which were additionally but not completely tinned, i.e. small plates were tinned only to the depth of 26 mm. This means that the total length of unprotected edges of small plates amounted to 21.5. mm.

The quantity of iron dissolved in the course of ISV determination, expressed in micrograms, amounted to 9 for each plate of the first group, 18 for the second group and 90 for the third group.

Determination of ISV of small plates of tinplate ISV (Iron Solution Value) was determined by the Tin Research Institute method (Hoare W. E., Britton S. C.: Tinplate Testing, 1962). (4)

The process of curing was carried out in plastic bags at + 4° C. After curing for 1, 3, 5, 7, 9, 17 and 21 day, a respective number of glass tubes was filled with 10 g. of cured meat each. For each initial concentration of $NaNO_2$ (from both parts of cured meat, i.e. with and without $NaNO)_3$, three glass tubes were filled with small plates. The first glass tube contained a small plate from the a) group, the second glass tube a small plate from the b) group and the third one a small plate from the c) group.

Thermal treatment. — Immediately after the glass tubes had been filled with meat and a small plate of tinplate, they were kept in a water bath at 76° C/360 minutes. After that period, the bath was turned off. The following day, the samples were left in a refrigerator at + 8° C. Seven days later, the content from glass tubes was taken out and the appearance of yellow-brown discolorations was registered by visual examination.

Determination of Nitrites was carried out by Griess's method.

Determination of Nitrates was carried out by a method with brucine.

Determination of Pigments. — Determination of total pigment, nitrosopigment and the percentage of total pigment turned to nitrosoform was carried out by Hornsey's method — modification by Möhler (3).

RESULTS AND DISCUSSION

Ppm of added $NaNO_2$	Composition of curing mixture: NaCl-2,8% Polyphosphates-0,5%																NaCl-2,8% Polyphosphates-0,5% $NaNO_3$-0,01%																	
	Iron solution value (micrograms Fe) of small plates: 9							18							90							9							18						
	Duration of curing (in days)																																	
	1	3	5	7	9	17	21	1	3	5	7	9	17	21	1	3	5	7	9	17	21	1	3	5	7	9	17	21	1	3	5	7	9	17
2.34	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
4.69	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
9.37	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	⊕	−	−	−	−	−	−	−	−	−	⊕	−	−	−	⊕	⊕	⊕	−
18.75	−	−	−	⊕	−	−	−	−	⊕	⊕	⊕	−	−	−	−	⊕	⊕	⊕	⊕	⊕	−	−	−	⊕	⊕	⊕	⊕	⊕	−	⊕	⊕	⊕	⊕	⊕
37.50	−	⊕	⊕	⊕	⊕	⊕	⊕	−	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	⊕	⊕	⊕	⊕	⊕	⊕	−	⊕	⊕	⊕	⊕	⊕
75.00	−	⊕	⊕	⊕	⊕	⊕	⊕	−	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
150.00	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
300.00	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
600.00	⊕	−	−	⊕	−	⊕	⊕	⊕	−	⊕	⊕	−	⊕	⊕	⊕	−	⊕	⊕	−	⊕	⊕	⊕	−	−	⊕	−	⊕	⊕	⊕	⊕	⊕	⊕	−	⊕	⊕	⊕
1200.00	−	−	−	−	−	⊕	⊕	−	−	−	−	−	−	⊕	⊕	−	−	−	−	−	−	⊕	−	−	−	−	−	−	⊕	−	−	−	−	−	−	⊕

⊕ = Appearance of yellow-brown discolorations
− = No yellow-brown discolorations

Table 1 shows the influence of curing ingredients (NaCl — 2.8 %; Polital M — 0.5 %) of various $NaNO_2$ concentrations and tin conating damage on the appearance of yellow-brown discolorations 7 days after thermal treatment.

From the results (presented in the Table) we can see that at initial concentrations of $NaNO_2$ of 1200 ppm discolorations do not take place except where

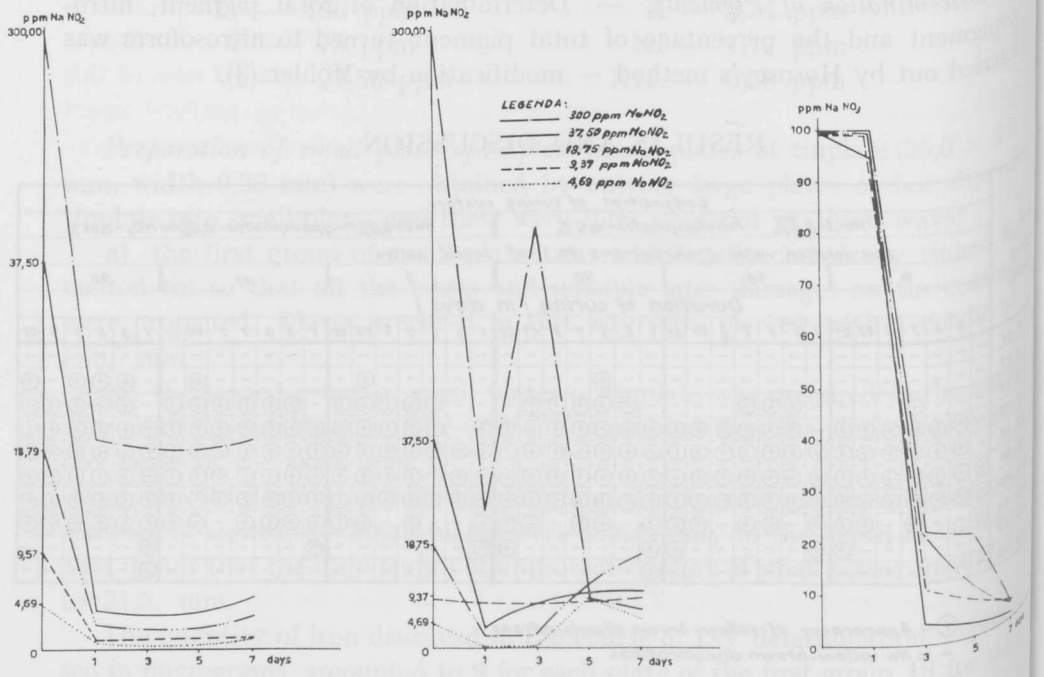
the samples cured for 24 hours are concerned. The exception were samples with the highest damage of small plate. We can look for an explanation of this phenomenon in the fact that a determined quantity of nitrosopigments sufficient for the appearance of yellow-brown discolorations was present the first day. The oxidation of nitrosopigments into holeglobin takes place later (the green color of meat). From this fact we may conclude that apart from the lowest level of the quantity of nitrites there also exists a topmost one above which yellow-brown discolorations do not appear and this can be explained by the absence of nitrosopigments.

In the case of the lowest level of added $NaNO_2$, i.e. the minimal quantities which bring about the appearance of discolorations, the results are in accordance with those of a previously edited study (8). Here too we may conclude that below the initial concentration of 4.69 ppm there are no yellow-brown discolorations even where the IS value is 90.

FIG. 1. QUANTITY OF $NaNO_2$ DURING CURING IN SAMPLES OF WHICH $NaNO_3$ HAS NOT BEEN ADDED.

FIG. 2. QUANTITY OF $NaNO_2$ DURING CURING IN SAMPLES TO WHICH $NaNO_3$ HAS BEEN ADDED.

FIG. 3. QUANTITY OF $NaNO_3$ DURING CURING IN SA... DIFFERENT INITIAL CONCENTRATIONS OF ...



Alongside with these experiments, we have determined:

— the quantity of $NaNO_3$ (in the part in which it was added);

— the quantity of $NaNO_2$ in the samples of both parts, before heating;

— the total pigment and nitrosomyoglobin, in other words the percentage of pigment turned to nitroso-form.

We should add that our detrminations were carried out in samples containing the following initial concentrations of $NaNO_2$ (with and without $NaNO_3$):

III — 300 ppm
VI — 37,5 ppm
VII — 18,75 ppm
VIII — 9,37 ppm
IX — 4,69 ppm

We have restricted these determinations only to those samples in which the initial concentration of $NaNO_2$ ranged within the highest namely the lowest limits in relation to the appearance of yellow-brown discolorations. These examinations were carried out 1, 3, 5 and 7 days after curing.

By comparing Fig. 1, 2, 3, 4 and 5 and the Table, it can be noticed that

FIG. 4. PERCENTAGE OF TOTAL PIGMENT TURNED INTO NITROSOMYOGLOBIN DURING CURING IN SAMPLES TO WHICH $NaNO_3$ HAS NOT BEEN ADDED

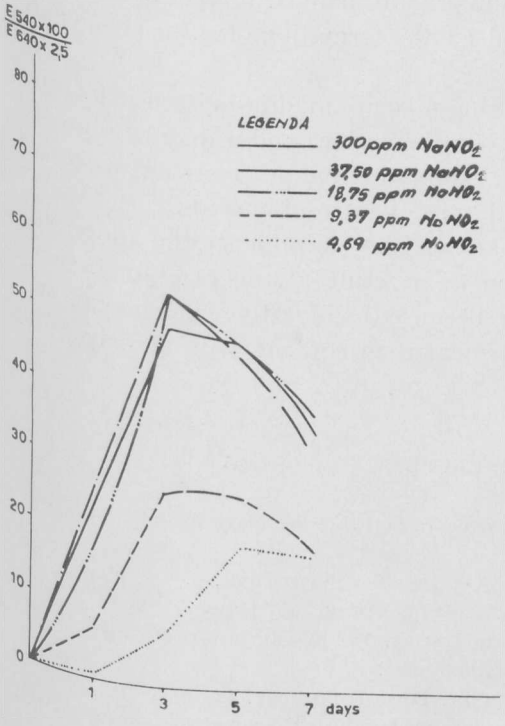
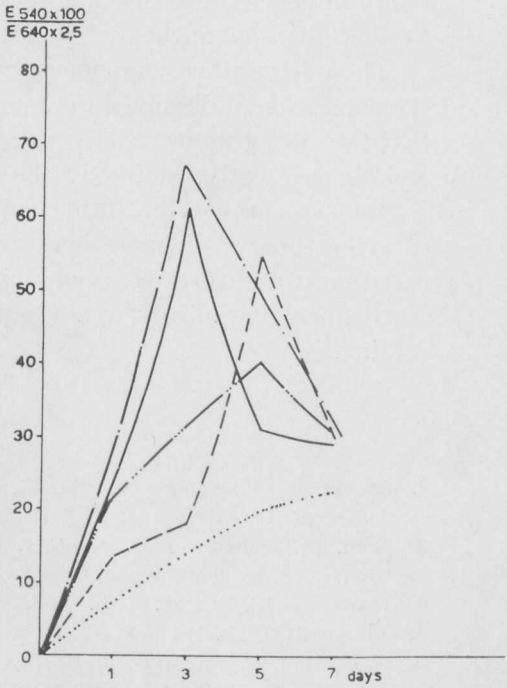


FIG. 5. PERCENTAGE OF TOTAL PIGMENT TURNED INTO NITROSOMYOGLOBIN DURING CURING IN SAMPLES TO WICH $NaNO_3$ HAS BEEN ADDED



yellow-brown discolorations appear only when the percentage of total pigment turned to nitrosopigments approaches 20. We can also conclude that in samples

containing $NaNO_3$, nitrosopigments are formed more quickly (Fig. 5) and the remaining quantities of $NaNO_2$ are somewhat larger (Fig. 2) what is understandable when we take into account that nitrate turns to nitrite. From the Table we notice that discoloration appears in samples to which nitrate was added as well as in those to which small plates with the highest IS value were added. The minimum quantity of formed nitrosopigments sufficient for the appearance of yellow-brown discolorations depends on the size of damaged tin coating. If the damage is considerable (ISV = 90) a smaller quantity of nitrosopigments is sufficient, and vice versa, if the damage is slight (ISV = 9) larger quantities of nitrosopigments are required.

Looking at the obtained results as a whole, we may conclude that the presence of certain minimal quantities of formed nitrosopigments is of primary importance for the appearance of yellow-brown discolorations on the content surface. The second important factor is nitrite or intermediary products of its decomposition, i.e. NO_2. The presence of iron as a catalyst enables the oxidation of nitrosopigments into brown metmyoglobin.

The quantity of added nitrite within already defined limits (4,69 n — 300 ppm) influences only the time required for the formation of sufficient quantities of nitrosopigments.

The role of other components of curing mixture manifests itself in favoring the deposition of dissolved iron on the content surface and it may be supposed that the curing mixture influences the oxidoreductive processes during curing and, consequently, indirectly the oxidation of nitrosopigments.

We can suppose that other yet unknown factors influence the appearance of yellow-brown discolorations formed as a result of the reaction between cured meat and tinplate, even more so because discolorative changes can take place when thermically treated cured meat is in contact with damaged tin coating.

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