

## CURRENT STATUS OF NITRITE-FREE MEAT CURING SYSTEMS

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### INTRODUCTION

Nitrite has been used for centuries and permitted by regulations for over 60 years for meat curing. Nitrite is responsible for the development of specific sensory characteristics namely colour and flavour in meats. By acting as a strong antioxidant, nitrite prevents the formation of "warmed-over" flavour in cured products. More importantly, nitrite acts as an antimicrobial agent and specifically retards the germination of spores and toxin formation by Clostridium botulinum.

Unfortunately, nitrite also has some serious disadvantages. It is responsible for the formation of carcinogenic N-nitrosamines in certain cured products, upon frying. On ingestion it may also cause the formation of N-nitrosamines in the stomach. Recently Schweinsberg and Bürkle (1985) reported that nitrite enhances the carcinogenic action of N-nitroso-N-methylbenzylamine in the production of esophageal tumors. Therefore, it is a desired goal to find suitable alternatives for nitrite in the preparation of cured products.

Since it is unlikely that a single compound will be found that can perform all of the functions of nitrite, efforts in the past have been concentrated to develop alternatives which performed a selected function of nitrite. Thus, a large number of colourants to substitute nitrite have been developed (NAS, 1982a). However, toxicity problems, etc., has prevented their use in meat processing. Relatively, a smaller number of antimicrobial agents have been identified that could

potentially replace nitrite (NAS, 1982 b).

In this paper, current status of our research for the development of nitrite-free curing agents, particularly preparation of multi-component systems responsible for cumulative action of nitrite will be discussed.

### NITRITE ALTERNATIVES

#### Colour of Cured Meats and Substitutes for Colouring Effects of Nitrite

The colour of meat is attributable mainly to the hemoprotein, myoglobin (Fox, 1966). Addition of nitrite, upon heat treatment, produces a relatively stable pink-coloured pigment in the processed meat products. The precise sequence of events resulting in the formation of the cured-meat pigment is not fully understood. While Lee and Cassens (1976) and Renerre and Rougie (1979) have concluded that dinitrosyl ferrohemochrome is the actual cooked cured-meat pigment, Killday *et al.* (1988) have shown that a mononitrosyl compound is responsible for the characteristic colour of cured meats. Definite formation of a substituted dinitrosyl ferrohemochrome, under a positive pressure of nitric oxide, has been reported by Wayland and Olsen (1974).

Recently preparation of the cooked cured-meat pigment from the reaction of beef red blood cells with a nitrosating agent directly or indirectly through a hemine intermediate was reported (Figure 1) (Shahidi *et al.*, 1984, 1985, Shahidi and Pegg, 1988). Although dinitrosyl ferrohemochrome was prepared under a positive pressure of nitric oxide, the exact nature of this pigment upon removal from this environment and application to meat is unknown. In this area, more concerted and detailed studies are currently underway in our laboratories.

To reproduce the antioxidative effect of nitrite, we have examined a number of antioxidants (Shahidi *et al.*, 1987b), sequesterants (Shahidi *et al.*, 1986) and their combinations (Shahidi *et al.*, 1987c). Among the antioxidants used BHA and TBHQ were the most effective, even at 30 ppm, for retarding oxidation during a 5-weeks storage at 4°C, as measured by the 2-thiobarbituric acid test (Table 2). Among the food-grade

Table 2. TBA numbers of cooked meats treated with different additives.<sup>a</sup>

Experiment No.	Additive(s)	Storage Time at 4°C, Days	
		1	35
1	Control (No additives)	4.39	15.46
2	BHA (30ppm)	0.25	0.44
3	TBHQ (30ppm)	0.32	0.35
4	STPP (3000ppm)	0.22	1.86
5	SPP (3000ppm)	0.24	1.66
6	SHMP (3000ppm)	1.20	7.21
7	Na <sub>2</sub> EDTA (500ppm)	0.31	0.96
8	(4)+ Asc (550ppm)	0.17	0.27
9	(5)+ Asc (550ppm)	0.19	0.23
10	(6)+ Asc (550ppm)	0.21	0.29
11	(8)+ BHA (30ppm)	0.16	0.20
12	(8)+ TBHQ (30ppm)	0.19	0.18
13	Pigment (12ppm)	0.39	9.89
14	(11)+ pigment (12ppm)	0.22	0.34
15	(12)+ pigment (12ppm)	0.25	0.24
16	(14)+ SHP (3000ppm)	0.28	0.28
17	(15)+ SHP (3000ppm)	0.22	0.21
18	NaNO <sub>2</sub> (150ppm)	0.50	0.63

<sup>a</sup> Additives were: hydroxyanisole, BHA; tert-butylhydroquinone, TBHQ; sodium triphosphosphate, STPP; sodium pyrophosphate, SPP; sodium hexametaphosphate, SHMP; disodium salt of ethylenediaminetetraacetic acid, Na<sub>2</sub>EDTA; sodium ascorbate, Asc; and sodium hypophosphite, SHP.

sequesterants, sodium pyrophosphate (SPP), sodium tripolyphosphate (STPP) and ethylenediaminetetraacetic acid (EDTA) were most effective. A strong synergistic effect was noted when ascorbates were added to polyphosphates (Table 2). Addition of small amounts (30ppm) of an antioxidant such as BHA or TBHQ to the above systems, although having a minor effect on the TBA values, but conferred a positive influence on their sensory characteristics as noted by untrained panelists (Yun *et al.*,

1987). Interestingly, the preformed cooked cured-meat pigment had a weak, but noticeable antioxidative effect of its own (Shahidi *et al.*, 1987b). Good correlations between the TBA values and the sensory data, as well as between the hexanal content of the meats and their sensory acceptability existed (Shahidi *et al.*, 1987a).

#### THE ROLE OF NITRITE AND ITS ALTERNATIVES ON FLAVOUR

The cured-meat flavour is perhaps a composite sensation arising from the cumulative effect of many odoriferous compounds. Although presence of yet unappreciated substances, in minute quantities, may be responsible for the cured flavour, there is perhaps no doubt that nitrite influences the flavour of cured meats by virtue of its antioxidative properties. Indeed the concentration of carbonyl compounds produced from autoxidation of meat lipids was markedly reduced by the addition of nitrite (Shahidi, 1989) (Table 3). Similar results were obtained when combinations containing polyphosphates, ascorbates and low levels of an antioxidant were used (Shahidi *et al.*, 1988).

Table 3. Effect of curing with nitrite on the concentration of carbonyl compounds of meat.

Carbonyl Compound	Relative Concentration	
	Uncured	Cured
Hexanal	100	7.0
Pentanal	31.3	0.5
Heptanal	3.8	<0.5
Octanal	3.6	<0.5
2-Octenal	2.6	--
Nonanal	8.8	0.5
2-Nonenal	1.0	--
5-Decenal	1.1	--
2-Undecenal	1.4	0.5
2,4-Dodecadienal	1.1	--

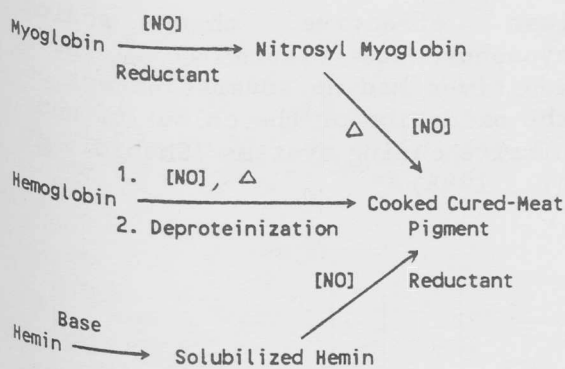


Figure 1. Reactions of myoglobin and hemoglobin with a nitrosating agent.

The preformed cooked cured-meat pigment had identical spectral characteristics to that of the pigment extracted from a commercial sample of ham (Figure 2). Upon its addition to meat and cooking, the characteristic colour of nitrite-cured meat was reproduced (Table 1).

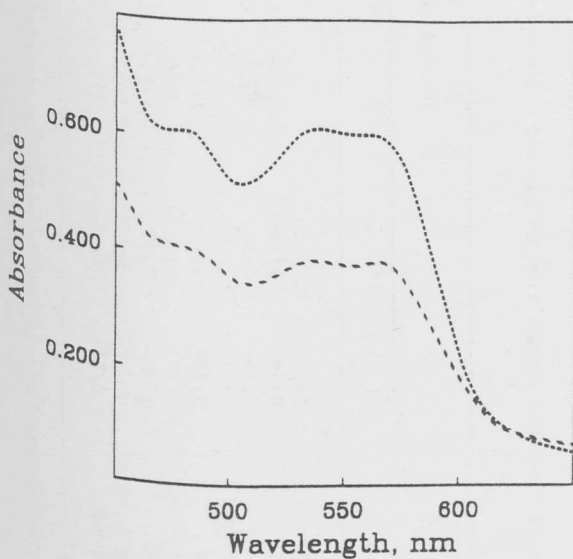


Figure 2. Absorption spectrum of the cooked cured-meat pigment: preformed, ————— ; extracted from ham, - - - - -.

Although other compounds have been found and various patents have been filed on such compounds and processes, none of these colour substitutes has reached the commercial stage (NAS, 1982a). Recently Smith and Burge (1987) studied the addition of protoporphyrin-IX to meats; however,

this compound did not reproduce the desired colour. As expected, presence of iron in the protoporphyrin ring is essential for the development of the typical cured colour in meats. Perhaps the preformed cooked cured-meat pigment, being the natural colourant of cured meats, could break the barrier.

Table 1. Hunter L,a,b values of nitrite-cured and pigment-treated cooked meats.

Additive	Hunter Values		
	L	a	b
Control (no additive)	63.3	4.1	11.6
Nitrite (150 ppm)	62.4	11.6	9.5
Preformed pigment (12 ppm)	60.7	11.8	9.4

### CONTROL OF LIPID AUTOXIDATION IN CURED MEATS

Nitrite acts as a strong antioxidant in cured meats and thus, prevents lipid autoxidation in processed products. Although lipid component of freshly cooked meats contribute to their desirable and characteristic flavour, their oxidation affects palatability and products so formed may have adverse health effects (Shamberger *et al.*, 1974). Phospholipids are most susceptible to autoxidation and form products such as malonaldehyde, pentanal and hexanal (Cross and Zeigler, 1965; Shahidi *et al.*, 1987a) which are responsible for off-flavour development in uncured meats.

The 2-thiobarbituric acid (TBA) number of meats treated with 25,50 and 150 ppm of sodium nitrite has been reported (Shahidi *et al.*, 1987b). While, at 150 ppm level of addition, sodium nitrite almost entirely eliminated the oxidation of lipids during a 5-weeks storage period, at 25 and 50 ppm nitrite reduced the TBA values by about 25% and 44%, respectively.

## ANTIMICROBIAL ACTION OF NITRITE AND ITS ALTERNATIVES

Nitrite exerts a concentration-dependent antimicrobial effect in cured meat products and inhibits the outgrowth of *Clostridium botulinum*. (NAS, 1982b; Pierson and Smoot, 1982). The degree of protection provided depends on the concentration of residual nitrite present, duration of temperature abuse and contamination. Nitrite also retards microbial spoilage of cured meats by anaerobic and aerobic spore-forming bacteria. The mechanism(s) by which nitrite inhibits the outgrowth of spores and the growth of vegetative cells and microorganisms is not fully understood. However, it appears that a reaction with iron-containing enzymes is involved. A better understanding of the exact mechanism(s) of the antimicrobial role of nitrite is still required.

Several alternatives to nitrite for its antimicrobial action have been tested. These include sorbic acid and its potassium salt, sodium hypophosphite, fumarate esters, parabens, and lactic acid-producing organisms. These could be used either alone or together with low concentrations of nitrite (NAS, 1982b).

Sorbic acid and its potassium salt have been found to be relatively safe food additives and are permitted in a variety of foods. In meats they are effective at 2600 ppm. Sodium hypophosphite is a GRAS substance and may be used at 3000 ppm level in meats. Fumarate esters are effective at 1250 or higher levels while parabens had little antibotulinal activity in frankfurters. Wood *et al.*, (1986) recently evaluated the antibotulinal activity of some of these compounds in nitrite-free curing systems. The treatment containing 3000 ppm sodium hypophosphite most closely resembled that of nitrite at 150 ppm in its ability to prevent spore outgrowth and toxin production. Monomethyl fumarate at 1250 ppm was slightly

less effective than sodium hypophosphite (Table 4). These additives had no adverse effect on the oxidation or the colour of non-nitrite curing systems (Shahidi, *et al.*, 1988).

Table 4. Effect of treatment composition on gas and toxin production by *C. botulinum* in meats

Treatment <sup>a</sup>	Incubation at 27°C, Days										
	1	2	3	4	5	6	7	8	27		
1. Control	34/34+										
2. NaNO <sub>2</sub> (150ppm)	0/36-	11/36+	5/18+	8/13+	3/5+	2/2+					
3. NaNO <sub>2</sub> + Asc	0/36-	0/32-	15/30-	5/14+	3/9+	4/6+	1/2+	0/1-	0/1-		
4. Pigment	17/17+										
5. SHP + Pigment	1/18-	1/16+	2/14+	4/12+	3/5+	1/2+	0/1-	0/1-	0/1-		
6. SHP + Pigment + Asc + SPP + TBHQ	6/35-	3/27	1/24-	6/22-	3/16	5/13+	6/8+	1/2+	0/1-		
7. (6) but with Sorbate	0/39-	32/35+	3/3+								
8. (6) but with WMF	0/37-	1/33-	17/31+	9/18+	3/7+	3/4+	0/1+	0/1+	0/1-		

<sup>a</sup> For abbreviations see Table 2. WMF is monomethyl fumarate



## CUMULATIVE EFFECTS OF NITRITE ALTERNATIVE SYSTEMS

We have formulated several nitrite-free combinations consisting of the preformed cooked cured-meat pigment, a sequesterant, an antioxidant and an antimicrobial agent for meat curing (Shahidi *et al.*, 1988; Shahidi, unpublished results). These mixtures have been found effective in reproducing the colour, the oxidative stability and flavour, as well as the antimicrobial effects of nitrite. However, further studies are required, particularly for studying the possibility of reducing the addition level of the existing antimicrobial agents and to test other new and effective antimicrobial substances.

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