

Nitrite-free meat curing systems: Update and review

Fereidoon Shahidi & Ronald B. Pegg

Food Science Program, Department of Biochemistry, Memorial University of Newfoundland, St. John's. NF, Canada A IB 3X9

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Several nitrite-free meat curing systems consisting of the pre-formed cooked cured-meat pigment (CCMP), an antioxidant and/or a sequesterant and possibly an antimicrobial agent, have been formulated. Application of this pigment in different formulations to comminuted and solid cuts of muscle foods has been achieved. Colour, oxidative stability and flavour of the treated samples were similar to those of their nitrite-cured counterparts. Microbial stability of meat systems was assured by the incorporation of a known antimicrobial agent or low-dose, low temperature irradiation.

INTRODUCTION

The preservative effect of sodium nitrite in meats dates back to antiquity. However, the regulated use of sodium nitrite has been in effect only since 1925. Nitrite is responsible for the development of the specific cured flavour and colour of processed meats. By virtue of its strong antioxidant properties in meats, nitrite prevents the formation of warmed-over flavour in cured products. More importantly, nitrite acts as an antimicrobial agent and thus retards the germination of spores and toxin formation by *C. botulinum.*

Despite all of its desired properties, nitrite is also responsible for the formation of carcinogenic N-nitrosamines in some cured products under certain processing conditions. Recently, Schweinsberg and Bürkle (1985) reported that nitrite itself enhances the carcinogenic action of N-nitroso-N-methylbenzylamine in the production of esophageal tumors. To overcome these potentially serious problems, several approaches have been considered by researchers. Since the rate of nitrosamine production depends on the square of the concentration of the residual nitrite in meats, a reduction in the level of nitrite addition to meats has proved to be an effective measure in reducing the risk of nitrosamine formation. Use of nitrosamine-blocking agents such as α -tocopherol together with ascorbates has also been suggested (Gray *et al.,* 1982). However, the most reliable method is the total elimination of nitrite from

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the curing process. Therefore, it is a desired goal to find suitable alternatives for nitrite.

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 perform a selected function of nitrite. Thus, a large number of colorants to substitute nitrite has been developed (NAS, 1982a). However, toxicity problems, etc., have prevented their use in meat processing. A relatively smaller number of antimicrobial agents has been identified that could potentially replace nitrite (NAS, 1982b). Sweet (1975) was the first researcher to report the development of nitrite-free curing systems to provide different functions of nitrite.

This paper summarizes the development of nitritefree curing agents, particularly preparation of multicomponent systems responsible for the cumulative action of nitrite.

NITRITE ALTERNATIVES

Colour of cured meats and nitrite substitutes

The colour of meat is attributable mainly to the hemoprotein, myoglobin (Fox, 1966). Addition of nitrite, upon heat treatment, produces a relatively stable pinkcoloured 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)

Fig. 1. Formation of cooked cured-meat pigment from myoglobin and nitrite. Symbol P signifies protein. Hemoglobin may replace myoglobin.

have concluded that dinitrosyl ferrohemochrome is the actual cooked cured-meat pigment, Bonnett *et al.* (1980) and Killday *et al.* (1988) have shown that a mononitrosyl compound is responsible for the characteristic colour of cured meats (Fig. 1). Definite formation of a substituted dinitrosyl ferrohemochrome, under 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 hemin intermediate was reported (Fig. 2) (Shahidi *et aL* 1984, 1985; Pegg & Shahidi, 1987; Shahidi & Pegg, 1988). Although dinitrosyl ferrohemochrome was presumably

Fig. 2. Reactions of myoglobin and hemoglobin with a nitrosating agent.

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

Additives	Hunter values					
		а		Hue		
Control (no additive)	63.3	4.1	11.6	70.5		
Nitrite (156 ppm)	$62-4$	$11-6$	9.5	39.3		
Preformed pigment (12 ppm)	$60-7$	$11-8$	$9-4$	38.5		
Protoporphyrin-IX (60 ppm)	$52-1$	6.8	$9-4$	$54-1$		
Protected pigment (1.5 years)	58.5	11.7	10-1	40.8		

prepared under a positive pressure of nitric oxide, the exact chemical nature of this pigment before and after application to meat remains unknown. Stability of the preformed cooked cured meat pigment was limited when light and oxygen were present (Shahidi *et al.,* 1985; *vide infra).* However, the pigment remained stable for extended periods of time in sealed ampules under a positive pressure of nitric oxide (Shahidi & Pegg, 1991b). Furthermore, entrapment of the pigment in food-grade wall materials such as cyclodextrins and modified and/or hydrolyzed starches (Shahidi, 1976) was deemed beneficial. Thus, encapsulation of the cooked cured' meat pigment was considered. The entrapment of the pigment in single or mixed ingredients protected it for at least 1.5 years as shown by their spectra and the Hunter L , a , b and Hue values of the treated meats (Table 1, Shahidi & Pegg, 1991b).

The preformed cooked cured-meat pigment prepared directly or indirectly from beef red blood cells, had identical spectral characteristics to that of the pigment extracted from a commercial sample of ham (Fig. 3). Upon its addition to both comminuted and selected solid cuts of meat and cooking, the characteristic colour of nitrite-cured meat was reproduced (Table 1).

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 (Fig. 3 and Table 1). As expected, presence of iron in the protoporphyrin ring is essential for the development of the typical cured colour in meats. The preformed cooked cured-meat pigment, being the

Fig. 3. Absorption spectra of: CCMP prepared from red blood cells, -----; CCMP prepared from hemin, pigments extracted from commercial ham, -------; and pigments extracted from CCMP-treated cooked meats, ------.

natural colorant of cured meats, should be readily acceptable. Pilot-scale experiments for the preparation of wieners as well as evaluation of their colour quality by subjective or objective methods of analyses have recently been reported from our laboratories (Shahidi & Pegg, 1988, 1990; Shahidi *et al.,* 1990).

The colour intensity of wieners cured with different levels of nitrite or the cooked cured meat pigment (CCMP) was dependent on the myoglobin content of the original meat (Table 2) as well as the concentration of these additives (Tables 3 and 4; Shahidi & Pegg, 1991a). The pigment-treated samples generally had slightly lower Hunter L values than their nitrite-cured counterparts. The Hunter a values of the systems were more heavily dependent on both the added pigment and on the original myoglobin content of the meats (Tables 2 and 4). The original myoglobin in the sample is not fully converted to its nitrosated ferrohemochrome by nitrite and as such it is readily masked by the intense colour of the cooked cured-meat pigment. The Hunter Hue values of the treated meats reflected a similar trend as they decreased with the increasing level of myoglobin in the meat or the addition level of the nitrite or the preformed pigment.

The colour stability of the pigment-treated samples and their nitrite cured analogues was examined under intense (375 lux) fluorescent lighting. Both systems faded rapidly during the first 6 h and the final Hunter

Table 2. Dependence of Hunter colour values of cooked meats on their myoglobin content

Myoglobin (mg/g)	Nitrite-cured (156 ppm)		Pigment-treated (12 ppm)			
	a	Hue			Hue	
0.76 ± 0.02	$64.2 + 0.3$	10.8 ± 0.2	$43.0 + 0.6$	63.3 ± 0.4	$11.8 + 0.2$	39.4 ± 0.6
1.21 ± 0.03	57.9 ± 0.2	$13.4 + 0.2$	34.6 ± 0.2	57.4 ± 0.2	$13.2 + 0.2$	$34.8 + 0.4$
2.33 ± 0.06	53.5 ± 0.8	15.4 ± 0.2	31.5 ± 0.6	52.1 ± 0.2	15.3 ± 0.2	31.4 ± 0.4

Nitrite (ppm)		Hunter values					
		a	Hue				
25	$57.2 + 0.2$	$12.0 + 0.1$	38.1 ± 0.4				
50	57.2 ± 0.2	12.8 ± 0.1	36.0 ± 0.3				
100	$57.4 + 0.3$	13.2 ± 0.1	35.2 ± 0.4				
156	$57.4 + 0.2$	$13.4 + 0.2$	34.5 ± 0.4				

Table 3. Dependence of Hunter colour values of meat on the concentration of sodium nitrite

Table 4. Dependence of Hunter colour values of meat on the concentration of cooked cured-meat pigment

Hunter values						
L	a	Hue				
$62.4 + 0.2$	11.6 ± 0.3	39.4 ± 0.5				
62.0 ± 0.3	$11-2 \pm 0.2$	40.1 ± 0.5				
60.7 ± 0.5	$11.8 + 0.2$	$38.6 + 0.5$				
59.1 ± 0.2	12.2 ± 0.2	37.3 ± 0.4				
58.1 ± 0.3	12.5 ± 0.1	36.7 ± 0.3				
57.5 ± 0.2	12.7 ± 0.2	36.2 ± 0.5				

Hue values of the samples were increased by 15 to 20 units (Fig. 4; Shahidi & Pegg, 1991a, b). The colour fading rates of these systems were also found to be similar.

Application of the cooked cured-meat pigment to a wide range of meat emulsions and solid cuts ranging

Fig 4. Hue angle parameter (arctan b/a) for meats treated with CCMP: 3 ppm,-----; 12 ppm,-----; and 24 ppm, $-\cdots$; and 156 ppm sodium nitrite,-------; as a function of storage time under intense fluorescent light.

from cod surimi to seal meat has been completed. Results indicate that this pigment successfully reproduces the characteristic colour of nitrite-cured meats even in dark meats such as seal.

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 components of freshly cooked meats contribute to their desirable and characteristic flavour, their oxidation affects palatability and products soformed 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 & Zeigler, 1965; Shahidi *et al.,* 1987a) which are known to be correlated to offflavour 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 meat lipids during a 5-week storage period, at 25 and 50 ppm nitrite it reduced the TBA values by about 25% and 44%, respectively (Shahidi *et al.,* 1991a).

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

Table 5. TBA numbers of cooked meats treated with different additives after a 5-week storage period at 4°C a

Experiment no.	Additives(s)	TBA number
1	Control (no additives)	15.46
\overline{c}	BHA (30 ppm)	0.44
$\overline{\mathbf{3}}$	TBHQ (30 ppm)	0.35
4	SAPP (3000 ppm)	1.86
5	SPP (3000 ppm)	1.66
6	SHMP (3000 ppm)	7.21
7	$Na2EDTA$ (500 ppm)	0.96
8	$(4) +$ Asc (550 ppm)	0.27
9	$(5) + \text{Asc}(550 \text{ ppm})$	0.23
10	$(6) + \text{Asc} (550 \text{ ppm})$	0.29
11	$(8) + BHA (30 ppm)$	0.20
12	$(8) + TBHQ (30 ppm)$	0.18
13	Pigment (12 ppm)	9.89
14	(11) + pigment (12 ppm)	0.34
15	(12) + pigment $(12$ ppm)	0.24
16	$(14) + SHP$ (3000 ppm)	0.28
17	$(15) + SHP$ (3000 ppm)	0.21
18	NaNO ₂ (150 ppm)	0.63

Additives were: hydroxyanisole, BHA; tert-butylhydroquinone, TBHQ; sodium tripolyphosphate, STPP; sodium pyrophosphate, SPP; sodium hexametaphosphate, SHMP, disodium salt of ethylenediaminetetraacetic acid, $Na₂EDTA$; sodium ascorbate, Asc; and sodium hypophosphite, SHP.

Fig. 5. Synergistic effect of polyphosphates with sodium ascorbate in meat systems. Symbols (full) are: SHMP; \blacksquare STPP; \blacktriangle SPP; \blacklozenge SAPP. Corresponding open symbols are for the same polyphosphates with sodium ascorbate.

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-week storage at 4°C, as measured by the 2-thiobarbituric acid test (Table 5). Among the food-grade sequesterants, sodium acid pyrophosphate (SAPP), 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 (Fig. 5). Addition of small amounts (30 ppm) of an antioxidant, such as BHA or TBHQ to the above systems, had a minor effect on the TBA values but had a positive influence on their sensory characteristics as noted by untrained panelists (Yun *et al.,* 1987). Similar antioxidant effects were observed when plant phenolic compounds were used (Shahidi & Hong, 1989). Interestingly, the preformed cooked cured-meat pigment has a weak, but noticeable antioxidative effect of its own (Shahidi *et al.,* 1987b, 1988a). 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 NITRITE ALTERNATIVES ON FLAVOUR

The cured-meat flavour is perhaps a composite sensation arising from the cumulative effect of many compounds. Although presence of yet unappreciated **sub-**

Table 6. Effect of curing with nitrite on the concentration of carbonyl compounds of meat

Carbonyl	Relative concentration						
compound	Uncured	Nitrite- cured ^a	Nitrite-free cured ^b				
Hexanal	100	70	6.5				
Pentanal	31.3	0.5	0.5				
Heptanal	3.8	< 0.5	0.5				
Octanal	3.6	<0.5	0.5				
2-Octenal	2.6						
Nonanal	8.8	0.5	0.7				
2-Nonenal	$1-0$						
2-Decanal	$1-1$		< 0.1				
2-Undecenal	$1-4$	0.5	0.5				
2,4-Decadienal	$1-1$						

^a Sample contained 550 ppm sodium ascorbate.

Sample contained the preformed cooked cured-meat pigment, 12 ppm; STPP, 3000 ppm; Na ascorbate, 550 ppm and TBHQ, 30 ppm.

stances, in minute quantities, may be responsible for the cured flavour, there is no doubt that nitrite influences the flavour of cured meats by virtue of its antioxidative properties and stabilization of microsomal lipids and heme pigments. Indeed the concentration of carbonyl compounds produced from autoxidation of meat lipids was markedly reduced by the addition of nitrite (Shahidi, 1989a, b) (Table 6). Similar results were obtained when combinations containing polyphosphates, ascorbates and low levels of an antioxidant or some of our other combinations containing all-natural ingredients were used (Shahidi *et al.,* 1990). Typical results for the concentration of major carbonyl compounds in a nitrite-free cured meat system are given in Table 6. Furthermore, the concentration of some of the flavour components responsible for the meaty aroma of cooked meats was proportionally affected. Thus, the treated meats preserved their desired flavour characteristics and in most cases were indistinguishable in comparison with their nitrite-cured analogues (Shahidi, 1989a).

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 & 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

Treatment ^b		Incubation at 27° C (days)							
		\mathcal{L}	3	4	5.	6		8	27
1. Control	$34/34+$								
2. NaNO ₂ $(150$ ppm $)$	$0/36-$	$11/36+$	$5/18+$	$8/13+$	3/5c	$2/2+$			
3. $NaNO2 + Asc$	$0/36-$	$0/32-$	$15/30-$	$5/14+$	$3/9+$	$4/6+$	$1/2+$	$0/1-$	$0/1-$
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. $SHP + Pigment + Acc +$									
$SPP + TBHO$	$6/35-$	3/27c	1/24	$6/22-$	3/16c	$5/13+$	$6/8+$	$1/2+$	$0/1-$
7. (6) but with Sorbate	$0/39-$	$32/35+$	$3/3+$						
$8.$ (6) but with MMF	$0/37-$	$1/33-$	$17/31+$	$9/18+$	$3/7+$	$3/4+$	$0/1+$	$0/1 +$	$0/1-$

Table 7. Effect of treatment composition on gas and toxin production by *C. botulinum* in meats^{*a*}

Adapted from Wood *et al. (1986).* Number of packs showing gas production/total number of packs.

+, toxin present, -, toxin absent.

 h For abbreviations see Table 2. MMF is monomethyl fumarate.

, Presence of toxin was not tested.

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 perhaps be used at the 3000 ppm level in meats. Fumarate esters are effective at 1250 ppm 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 nitritefree curing systems. The treatment containing 3000 ppm sodium hypophosphite, together with low levels of TBHQ, 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 7). These additives had no adverse effect on the oxidation or the colour of non-nitrite curing systems (Shahidi *et aL,* 1988b). Furthermore, application of irradiation, at 5 or 10 kGy, to meats treated with the cooked curedmeat pigment not only ensured the keeping quality of the products, but did not have any negative effect on their colour stability (Shahidi *et al.,* 1991b).

CUMULATIVE EFFECTS OF NITRITE ALTERNATIVE SYSTEMS

Several nitrite-free combinations consisting of the preformed cooked cured-meat pigment, a sequesterant and/ or an antioxidant and an antimicrobial agent have been formulated for meat curing (Shahidi *et aL,* 1988b). 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 still 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. Other combinations composed of more readily acceptable formulations have recently been reported (Shahidi *et al.,* 1990).

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