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Nitrates/Nitrites and Preservative Replacements in Meat Products

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Clean Label Product Innovation Short Course

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Objectives

- To review the basic functions and importance of nitrites and nitrates as curing agents in meat products
- To present and discuss the various types of “clean label” processed meat products and their regulatory requirements
- To discuss alternatives to replace conventional nitrates/nitrites and antimicrobial preservatives in clean label processed meat products in the context of the technical challenges involved

Agenda

- History of Meat Curing
- Nitrate and Nitrite – The Basics
- Nitrate and Nitrite in the Diet
- Nitrate and Nitrite Content of Foods
- Functions of Nitrate and Nitrite in Meat Products
- Alternative Curing Systems
- Alternative Antimicrobial Systems
- Labeling of Clean/Simple Label Processed Meat Products

History of Meat Curing

- One of the oldest forms of food preservation
- Likely discovered by accident via contamination of salt with saltpeter (potassium nitrate)
- By 10th century, Romans were adding saltpeter intentionally to obtain distinctive color and flavor
- First USDA regulations for nitrite and nitrite use in meat products established in 1925
- Regulations last updated in 1970
- Bacon-specific regulations established in 1978 (to minimize potential for nitrosamine formation)

Nitrate and Nitrite

- Ionic forms:
  - Nitrate – NO_3^-
  - Nitrite – NO_2^-

- Sodium or potassium salts
  - $NaNO_3$ or KNO_3
  - $NaNO_2$ or KNO_2

Sodium Nitrate

- Source:
  - Can be mined or synthesized
- In meat products, functions as a source and reservoir of nitrite

Sodium Nitrite

- Source:
  - Commercially synthesized by treating sodium hydroxide with mixture of nitrogen dioxide and nitric oxide:

$$2\ NaOH + NO_2 + NO \rightarrow 2\ NaNO_2 + H_2O$$

- By definition, cured meats must contain nitrite
- Important public health function due to proven track record of *C. botulinum* prevention, which has been further validated by recent research

Nitrate and Nitrite in the Diet

- Two major sources in the body:
  - **Endogenous** → L-arginine-NO synthase pathway
    - NO (nitric oxide) generated by conversion of L-arginine to L-citrulline by nitric oxide synthase (NOS) is oxidized in blood and tissues to form NO_3^- and NO_2^-
  - **Exogenous** → Diet

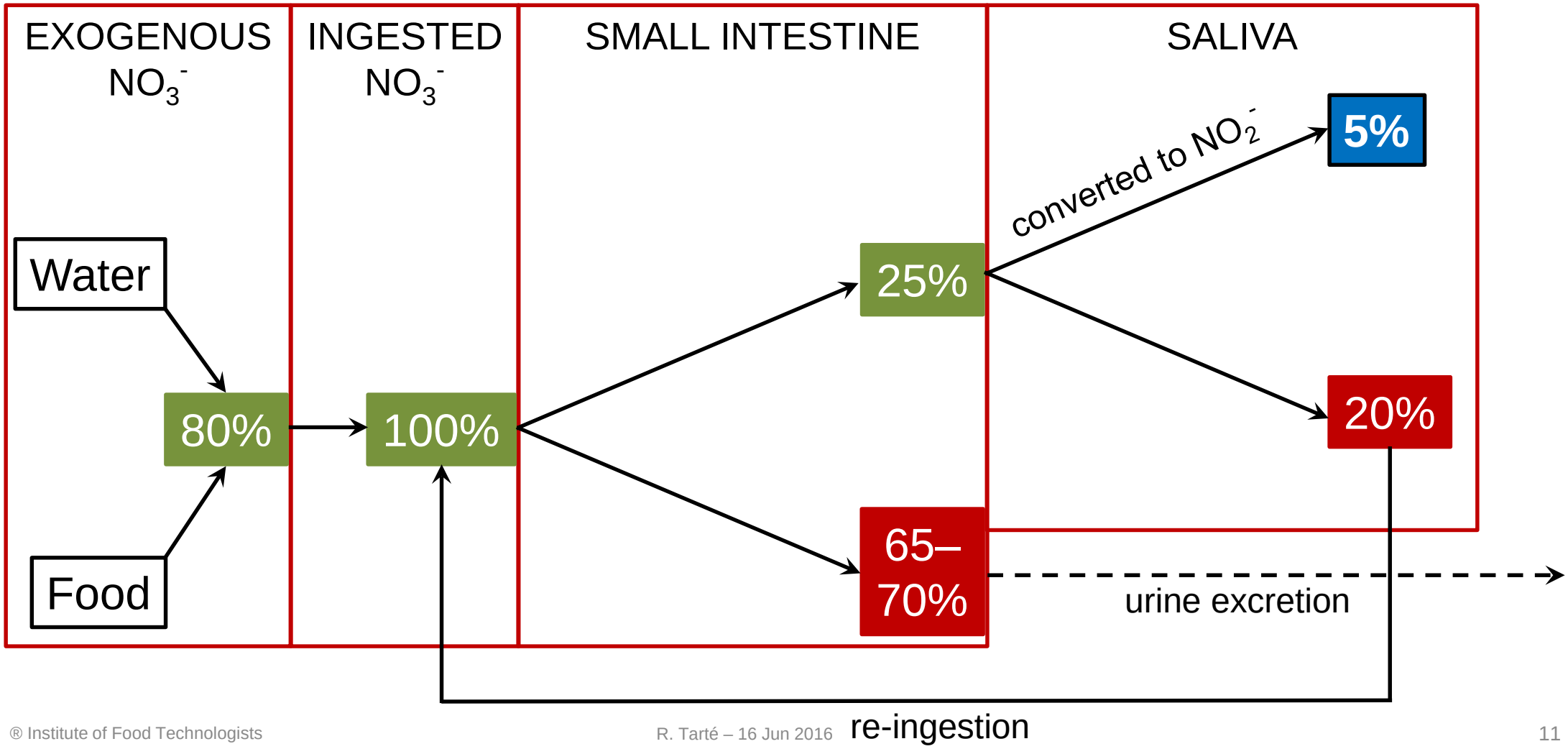
Nitrate in the Diet

- Mean daily intake = 43–141 mg (WHO, 2007)
- Total (exogenous) intake sources
  - Plant foods: ≈80%
  - Drinking water: 10–15%
- Food intake sources
  - Various vegetables
    - Largest contributors of dietary intake of nitrate; ≈85–90%
    - E.g., lettuce, cabbage, spinach, beets, celery, radishes

Nitrite in the Diet

- Mean daily intake = 1.2–3.0 mg (WHO, 2007)
- Total intake sources
  - Saliva: ≈93%
  - Vegetables: ≈2%
  - Cured meats: ≈5%
- Enterosalivary circulation of dietary nitrite
  - Ingested nitrate is absorbed in small intestine, 25% of which is secreted in saliva, ≈20% of which is converted to nitrite by oral cavity bacteria
    - Therefore ≈5% of ingested nitrate becomes converted to nitrite
      - » This amount accounts for ≈93% of total ingested nitrite
    - Nitrite in saliva may produce NO under acidic conditions (as in stomach) in sufficient amounts to protect against swallowed pathogens (Duncan et al. 1995).

Enterosalivary Circulation of Dietary Nitrate



Nitrite/nitrate concentrations of selected foods collected from five U.S. cities in 2009

	Nitrate (ppm)		Nitrite (ppm)	
	Mean	Range	Mean	Range
Broccoli	394	29–1140	0.6	0.01–9.5
Cabbage	418	37–1831	0.1	0.01–0.4
Celery	1495	20–4269	0.1	0.02–0.5
Lettuce	850	79–2171	0.6	0.01–9.7
Spinach	2797	65–8000	8.0	0–137
Cured, dried, uncooked sausage	113	0.1–2289	0.8	0.03–9.7
Cured, cooked sausage	32	0.8–541	8.0	0.1–29.3
Fermented, cooked sausage	46	1.8–320	0.8	0–26.7
Whole-muscle, brine cured, uncooked	14	3.5–32	6.8	0.2–36.5
Whole-muscle, brine cured, cooked	16	0.2–108	7.5	0–27.6
Whole-muscle, dry-cured, uncooked	106	0.4–1367	1.5	0.02–16.2

Source: Keeton JT et al. 2009.

Maximum ingoing nitrite and nitrate limits (in ppm) for meat and poultry products

	Curing Method			
Curing Agent	Immersion Pumped	Massaged or Pumped	Comminuted	Dry Cured
Sodium Nitrite	200	200	156	625
Potassium Nitrite	200	200	156	625
Sodium Nitrate	700	700	1718	2187
Potassium Nitrate	700	700	1718	2187

Source: USDA-FSIS Processing Inspectors' Calculations Handbook. 1995 revision. http://www.fsis.usda.gov/OPPDE/rdad/FSISDirectives/7620-3.pdf.

Potassium nitrate 5%

= 5,000 ppm

Concerns About Nitrite

- Toxicity
  - Very reactive; toxic at very high doses
    - Lethal dose ≈1 g (14 mg/kg body weight)
      - » Assuming 15 ppm residual nitrite, this would be equivalent to ingesting 1,086 56-g hot dogs (66.7 kg)
  - Concern for methemoglobinemia, primarily in infants (blue baby syndrome)
- Nitrosamines and Cancer
  - N-nitrosamines cancer-causing potential discovered during 1950s/1960s
  - Formed by reaction of nitrite with secondary amines near neutral pH and temperatures >130°C
  - For more information, consult Sindelar & Milkowski (2012)

Functions of Nitrite

- **Cured Color**
- **Cured Flavor**
- **Texture**

} Organoleptic effects

- **Antimicrobial**
- **Antioxidant**

Functions of Nitrite

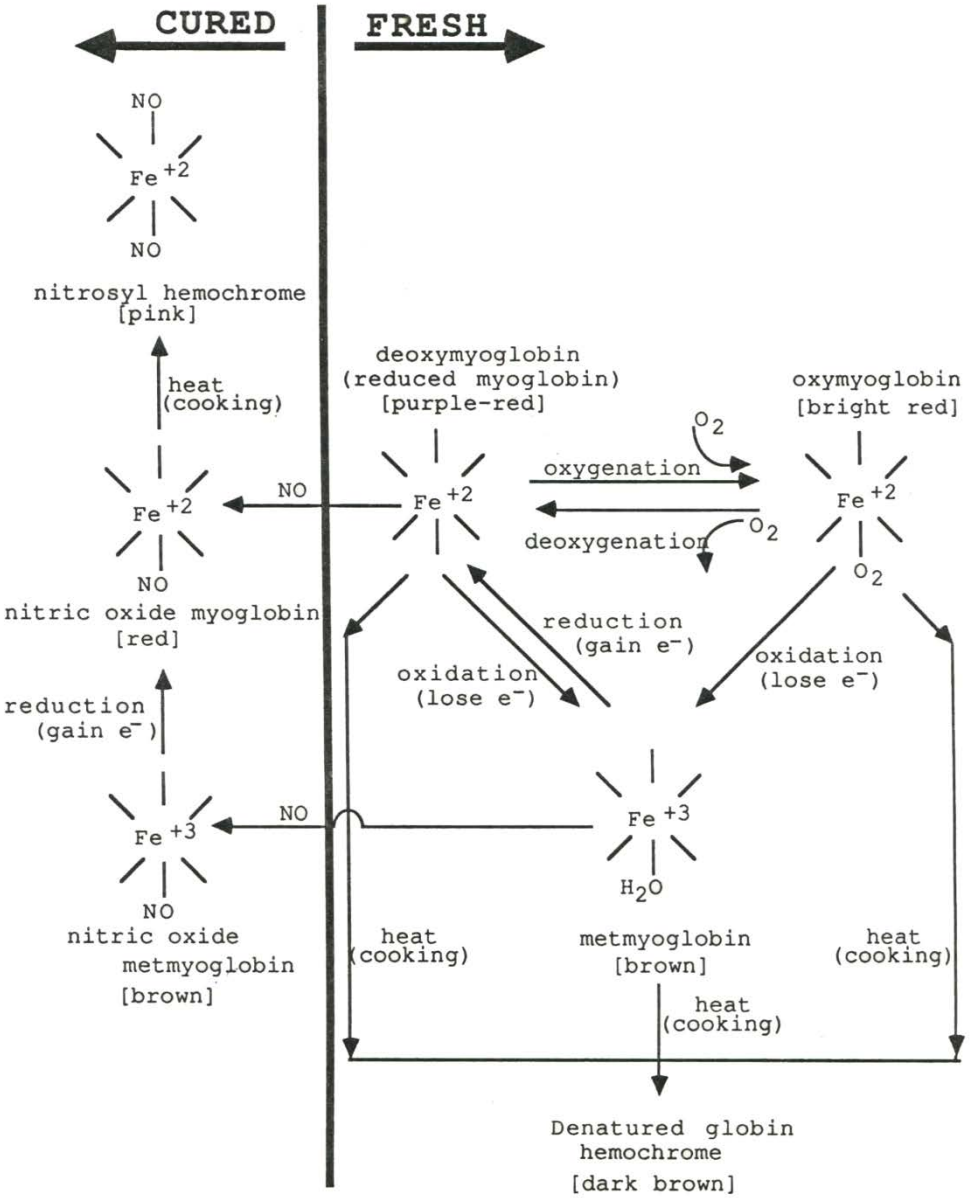
1. Color

- Due to nitric oxide (NO) production from NO_2^-

$$\underset{\text{nitrate}}{NO_3^-} \xrightarrow[\text{reductase}]{\text{nitrate}} \underset{\text{nitrite}}{NO_2^-} \xrightarrow[\text{accelerator}]{\text{cure}} \underset{\text{nitric oxide}}{NO}$$

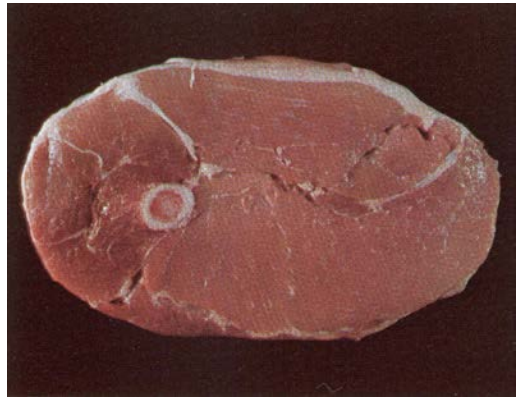
- <5 ppm NO_2^- required for this effect
- Promoted by acidic conditions
- Accelerated by reductants, salt, pigments (Fe)

MEAT COLOR FORMS



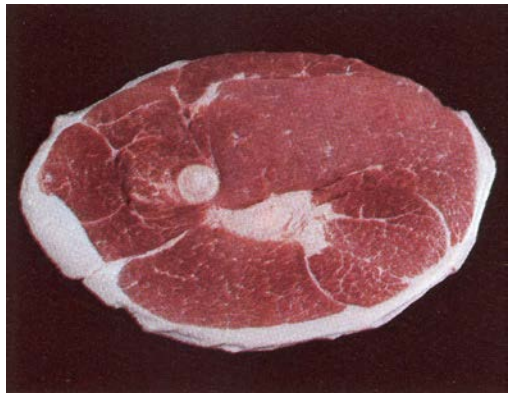
Functions of Nitrite

- Interaction of NO with meat pigment myoglobin



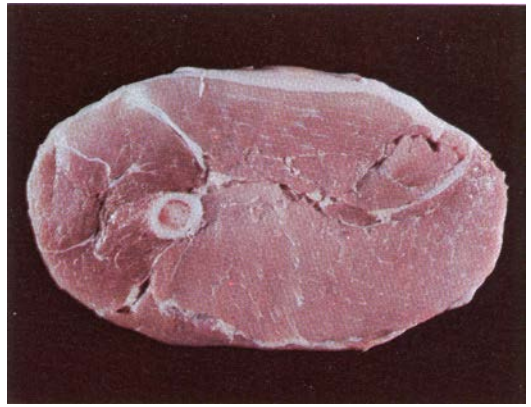
Myoglobin

NO_3^- → NO_2^- → NO →



Nitrosomyoglobin

Heat →



Nitrosylhemochrome
(pink cured meat color)

Functions of Nitrite

2. Antimicrobial

- Inhibitory activity towards many microorganisms, including *Clostridium botulinum*
- Acts in synergism with salt and other antimicrobials, e.g., lactate, to control *Listeria monocytogenes*

Functions of Nitrite

3. Antioxidant

- Effective for preventing rancidity
  - Decreases rate of lipid oxidation
  - Eliminates “warmed-over flavor” in cooked meats
  - Interacts with heme iron
  - NO scavenges free radicals
- Antioxidant activity of NO_2^- may play a role in cured flavor

Functions of Nitrite

4. Flavor

- Cured flavor not clearly understood
- Is it a specific flavor compound or *the absence* of other flavor compounds? Is it both?
  - Fewer flavor compounds have been isolated from cooked cured meats than from uncured cooked meats
  - Does antioxidant activity play a role?

5. Texture

- Protein crosslinking of sulfur-containing amino acids by nitrite

Functions of Nitrite

No other known substance possesses all of nitrite's unique properties

Functions of Nitrate

- Serves as nitrite precursor and/or reservoir
- Sometimes included in starter cultures as a cured color promoting agent
- Also available from natural sources, such as celery powder and swiss chard
  - “Natural” or “Alternative” curing
  - Requires conversion to nitrite
    - In-plant fermentation
    - Pre-converted

Nitrate/Nitrite Alternatives

- Health concerns over nitrite in the 1960s lead to development of truly uncured (nitrite-free) products in the 1970s
  - These provided inferior organoleptic, safety and shelf-life properties than their cured counterparts
- In response, in 1972 USDA established requirement that products "for which there is a standard and to which nitrate or nitrite is permitted or required to be added, may be prepared without nitrate or nitrite and labeled with such standard name when immediately preceded with the term 'Uncured'..."
- 1979 amendment include statement "No Nitrate or Nitrite Added."

Clean/Simple Label Alternatives in Processed Meats

- Elements to replace:
  - Curing system
    - Nitrate/nitrite, ascorbate/erythorbate
  - Antimicrobial system
    - Lactate/diacetate, benzoate, propionate, others
    - Any ingredient called by its chemical name
  - Other ingredients
    - Phosphates, binders (e.g., carrageenan, *modified* starches)
    - Any ingredient called by its chemical name
- This necessitates search for “natural” or simple-name versions of these ingredients or other ingredients with similar functionality

Alternative Curing Systems

- Three basic elements of an alternative curing system
  - Nitrate/nitrite source
  - Cure accelerator
  - Bacterial starter culture (not always necessary)

Alternative Curing Systems

1. **Nitrate / nitrite source**
   - Commercial vegetable juices and juice powders
     - Celery (most common); Swiss chard
     - Other sources (e.g., lettuce, spinach, beets) not yet exploited commercially for this purpose

Alternative Curing Systems

1. Nitrate / nitrite source, cont.

- Types:
  - Regular
    - » Commercial sources vary from 20,000–30,000 ppm NO_3^-
    - » Typically standardized to a specific NO_3^- content
    - » Require fermentation step during processing to convert NO_3^- to NO_2^-
  - Pre-converted
    - » NO_3^- converted to NO_2^- by supplier
    - » Typically standardized to specific NO_2^- content (up to >15,000 ppm)
    - » Eliminates the need for fermentation step

Alternative Curing Systems

1. **Nitrate / nitrite source, cont.**
   - Should try to maximize usage level to increase ingoing NO_2^- content
   - There's no regulatory limit, but, in most cases, self-limiting at 0.3–0.4% due to strong celery flavor
     - Maximum level is formulation specific, with blander-tasting products tolerating less
     - Opportunity for flavor research??

Alternative Curing Systems

1. Nitrate / nitrite source, cont.

- Concern
  - Does system generate enough nitrite to control *C. botulinum, C. perfringens* and *L. monocytogenes* ?
    - » E.g., pre-converted celery powder (22,500 ppm $NaNO_2$) at 0.4% would result in 90 ppm ingoing $NaNO_2$. Is that enough?
    - » It has been estimated that at least 70 ppm is needed for adequate antilisterial activity (Glass et al., 2008)
    - » Commercial alternatively-cured frankfurters, hams and bacon have been shown to have more potential for growth of *C. perfringens* (Jackson et al., 2011)
    - » Effectiveness of nitrite is affected by of other factors (e.g., other antimicrobials, salt level, temperature, a_w, etc.)

Alternative Curing Systems

2. Lactic acid starter culture

- Reduce NO_3^- to NO_2^- via production of nitrate reductase
- Commercially available strains
  - *Staphylococcus carnosus, S. utilis. S. vitulinus, Micrococcus varians*
- Requires fermentation step (1–2 h at ≈27–38°C) prior to cooking to allow for NO_2^- formation
  - Conversion not 100% efficient; difficult to control [NO_2^-]
- Not necessary when using pre-converted NO_2^- sources

Alternative Curing Systems

3. Cure Accelerators

- Natural sources of ascorbic acid
- Types
  - Cherry powder
  - Acerola powder
  - Lemon juice powder (to lower pH)

Antimicrobial Systems

- **Conventional**
  - Nitrite
  - Lactate
  - Diacetate
  - Benzoate
  - Propionate
- **Simple Name and or Natural**
  - Cultured sugars
  - Vinegar / buffered vinegar
  - Lemon juice / lemon juice solids
  - Plant extracts (e.g., rosemary, oregano, sage)

- Much commercial development activity in this area
- Need to confirm antimicrobial effectiveness (safety and shelf-life) on case-by-case basis by use of microbial challenge studies
- Some commercial microbial growth predictive models incorporate simple name antimicrobials

Labeling

1. Uncured Products

- "Any product, such as frankfurters and corned beef, for which there is a standard in this part and to which nitrate or nitrite is permitted or required to be added, may be prepared without nitrate or nitrite and labeled with such standard name when immediately preceded with the term ''**Uncured**'' in the same size and style of lettering as the rest of such standard name: *Provided*, That the product is found by the Administrator to be similar in size, flavor, consistency, and general appearance to such product as commonly prepared with nitrate and nitrite…" 9 CRF 319.2

Labeling

1. Uncured Products, cont.

- Products "which contain no nitrate or nitrite shall bear the statement ''**No Nitrate or Nitrite Added**.'' This statement shall be adjacent to the product name in lettering of easily readable style and at least one-half the size of the product name." 9 CFR 317.17(c)(1)
- These products must also bear the statement ''**Not Preserved—Keep Refrigerated Below 40°F At All Times**'' unless they have been thermally processed to F_o of 3 or more; they have been fermented or pickled to pH of 4.6 or less; or they have been dried to a water activity of 0.92 or less." 9 CFR 317.17(c)(2)

Labeling


NO ARTIFICIAL PRESERVATIVES
*SEE BACK PANEL FOR INGREDIENTS USED TO PRESERVE QUALITY
GLUTEN FREE | FULLY COOKED
Oscar Mayer
SELECTS
U.S. INSPECTED AND PASSED BY DEPARTMENT OF AGRICULTURE
ANGUS BUN LENGTH
UNCURED
BEEF FRANKS
NO NITRATES OR NITRITES ADDED EXCEPT THOSE NATURALLY OCCURRING IN CELERY JUICE
NOT PRESERVED—KEEP REFRIGERATED BELOW 40°F AT ALL TIMES
NET WT 14 OZ
PER 1 LINK
170 CALORIES
6g SAT FAT 30% DV
370mg SODIUM 15% DV
<1g SUGARS

Labeling

2. “Natural” Products

- USDA-FSIS Food Standards and Labeling Policy Book:
  - The term “natural” may be used on labeling for meat products and poultry products, provided the applicant for such labeling demonstrates that: (1) the product does not contain any artificial flavor or flavoring, coloring ingredient, or chemical preservative (as defined in 21 CFR 101.22), or any other artificial or synthetic ingredient; and (2) the product and its ingredients are not more than minimally processed.
  - Therefore, sodium nitrate or nitrite are not allowed
    - » Products must be labeled “uncured”

Labeling

2. “Natural” Products, cont.

- USDA-FSIS Food Standards and Labeling Policy Book:
  - Minimal processing may include: (a) those traditional processes used to make food edible or to preserve it or to make it safe for human consumption, e.g., smoking, roasting, freezing, drying, and fermenting, or (b) those physical processes which do not fundamentally alter the raw product and/or which only separate a whole, intact food into component parts, e.g., grinding meat, separating eggs into albumen and yolk, and pressing fruits to produce juices.

Labeling


APPLEGATE.
CHANGING THE MEAT WE EAT®
NATURAL*
UNCURED
BEEF HOT DOG
NOT PRESERVED • KEEP REFRIGERATED BELOW 40°F AT ALL TIMES
NO NITRATES OR NITRITES ADDED EXCEPT FOR THOSE NATURALLY OCCURRING IN SEA SALT & CELERY POWDER
NO ANTIBIOTICS USED** • HUMANELY RAISED***
VEGETARIAN GRAIN-FED DIET • GLUTEN & CASEIN FREE • NO FILLERS
Nutrition Facts
NET WT. 12 OZ. (340g)

Labeling

3. Organic Products

- Governed by Organic Foods Production Act (1990) and managed by the National Organic Program (NOP)
  - Establishes prohibited practices, requirements and allowed substances
- Synthetic and non-organic substances that may be used are listed in the National List of Allowed and Prohibited Substances (7 CFR 205.605 and 606)
- Sodium nitrate or nitrite specifically prohibited
  - Products must, therefore, be labeled “uncured.”

Labeling

3. Organic Products, cont.

- Regulated by Organic Foods Production Act (1990):
- "100% Organic"
  - Only organically-produced ingredients and processing aids
  - Water and salt are excluded
  - Can use USDA organic seal
- "Organic"
  - 95%+ organically-produced ingredients, excluding water and salt
  - Can use USDA organic seal
- "Made with Organic Ingredients"
  - 70+ organically-produced ingredients
  - Cannot use USDA organic seal

Labeling


APPLEGATE
CHANGING THE MEAT WE EAT®
THE GREAT
ORGANIC
UNCURED
BEEF HOT DOG
MADE WITH GRASS-FED BEEF
NOT PRESERVED • KEEP REFRIGERATED BELOW 40°F AT ALL TIMES • NO NITRATES OR NITRITES ADDED*
NO ANTIBIOTICS USED** • HUMANELY RAISED*** • GLUTEN & CASEIN FREE • NO FILLERS • GRASS-FED BEEF
FULLY COOKED • BEST WITHIN 4 DAYS OF OPENING, MAY BE FROZEN FOR UP TO 9 MONTHS
Nutrition Facts
Serving Size: 1 hot dog (56g)
Servings Per Package: 8
Calories 110
Calories From Fat 80
Amount Per Serving % DV*
Total Fat 8g 12%
Sat. Fat 3g 15%
Trans Fat 0g
Cholesterol 30mg 10%
Sodium 330mg 14%
Amount Per Serving % DV*
Total Carbohydrate 0g 0%
Dietary Fiber 0g 0%
Sugars 0g
Protein 7g
Vitamin A 2% • Vitamin C 0% • Calcium 0% • Iron 4%
00570 00571 00970
INGREDIENTS: ORGANIC GRASS-FED BEEF**, WATER. CONTAINS LESS THAN 2% OF THE FOLLOWING: SEA SALT, ORGANIC SPICES, ORGANIC DEHYDRATED GARLIC AND ONION, ORGANIC PAPRIKA, CELERY POWDER. GLUTEN & CASEIN FREE.
Questions? Comments? Call 866-587-5858 or visit www.applegate.com
DISTRIBUTED BY APPLEGATE FARMS, BRIDGEWATER, NJ 08807
Certified Organic by Quality Assurance International
*Except for those naturally occurring in sea salt and celery powder. **Beef never administered antibiotics, added growth hormones or animal by-products. Grass-fed beef. ***Beef raised on sustainable family farms in a stress-free environment that promotes natural behavior and socialization.
HEATING INSTRUCTIONS: GRILL: Place over medium heat and turn until browned. BOIL: Bring water to a boil, reduce heat, carefully add hot dogs. Simmer for about 5 minutes. For kids under 5 years: cut lengthwise, then slice.
Real Food has a Story. Visit us online and learn more about the people, places and practices behind our products.
USDA ORGANIC
U.S. INSPECTED AND PASSED BY DEPARTMENT OF AGRICULTURE EST.9574
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Thank You

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