Additives and Ingredients in Ham Production

The manufacture of whole muscle cooked meat products uses a wide variety of ingredients and additives to enhance flavour, texture, appearance and smell Lorenc Freixanet from the Intelligence Department at equipment manufacturer Metalquimia unravels some of the uses and the pitfalls that can be met in their use.

In the production of cooked ham there is a distinction between ingredients and additives. Ingredients are those constituents, which are present in nature and are consumed as a matter of course in a normal diet, while additives are any substance not normally consumed, which is added intentionally for technological or organoleptic purposes.

INGREDIENTS

Meat and Water

Meat preparation for the production of ham varies widely depending on production goals, ranging from bone-in, skin-on ham with no trimming, to products completely cut into separate muscles or smaller pieces, completely trimmed of all fat, tendons and nerves.

The meat used in the manufacture of whole muscle cooked meat products may be the ham or shoulder, bone-in or boneless, skin-on or skinless, and with varying degrees of fat, nerves and tendons trimmed, which will depend on the product to be produced and on the consumer tastes of each particular country.

In most cooked ham products, the second most important ingredient is the water added. Technologically, the water in brine preparations must comply with a number of requirements. First, it must be hygienic, sanitary water of high chemical quality, given its use in a food product destined for human consumption.

From a technological point of view, the water must be as soft as possible (free of Ca 2+ and Mg 2+ ions and heavy metals).

Knowing the degree of hardness of the water that is used is very important, because a high concentration of ions can negatively affect the water holding capacity of the finished product. Also, the presence of iron, copper and other metals in saline solutions, as well as having toxicological risks, can partially destroy the ascorbate, present in brine as an antioxidant, and affect colour stability in the finished product.

Salt

Table salt or sodium chloride has been used since ancient times in the preparation of meat, because of its capacity to reduce water activity, helping to preserve the product as well as contributing to its flavour.

Salt is now used in cooked ham in concentrations that fluctuate around two per cent, and its use is restricted only in those dietetic products labelled as having a low sodium content. In the case of cooked dietetic ham, salt is partially replaced by other ingredients, in particular potassium chloride, a product with a similar water activity depressor capacity but which gives the ham a bitter metallic taste that must be counteracted with flavouring agents.

In addition to these functions, technologically salt plays an important role in making meat proteins soluble and expanding their quaternary structures, because it provides the principal aid to the product's ionic strength, weakening the electrostatic unions existing among the groups carboxyl and ammonium and therefore contributing to water holding capacity and muscular binding in the finished cooked meat product.

Sugars

Sugars are used in cooked ham basically as water activity depressors, although they also play an important role in product taste. Sugars are usually used in mixtures with compositions that vary according to what effects are desired in the finished cooked product. The properties and effects of the sugars commonly used in manufacturing cooked ham are:

- **Saccharose:** The principal purpose of sucrose, or sugar, in sugar mixtures for cooked ham is to contribute to the finished product's flavour, since its use as a water activity depressor is limited by its sweetening power. In cooked ham its concentration must not exceed 0.8-0.9 per cent, higher concentrations result in an abnormally sweet taste that cannot be counteracted by the addition of salt. A lesser proportion (about 0.5 per cent) compensates for relatively high salt concentrations, which alone would make the ham too salty, and gives the product a pleasant background flavour.
- **Dextrose:** Because dextrose, or glucose, has much less sweetening capacity than sugar and a greater osmotic pressure in solution, it is commonly used as a water activity de-

pressor in brine. With well-balanced brines, it can reach concentrations of more than three per cent in the finished product without negatively affecting the product's taste. The main disadvantage of using dextrose occurs in countries with a hot climate in which proper refrigeration facilities cannot be guaranteed throughout the duration of product storage.

Dextrose is a monosaccharide, which is digested directly by many microorganisms, including lactobacilli, thereby accelerating their growth rate, especially if refrigeration is inadequate, shortening the product's shelf life and presenting problems of excessive acidity caused by lactic acid.

• **Lactose:** Its use and characteristics are very similar to those of dextrose, although it has a somewhat different taste, which is reminiscent of its original source, milk. One of its forms, a-lactose, is also digested directly by lactobacilli, so that there is also some risk in using lactose in countries with a hot climate.

• **Fructose:** The use of fructose is limited because its sweetening effect is much more powerful than sugar's.

• **Glucose syrups:** Glucose syrups are sugar mixtures obtained by hydrolysis of starches. The principal ingredient in these mixtures is dextrose, in proportions that range from 30 per cent to 60 per cent, and the remainder is composed of monosaccharides and oligosaccharides with varying chain sizes. Their use and characteristics are similar to those of dextrose and glucose, although their use involves less bacteriological risk in countries with insufficient cooling facilities. Another basic advantage of glucose syrups, as compared to dextrose and glucose, is that they are usually significantly more economical.

• **Dextrins:** Dextrins are also produced by starch hydrolysis, usually thermal hydrolysis, and differ from glucose syrups in that they are higher in the content of oligosaccharides with a higher molecular weight. The dextrose content of these products is usually between two per cent and 20 per cent. Their use in manufacturing cooked ham has the disadvantage of sometimes causing colourings with iodine/potassium iodide solution, similar to those of starches, so that their use in non-starch products is limited to such small amounts that they serve little purpose. They are not very useful in starch products either, since they lose their gelling capacity during the hydrolysis process.

Proteins

Proteins and hydrolyzed proteins are used in cooked ham for two main reasons: to increase the finished product's protein content, and for their water holding capacity. Their use can be limited by legislation as well, because of organoleptic reasons—the flavour they confer to the cooked product. As functional proteins, the most commonly used in the manufacture of cooked ham are:

Milk Proteins:

• **Milk wheys:** These correspond to the soluble fraction of milk proteins and present concentrations of 10 per cent to 40 per cent, otherwise made up mainly of lactose. They have the disadvantage of a low protein content and little (compared to other proteins) water holding capacity. They have the advantage of causing little alteration to the finished product's flavour.

• **Lactoalbumins:** These are milk wheys purified by ultra-filtration, in which protein concentrations can reach up to 80 per cent. Also with little effect on the product's flavour, a better water holding capacity is attained with their use than with normal milk wheys. They have the disadvantage of a high capacity for emulsifying air and forming stable foams, and they are expensive.

• **Caseinates:** With a moderate water holding capacity, they contribute well to protein content, because they have protein concentrations of more than 90 per cent. They give a pleasant taste to cooked ham, but have the disadvantage of interfering with solubility of muscular proteins, when used in high concentrations, which can give rise to poor binding. They are also expensive.

Blood proteins:

• **Blood plasma:** Through its coagulative properties, blood plasma has an improved water holding capacity and an acceptable level of protein content (about 70-80 per cent in powdered form). When liquid or frozen blood plasma is used, there are serious microbiological risks that require very careful handling of the product. These risks disappear when sterilised powdered plasma is used, but the desiccation process results in an unpleasant flavour, noticeable in cooked ham with high concentrations of powdered blood plasma.

Collagen protein:

• **Partially hydrolysed collagen:** This is obtained by the partial hydrolysis of collagen. In contrast with natural collagen, these proteins are soluble in water or brine and have a high protein content (84-90 per cent). Their use in cooked meat products is because of their water holding capacity, their gelling properties and their high protein content.

• **Dried skin powder:** Made from dehydrated ground pork skin, it has a good water holding capacity and a high protein content (over 80 per cent) because it is basically collagen that still retains its functional properties. The main disadvantage is that the proteins are basically insoluble and therefore, not easily incorporated into injection brines without obstructing filters and needles of injection equipment.

Egg proteins:

Egg albumins can be used in cooked meat products. They have a good water holding capacity, gelling power and high protein content (over 85 per cent). They also confer good flavour to the finished product, but are expensive.

Vegetable proteins:

The most commonly used vegetable proteins are soy proteins, either as isolates or in concentrates. Isolate proteins offer a number of advantages over concentrates including higher protein content (90 per cent as compared to 60-70 per cent), better solubility (concentrates usually have a significant amount of insoluble substances, which can cause blockage of equipment during the injection process), and better flavour. Soy proteins have an improved water holding capacity and are fairly inexpensive, making them widely used in those products in which their addition is permitted by law.

They have the disadvantage of sometimes giving the ham a disagreeable flavour when used in high concentrations. Due to the controversy that has arisen in regard to Genetically Modified Organisms, the use of soy proteins has been affected, and in some products their use is avoided altogether.

In general, all the above-mentioned proteins have both positive and negative effects, so that they are best used in cooked ham in mixtures that combine the desirable properties in such a way that their negative effects are reduced to a minimum.

Protein hydrolysates:

Because hydrolysed proteins have no water holding capacity, except for their effect as water activity depressors, their function is limited to protein addition and flavouring. The most common-

ly used for their contribution to protein content are hydrolysed collagens and proteins from mechanically-recovered meat. Collagen contributes more than 100 per cent in proteins, since in the analysis of collagen the nitrogen must be multiplied by 5.5 in order to obtain the total protein, while in the meat products the nitrogen content is multiplied by 6.25, and the hydrolysed collagens usually have more than 90 per cent in proteins.

Hydrolysed vegetable proteins are also used in small doses for their contribution to flavour, and so are considered within the group of flavourings.

Starches

In high-yield products, and in countries where their use is permitted by law, starches are used for their water holding capacity. Normally used in cooked ham without chemical modifications, these starch products are polysaccharides that gel when exposed to heat, forming a three-dimensional network that holds great amounts of water.

Most starches gel at temperatures of between 65°C and 75°C, the gelling temperature depending on the size of particles. The most commonly used starches are those derived from wheat, potato, corn and manioc. Wheat starch, with a gelling temperature of 65°C, has the advantages of giving good flavour and providing good product texture. Potato starch, with a gelling point of around 70°C, has a very high water holding capacity, but results in a rather unpleasant product flavour and not very satisfactory texture. Corn starch and starches derived from yucca or manioc, widely used in Latin America, all have properties somewhere in between those of wheat and potato starches.

Fibres

Vegetable fibres are types of polysaccharides, other than starches, that constitute the cellular walls of cereals and vegetables, and which cannot be assimilated by the human digestive system. Depending on the raw material and on the extraction process, they include cellulose, hemicellulose, pectins, lignin, etc., in quantities that can range from 55 to 85 per cent. Thanks to their chemical structure, vegetable fibres provide a number of advantages from a technological point of view, such as a good water holding capacity and improved product texture.

They are currently in use in meat products as a substitute for fatty material, to reduce their calorific value.

Flavourings

The last ingredient used in manufacturing cooked ham are flavourings. The types of flavouring used vary widely and include liqueurs and wines, fruit juices, hydrolysed vegetable proteins, Mallard reaction products, oleoresins derived from

natural spices, fruits, vegetable and spice infusions, smoke extracts, etc.

ADDITIVES

Colourings

Cochineal Carmine is universally the colouring most commonly used in the manufacture of cooked ham, since it gives the ham a natural-looking pink tone. It is a natural red colouring extracted from the desiccated bodies of female insects of the *Coccus Cacti* Species, grown on the cactus, *Nopalea coccinellifera*, which is found in Peru, Guatemala, Mexico and the Canary Islands. It takes 140,000 insects to obtain 200 g of Cochineal carmine with a 50 per cent concentration.

The main colouring agent present in carmine is carminic acid ($C_{22}H_{20}O_{13}$).

Its most advantageous characteristic is its capacity to remain stable when exposed to light, pH variations, and thermal processes. It is usually extracted from carminic acid in the form of aluminum-calcium lake, with a minimum carminic acid content of 50 per cent. Since this form is not water-soluble,

in order to be used in brines it must first undergo dissolution in diluted alkalis, such as ammonia or carbonate.

The main colouring agent in the water-soluble extract from bixa, or annatto, is norbixin sodium salt, a colouring that belongs to the carotenoid group. In spite of its orange colour, it is redder than most other carotenes, and for this reason is sometimes used in meat products. One disadvantage, when used in cooked ham, is that at the pH usually present in this product it become yellowish and unstable when exposed to light. It also has the problem of causing coloration of the fatty tissues.

Beet Red, made up principally of Betanin, has the disadvantage of poor stability when exposed to light and heat.

Stabilized hemoglobin, sterilised and dehydrated, is also sometimes used in cooked ham. Its main disadvantage is that when used in sufficient amounts to have a visible effect on the finished product's colour, it has poor stability when exposed to light and oxygen, causing the slice to become brownish within minutes.

Caramel is used in cooked ham as a colouring only in the product's outer gelatin covering or as a simulated smoke substitute.

Like the rest of artificial colouring agents (Red 2G, Red 40, Ponceau 4R, etc.), its use is becoming more restricted all the time, given the worldwide tendency to prohibit the use of artificial colourings in cooked ham.

Nitrites

Although its action is basically as a preservative, nitrite has a variety of effects on cooked ham. Nitrite as such does not act on the meat. It is the nitrous oxide molecule that is the principal agent responsible for the effects produced. This molecule is formed from nitrite reactions.

Free nitrous oxide formed in this way is highly reactive and

partially reacts with myoglobin to form nitrosomyoglobin, the pigment responsible for cooked ham's characteristic pinkish colour. The rest of the nitrous oxide, not fixed by the myoglobin, undergoes a number of different processes. A part is lost through direct evaporation, while another part continues the reduction process until nitrogen is formed which also evaporates. Another part reacts with the muscular proteins and fats. The remainder reacts with the antioxidising additives, especially with ascorbate and erythorbate.

Colour formation begins when nitrous oxide reacts with the myoglobin to form nitrosomyoglobin, which subsequently decomposes into globin and nitrosomyochromogen, the real colouring agent responsible for the pinkish colour typical of these products.

Although the chemical process involved in making nitrite an effective preservative is not fully understood, nitrite has a proven bacteriostatic effect on Enterobacteria, *Clostridium Perfringens* and *Staphylococcus Aureus*, and is particularly lethal for *Clostridium Botulinum*. Since the latter microorganism is very resistant to thermal processing, the addition of nitrite is practically the only way to prevent transmission of botulism through meat products.

Nitrates

Potassium nitrate was the first nitrifying agent to be used in manufacturing salted meat products. This substance is found, in small amounts, in rock salts used in ancient times for salting meat.

Nitrate as such does not have a nitrifying action on meat. Its effects are derived from its transformation into nitrite through the action of nitrate-reductases, enzymes produced by lactobacilli, enterobacteria, and other microorganisms.

The use of nitrate in cooked ham has often been questioned since, during the cooking process, the nitrate-reductase-forming bacteria are reduced to a very low level and, at the same time, maturation times prior to cooking tend to be very short, 72 hours at most, so that the conversion of nitrate to nitrite is minimal.

Cooking destroys most, but not all, of the bacterial flora.

Preservatives

The use of preservatives represents one of the earliest preservation methods used, but thanks to advances in thermal processing, refrigeration networks and improved manufacturing conditions, the need for their use has been reduced and most legislation is very restrictive in this respect.

Antioxidants

Of all the antioxidants authorised for use in cooked ham by differing legislation, the most universally used are sodium L-ascorbate and its optical isomer, sodium erythorbate. Of the two, the former is permitted by all existing legislation, while the latter is not allowed in some countries. The reason for the ban is that is that sodium L-

ascorbate is a product consumed in a normal diet as vitamin C or ascorbic acid, whereas sodium erythorbate is not and has only five per cent the vitamin action of ascorbate.

Sodium ascorbate has three basic functions in its application to the manufacture of cooked ham, which are derived from its chemical behaviour as a powerful reducing agent.

The first of these functions is its action as a nitrite reducer.

Ascorbate reduces nitrite to nitrous oxide, facilitating nitrosomyoglobin formation, and thereby accelerating the formation of the pink colour. Without the presence of ascorbate, this reaction would be produced in the same way, by the natural reducing agents existing in the meat, but this would require much longer maturation periods and much greater amounts of nitrite in order to obtain a satisfactory colour.

Ascorbate also contributes to colour stability in the finished meat product.

Finally, ascorbate contributes to preventing the formation of cancer-promoting nitrosamines by blocking the formation of nitrosating agents (N_2O_3) being originated from the nitrous oxide.

In manufacturing cooked ham, the addition of ascorbate should always be done in the form of salt.

Because sodium ascorbate is insoluble in fatty tissues, it has little antioxidising effect on them. In manufacturing cooked ham, the types of antioxidants for fat, such as tocopherols, butylhydroxianisole (BHA), or butyl-hydroxitoluene (BHT), are not usually used.

Of the substances classified as antioxidant reinforcing agents, the only ones used in cooked ham are tri-sodium citrate and sodium lactate. The former is used primarily for its buffering and chelating properties, and the latter for its action as a water activity depressor agent and for its inhibiting effects on bacterial growth, in particular, on lactobacilli.

Phosphates

Phosphates have two basic functions in cooked ham. They produce a spectacular increase in water holding capacity, and they help the process of solubility and extraction of myofibrillar proteins, responsible for intermuscular binding in cooked ham.

The polypeptidic chains of proteins are joined together in their tertiary and quaternary structures by electrostatic bonds, hydrogen bridges, disulfide bridges, and bridges made up of divalent cations, especially calcium and magnesium. The protein's hydrating capacity (and therefore, its water holding capacity during the cooking process) will usually increase proportionally as this tertiary and quaternary structure becomes less compact (in the same way a sponge, with the meat's proteins being like a squeezed sponge, must be allowed to expand in order to be able to retain water). This expansion is obtained by breaking the greatest number possible of these bonds. The reduction of the electrostatic bonds is achieved by increasing the medium's ionic strength, basically through the action of salt. One of the known mechanisms of phosphates is their chelating action on calcium and magnesium, loosening the bonds formed by these metals and allowing protein expansion.

Phosphates also act to influence the pH conditions. Even though in concentrations commonly used, the injected mass's pH increases no more than 0.5 points, phosphates contribute with their buffering effect to homogenising the pH in different muscles, lessening the exudative effects of PSE (Pale, Soft, Exudative) muscles.

It is generally accepted that effective action is produced only in the form of pyrophosphate (diphosphate). Because this product is highly insoluble in water (and more so in the saline conditions of brine), mixtures of tripolyphosphate, pyrophosphate and hexametaphosphate are usually used in cooked ham. Both hydrolys in aqueous mediums, gradually releasing pyrophosphate.

Effectiveness is usually achieved with doses of no more than 5 g/kg phosphate added, although the mixture's proportions must be controlled carefully depending on product objectives.

Stabilisers

Both carrageenans and alginates are algae extracts. Carrageenans (derived from red algae) are polysaccharides formed by linear galactose chains with varying degrees of sulphation that determine different fractions (Kappa, Lambda and Iota carrageenans). They are obtained by boiling the algae in water or alkaline solutions for several hours, followed by drying or alcohol precipitation. Alginates, extracted from brown algae, are polysaccharides formed by linear chains of D- Mannuronic and L-Guluronic acids. To obtain these polysaccharides, the algae are treated in an acid medium in order to eliminate the calcium, which insolubilizes alginates, then dissolved by an alkaline treatment to obtain sodium alginate, which can then be transformed into alginic acid or calcium alginate.

Of these substances, the most commonly used in the manufacture of cooked ham are carrageenans. Commercial mixtures are usually made up of varying proportions of the three fractions, Kappa, Lambda, and Iota, complemented by small amounts of gums and some salt, usually potassium chloride.

The properties of these mixtures and, therefore their applications, vary according to their compositions. Some mixtures have an enhanced viscosity so that they can be used as brine stabilisers.

Carrageenan mixtures are used in injection brines as well as being added during the massaging phase. The main purpose of their use is their stabilising effect. Carrageenans gel, retain a great deal of water in the gels that are formed.

The mixture's composition decisively affects the characteristics of the gel formed, influencing its hardness, flexibility, transparency, colour and syneresis. For example, including potassium chloride in the mixture will significantly increase the gel's hardness.

Carregeenans also have synergic effects with some gums, such as caruba gum, which greatly increases the water holding capacity of carrageenan gels, as well as reducing syneresis. For this function, as water retainers, carrageenans are usually used in concentrations of between 1 and 5 g/kg in the finished cooked meat product.

Gums are commonly used as stabilizers in brine. Chemically, they are also saccharides, but usually have a branched structure, and are derived from various sources. Arabic gum (produced by acacias) and tragacanth gum, both vegetable exudates, are rarely used in manufacturing cooked ham.

Some gums are extracted from grains, such as caruba gum (extracted from carob trees) and guar gum (extracted from guar seeds).

Flavour enhancers

Flavour enhancers are substances that, without altering the product's innate flavour, increase the smell and taste of this flavour. The mechanism that produces this phenomenon is not at all clear. On the one hand, it seems that they act directly on the nerve endings, making them especially sensitive to flavours, but on the other hand, it can be demonstrated that they have no effect whatsoever on the four basic flavours (sweet, salty, acid, and bitter).

The most universally used flavour enhancer is monosodium glutamate, industrially produced by fermentation of molasses.

In cooked ham, doses of between 0.2 and 1 g/kg finished product are used.

MPG