

Paper No. 13 FOOD ADDITIVES

Module No. 12

Emulsifying salts for the dairy and food industry

Introduction

Dairy products like processed cheese and processed cheese spreads and food products like cheese analogues rely on the action of one important food additive – emulsifying salts (ES). Cheese analogues are substitute of natural cheese that are made using processed cheese manufacturing technique, but utilizing raw materials like rennet casein or acid casein or Na-caseinate or vegetable proteins as protein source, and vegetable fat or even milk fat as the fat source, along with other ingredients (viz., cheese flavor, NaCl, acid, color, preservative, etc.). Each food additive has its own contribution in cheese systems. Among various food additives, ES play a major role in the manufacture of processed cheese, processed cheese spread and cheese analogues. Similar to the proprietary blend of stabilizer-emulsifiers for the ice cream industry, several manufacturers are taking advantage of the proprietary blend of emulsifying salts that are claimed to give excellent functionality to the processed cheese makers.

Understanding of the role of emulsifying salts in such products can help the cheese maker to improve the product quality and may enable the food processors to ‘tailor-make’ the cheese as per the whims and wishes of the retailers and consumers.

Emulsifying salts

Emulsifying salts (ES), also referred to as ‘melting salts’ or ‘chelating salts’ are Na, K or Ca-salts of citrate or phosphates (short or long chained), preferentially used as an ingredient in the manufacture of processed and imitation cheeses. Such additive helps in forming the structure of food and exerts positive influence on the melting properties by aiding emulsification of milk/vegetable fat in the protein matrix. They provide uniform structure during the melting of process cheese and also affect the physical, chemical and microbiological quality of resultant product.

Processed cheese and cheese spreads

The ripened cheeses of various ages are mixed in certain proportion and processed in presence of ES to yield ‘processed cheese (PC)/processed cheese spread (PCS)’ having enhanced shelf life. The PCS is formulated to have higher milk fat and moisture content so that it has the property to ‘spread’ during food applications. PC or PCS is manufactured by blending shredded natural cheeses of different types and degrees of maturity with emulsifying salt, adding water, salt, milk fat and heating the blend (80-85°C/4-8 min) with constant agitation, until a homogeneous mass is obtained. The product is subsequently stored at 5-10°C after packaging and cooling. The legal

requirements (Food Safety and Standards Authority of India, FSSAI) for processed cheese and cheese spread in India specifies use of emulsifying salts such as Na, K, Ca-salts of citric acid, orthophosphoric acid, polyphosphoric acids at a level not exceeding 40,000 ppm (i.e. maximum 4.0% by weight).

In processed cheese industry, a term commonly used to describe the emulsification of cheese and water into a continuous system is 'creaming reaction'. The creaming reaction is related to the protein-protein interactions and the properties of the final product can be related to the level of protein dispersion and reassociation during processing.

Cheese analogues

'Cheese analogues' also referred to as 'imitation cheeses' are the products made out of dairy, partial dairy or even non-dairy ingredients, that tend to resemble a particular cheese variety. Examples of analogue cheeses are Mozzarella cheese, cream cheese, process cheese, etc. Cheese analogues are prepared by blending dry ingredients (e.g. rennet/acid casein or caseinates, common salt, starch, cheese flavour) in the aqueous solution of ES, followed by heat processing (~80-82°C/3-5 min) with simultaneous incorporation of vegetable or dairy fat. An appropriate acid (in solution form) is used to adjust the pH of cheese analogue. Further processing is carried out in a manner similar to processed cheese. Imitation cheese products are mainly used in the catering industry and in the processing sector, e.g. in preparation of pizza and prepared dishes.

Need to emulsify fat in cheese systems

All cheese products are essentially 'oil-in-water' emulsions. Natural cheese is a nearly perfect emulsion stabilized by natural surfactants, the cheese proteins. The principal caseins in cheese (α_{S1} -, α_{S2} -, β) have non-polar, lipophilic C-terminal segments, while the N-terminal regions containing calcium phosphate are hydrophilic. This structure allows the casein molecules to function as an emulsifier. However, in absence of ES, heating of natural cheese blend (i.e. of different maturity) above 65°C can result in separation of oil and water phases. To incorporate the fat source (butter/vegetable fat for process cheese and cheese analogue respectively) in the proteinaceous cheese matrix, ES helps in this regard. Emulsification of fat in cheese is affected by factors like amount of calcium in the CaPO_4 end, pH, age of cheese and temperature during cheese processing.

In natural cheese, caseins do not possess their emulsifying properties, because they are bound in three-dimensional calcium bond matrix. Therefore, ES are used during processed cheese production. They are capable of exchanging ions and from insoluble calcium para-caseinate more soluble sodium para-caseinate is created, which possesses emulsifying and stabilization function in processed cheese matrix.

Classification of emulsifying salts

The ES used for processed cheese systems are mainly classified into following two types, viz.,: (i) citrates, and (ii) phosphates.

Citrates: They are salts of citric acid e.g. tri-sodium citrate (TSC) which are preferred in 'block type cheese' and 'sliceable cheeses'. Citrates are highly soluble with fairly good protein dissolving power. They contribute to long, elastic structure to processed cheese; the structure of cheese remains firm and heavy. Few disadvantages of citrates are lack of creaming, lack of bacteriostatic action, and risk of sandiness and mottling in cheese.

Phosphates: They are salts of phosphoric acid. There are two types of phosphates i.e. (i) Mono phosphates (orthophosphates) e.g. NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4 and (ii) Condensed phosphates e.g. $\text{Na}_6\text{P}_4\text{O}_{13}$; $(\text{NaPO}_3)_n$.

Monophosphate/orthophosphates: These include mono-sodium, di-sodium and tri-sodium orthophosphates (TSP). Mono-phosphates are water-soluble and have excellent buffering properties, but do not exert any creaming effect. Mono-sodium and TSP are most commonly used for pH adjustment.

Condensed phosphates: These are classified into chain forming polyphosphates, ring-forming metaphosphates and cross-linked ultraphosphates. The chain forming polyphosphates are classified as short- and long-chain polyphosphates. Polyphosphates have strong creaming action and exert bacteriostatic property. Their buffering capacity depends on their chain length.

Short chain polyphosphates: These are mainly the diphosphates and tripolyphosphates with pH value of 1.0% solution ranging from 2.7 to 10.2. The commonly used salts are mono-sodium, di-sodium, tri-sodium and tetra-sodium diphosphates.

Long chain polyphosphates: They have an average degree of condensation ranging from 4 to 25. Graham's salt (i.e. Sodium hexa Meta Phosphate – SHMP) with a degree of condensation of 10-25 has outstanding ion-exchange ability. The disadvantage is their proneness to partial hydrolysis during processing.

Role of ES in cheese system

In order to modify the cheese proteins in natural cheese so that they can emulsify the fat during processing and to develop certain characteristics in processed cheeses like uniform body, melting of cheese during its application, ES are made use of.

The mechanism of action of emulsifying salts in any cheese system involves the following:

- Removal of calcium from the protein system

- Peptizing, solubilizing and dispersing the proteins
- Hydrating and swelling of the proteins
- Emulsifying the fat and stabilizing the emulsion
- Controlling pH
- Forming an appropriate structure of the product during or after cooling

The monovalent Na and bivalent Ca ions are antagonistic with regard to their action on proteins. The calcium bound to casein fragments depresses their water solubility. ES removes calcium by exchanging it for sodium or by binding to it. The functional behavior of cheese products are strongly influenced by the type of ES and its physico-chemical properties, including its ability to bind calcium, casein dispersion during cooking, and creation of cross-links with casein during cooling.

Type of emulsifying salts

The most commonly used ES for process cheese manufacture are TSC and disodium phosphate (DSP). TSC is the preferred ES for 'Slice-on-slice' process cheese varieties, whereas DSP (or appropriate combinations of di- and trisodium phosphates) is used in 'Loaf-type process cheese' and 'Process cheese spreads'. Sometimes, low levels of SHMP are also used along with these ES.

The quality of ES added to processed cheese blend depends not only on the type and age of cheese used in the blend (proportion of water and calcium), but is also determined by the final product group (i.e. block, spread, slices, etc.). The ES that help in structure building (not creaming) include high molecular polyphosphate like C, SE, S7, PZ (ES of Joha company) and citrate, which leads to firm, slicing processed cheese. ES that lead to creaming, e.g., lower and medium molecular polyphosphate, S9, S9 special, S10, S90 (ES of Joha company) are suitable for spreadable processed cheese.

The ability to exchange ions and form three-dimensional structure during cooling is different for individual ES and decreases in the order: polyphosphates > triphosphates > diphosphates > monophosphates \approx citrates. Citrates have higher ability to exchange ions than monophosphates. Longer phosphates lead to a higher dispersion of casein due to more intensive ability of ion exchange.

A combination of Joha S9S + Joha NO (1:1) ES @ 3.0% w/w was found suitable to produce desired PCS containing whey protein concentrate (WPC).

Rate of addition of an emulsifying salt

The amount of ES that can be added to the cheese base are regulated by many countries and usually do not exceed 3.0 or 4.0%. Increased levels of polyphosphate in ES mixtures (with

pyrophosphate or orthophosphate) resulted in a firm PCS based on Ras cheese, whereas increased levels of pyrophosphate produced softer cheeses; buffering capacity increased with increasing levels of orthophosphate and pyrophosphate. The degree of casein dissociation, pH and hardness of PC increased as the concentration of ES was raised. The PC prepared with TSC was whiter than those prepared with other emulsifying salts.

The hardness of non-fat Pasta filata cheese decreased, while the meltability increased with increasing concentrations of TSC (1.0 to 5.0%). The effect was attributed to a decrease in the number of colloidal calcium phosphate cross-links and an increase in electrostatic repulsion in the cheese system. Addition of 1.0% TSC increased the stretchability of cheese, by partially loosening the protein matrix.

The concentration of the ES affected the sensory properties of the cheese product. The meltability of processed cheese increased with an increase in the ES content. The hardness of processed cheese decreased as the ES content was raised.

Combining emulsifying salts

A single ES is not capable of providing all of the desirable characteristics to process cheese or cheese analogues. The right proportion of individual ES should be arrived at and adopted. TSC and DSP when added in 1:2 ratio yielded an excellent quality processed cheese with desired firmness, sliceability and smoothness. Such combination helped to strike a balance between the water absorption properties of diphosphate, and the protein solubilizing property of citrates.

Processed cheese produced using mixtures of sodium diphosphate, sodium polyphosphate and sodium tripolyphosphate (STPP) (30:40:30) yielded better quality product than that made using Joha salts SE and PZO.

The proprietary blends of emulsifying salts available in the market include JOHA HBS, JOHA S 9, JOHA® – SOLVA®, SELF 690, SELF® SR, CREMOSAL, CHEESEFOS and so on.

Impact of emulsifying salts on properties of cheese

Inclusion of an ES has influence on milk proteins and hence its interaction with milk fat in cheese system; variation in the type and/or amount of ES is bound to affect the cheese properties. The influence of ES on some important properties of cheese system is dealt hereunder.

Appearance: Increasing the concentration of ES tended to improve the whiteness of processed cheese spreads based on Ras and Quark cheeses.

pH and pH stability: Applying an appropriate mixture of ES causes an increase of the cheese blend pH from 5.0–5.5 up to 5.6–5.9 and, furthermore, contributes to pH stabilization due to its buffering capacity. Due to this particular pH increase, the calcium-masking ability of the ES is

increased by the negative charges on the para-caseinate, thus promoting a concomitant increase in hydration and solubility of para-casein and the formation of a stable product.

Textural properties: The influence of phosphate type emulsifying salts on cheese firmness increased in the order: orthophosphate, polyphosphate, diphosphate and triphosphate. TSC and DSP exhibited similar behaviour and produced the softest, most adhesive, least elastic and most liquid-like final processed cheese products that showed reduced apparent viscosity during processing. TSPP gave harder, less adhesive, more elastic and more solid-like samples compared to use of penta-Na-tripolyphosphate.

Melt, flow properties and sliceability: The variation in the TSC concentration (2.0-3.0%) influenced only the melt and flow characteristics, but did not affect the unmelted textural properties of processed cheese. TSC contributed to greater '*meltability*' and '*sliceability*' to process cheeses compared to several other emulsifying salts; the process cheese had a firm, gel-like structure. TSC in combination with DSP @ 3.0% level produced significantly softer cheeses and melted more easily than those prepared with condensed phosphate Joha salts. Meltability of cheese was in decreasing order for ES: trisodium pyrophosphate > DSP > TSC.

TSP and DSP were reported to produce the most pronounced melting effects. Sodium citrate induced significant melting only at the highest tested concentration (3.0%).

Bacteriostatic action of emulsifying salts

ES such as orthophosphate and polyphosphate may inhibit growth and toxin production by *Clostridium botulinum* by sequestering Fe, Mg or Ca ions. Polyphosphates may also interact physically with bacterial cells by forming channels, increasing their permeability to inhibitory compounds, and promote leakage and cell lysis. Growth and gas formation by *Cl. tyrobutyricum* were prevented by addition of 0.5 - 1.0% polyphosphate to process cheese. Use of 0.5% long chain polyphosphate formulation (JOHA HBS-1, HBS-9) maybe sufficient to control *Cl. tyrobutyricum* growth under normal conditions, where initial spore counts are low and storage temperature is 20°C.

Reduced sodium processed cheese

The average sodium content was reported to be 402 mg, 335 mg and 382 mg per 28 g each of processed cheeses, cheese food, and cheese spread respectively. The proposed sodium labeling for foods combined with a recommended dietary goal of substantially reducing sodium intake in several countries has focused attention on technological means to reduce sodium in processed foods. ES such as potassium citrate, potassium acetate, and mixtures of these at ratios (i.e. 1:1, 2:1 and 1:2), @ 3.0% by weight have been used in order to reduce the sodium content of cheese.

Defects related to emulsifying salts

If the ES is not utilized judiciously in cheese formulation, it may lead to some defects.

Fish-eye defect: 'Fish-eyes' (hard, glassy lumps of protein) may be formed in processed cheese due to poor hydration of the protein.

Bitterness in cheese: An overdose of specific emulsifying agents (i.e. high in phosphorus content) can lead to bitterness in processed cheese slices. Such bitter slices showed very weak α s1- and β -caseins region, had only γ -casein and low-molecular weight peptides, and showed high concentrations of hydrophilic and hydrophobic peptides.

Crystals: Crystals of ES (i.e. calcium phosphate/diphosphate, calcium lactate/citrate) may be observed in processed cheese as a result of: (i) excess use of emulsifying salt, (ii) an unsuitable mixture of emulsifying salts, or (iii) insufficient dissolution of the latter in the mixture during processing.

Emulsifying salts for cheese analogues

When using rennet casein or caseinates, they must first be solubilized by the addition of emulsifying salts, in the manufacture of cheese analogues.

The hot solution of calcium chelating salts (i.e. ES) are used to facilitate hydration of the protein which subsequently acts as an emulsifier for the oil phase dispersed in the protein/aqueous phase of the cheese analogue. The rheological properties of the rennet casein during hydration are dependent on the concentration of ES in the hydrating solution. In the manufacture of rennet casein based cheese analogues, ES are used to disrupt the calcium mediated protein-protein cross-bridges, thereby allowing the protein to hydrate. Such improved hydration enhances the emulsifying ability of rennet casein in cheese analogues. In the formulation of cheese analogue, the type of ES used is dictated by the protein source used (i.e. rennet casein/acid casein/caseinates); the level of incorporation of ES decides the functionality and sensory properties of resultant cheese analogues.

Sodium aluminum phosphate is commonly used in rennet casein/Na-caseinate based mozzarella type imitation process cheese since it provides desirable functional properties for pizza applications. TSP and DSP were found to exert most pronounced melting effects in such systems.

Orthophosphates, such as DSP and TSP, and polyphosphates, such as tetra sodium pyro and SHMP, are approved for cheese use. For standardized cheese products, 3.0% phosphate is allowed, though usually 1.8 to 2.5% phosphate is sufficient. Beyond this level, phosphate can cause crystals to appear in the cheese. If crystals are a problem, sodium aluminum phosphate can be used to avoid them.

Other applications of emulsifying salts

Cheese powder: Cheese powders are used in the food industry as natural functional and flavour ingredients in applications such as biscuits, savoury snacks, bakery products, sauces, dressings, ready meals and processed cheese, typically added at levels of 2-12%. In cheese powder production, cheese is comminuted and melted with addition of water and ES. This cheese slurry, cheese feed, is then heat-treated and finally most of the water is removed by spray drying. ES, primarily sodium phosphate, are added to create an emulsion that remains stable until spray drying and also to ensure a final powder with good keeping quality.

The raw material for cheese powder manufacture is usually a carefully selected blend of cheeses, of different ages. The cheese is comminuted and mixed with water to produce slurry containing 35-45% solids. Stabilizing salts (phosphates, citrates) are added in small amounts (i.e. 2%), to modify the physical characteristics of milk protein so that the fat is effectively emulsified and the slurry melts evenly on heating to give a smooth body. The slurry is pasteurized and homogenized (2000 + 500 psi) before spray drying to produce a powder containing < 3% moisture.

Other applications in dairy industry

Emulsifying salts are used as agents for preventing undesirable changes of ultra high temperature (UHT)-treated milk, UHT-treated cream, coffee cream, concentrated milk, etc. DSP can be used to reduce UHT milk protein coagulation. Long chain SHMP inhibits UHT milk age gelation. UHT milk, cream and coffee creamers gain stability and shelf life by treatment with JOHA[®] specialties. Such ES contribute to consistency and texture while reducing heat-induced protein coagulation. In non-dairy coffee whiteners, a phosphate buffering system contributes to stability and prevents '*feathering*' and '*fat separation*', when the coffee whitener is added to the hot acidic coffee medium.

DSP is added to fluid milk prior to pasteurization or spray drying to inhibit protein denaturation during heat treatment and to allow efficient protein dispersion upon rehydration. The purple discolouration of strawberry flavoured milk may be inhibited by addition of sodium tripolyphosphate (STPP) to bind the iron. Chocolate milk may benefit from the presence of trisodium polyphosphate (TSPP), which keeps the cocoa in suspension.

In dairy preparations using alginate as a texturizer, phosphates are ideal for controlling calcium release and consequently, gel setting.

DSP, TSPP or SHMP may be added to ice cream to prevent churning of the milk fat.

Sodium citrate is also an important stabilizer in whipping cream and vegetable based dairy substitutes. Non-dairy creamers frequently use dipotassium phosphate (DKP) to inhibit feathering, when the whitener is added to the warm, acidic coffee.

Applications other than in dairy industry

Sodium and/or potassium salts of phosphates and/or polyphosphates are regularly used in the food industry, namely meat and bakery industries.

Meat, poultry and sea foods: Phosphates play an important role in pH adjustment in meat, poultry and sea foods. Alkaline phosphates increase meat pH approximately 0.1-0.6 units, depending upon the particular phosphate used. Processors add phosphates to meat, poultry and fish to achieve moisture retention, along with higher yield and flavor protection, especially in processed meats. Phosphates can reduce oxidation, help retain marinade and cook juices, chelate metals, preserve colour and lend freeze-thaw stability. Adding phosphates enhances stability in finely chopped meat systems, such as bologna or hot dogs, by influencing the pH, ionic strength, protein extraction, divalent cation binding and viscosity. Phosphates help extract proteins from meat, whether chopped or whole muscle. Phosphate type and pH are critical for optimal performance in meats. Pyro is the most effective phosphate for meats; pH choice varies by application. TSPP extracts muscle proteins to a greater degree than other phosphate salts.

Baked goods: In the bakery industry, baking powder is an appropriate example to demonstrate the versatile use of phosphates in this area. Baked goods are leavened with phosphates that contribute to texture, colour, rise and desirable crumb characteristics. Bakery leavening systems commonly use anhydrous monocalcium phosphate (MCP), dicalcium phosphate dehydrate, sodium aluminium phosphate and sodium acid pyrophosphates. MCP can also act as a dough conditioner. Phosphate based acid reacts with an alkali (sodium bicarbonate), to produce carbon dioxide gas in batters and doughs of baked products. The resulting gas causes the matrix to form an open, honey-comb like structure that greatly influences texture.

Soft drinks: The soft-drink manufacturers add phosphate to cola drinks to enhance flavor.

Antibacterial effect: Antibacterial effects of polyphosphates have been observed. This especially applies to the effects on selected Gram-positive microorganisms (some strains of genera Staphylococcus, Bacillus and/or Clostridium), evaluated as contaminants in several foodstuffs.