

General Properties of the Alkaline Phosphates: Major Food and Technical Applications

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INTRODUCTION

The alkaline phosphates are used for many food and technical applications. Phosphates have two characteristics that explain their four main properties: buffer agent, sequestering power, dispersing power and water holding capability. Those properties allow phosphates to be used in many food and technical applications.

The main food applications are meat and seafood processing, baking and processed cheese, but others such as cereals, French fries, fruits and vegetables, beverages, noodles and so on also may need the use of phosphates. On the technical side, the main applications are the detergent products, the water treatment and the metal treatment. As for the food, many other applications require phosphates such as ceramics, bone china, paper and paints, ...

In meat products, phosphates salts interact in a unique way to bind water with proteins and improve the tenderness in meats. Treated products will maintain their juicy appearance as well as their natural nutritional properties texture and colour. In fish and seafood products, phosphates salts allow the retention of the natural juices of frozen fish fillets, prawns, shrimps, scallops and other seafood. Phosphates also help prevent the build-up of struvite crystals in tinned tuna and crabmeat.

In processed cheese, phosphates are crucially important in the production of processed cheese. These products ensure a homogeneous and uniform melt of raw cheese and product stability.

For bakery products, acid phosphates are well known leavening agents. Their reaction with sodium bicarbonate generates a controlled gas release that contributes to the volume, appearance and taste of types of cakes and pastry.

In detergent products, phosphates are essential components of I&I and household detergent. The formulations using phosphates have clear advantages compared to alternative formulations. The main properties of this "builder" are: the sequestering power (softener), the dispersing power, emulsifier and buffer agent, the synergy with tensio-actives and the alkaline content. The sodium tripolyphosphate is proved to be the most efficient builder.

Phosphates are used for the metal surface phosphatizing. This reduces the metal corrosion risks, to electrically isolate them and to improve the painting of the metals. On the other hand, phosphates are also used for the metal cleaning and the manufacturing of magnetic metal sheets.

Water treatment is the last major application. The use of phosphates also prevents scale formation, controls the black and red water phenomenon and reduces pipe corrosion risks. Moreover, some phosphates are used in the biological purification of industrial and used water.

GENERAL PROPERTIES OF THE ALKALINE PHOSPHATES

The alkaline phosphates are salts of the purified phosphoric acid; they are more or less polymerised and are acidic, neutral or basic.

Depending on the number of P atoms, the usual name will change as follow:

- 1 P atom: orthophosphates
- 2 P atoms: pyrophosphates or diphosphates
- 3 P atoms: tripolyphosphates
- >3 P atoms: polyphosphates

The tow main characteristics of the phosphates are their chain length and their pH. These characteristics define their four properties: buffer agent, sequestering power, dispersing power and water holding capability. These four properties will explain all uses of phosphates in food and technical applications.

Buffer agent: phosphates are able to buffer a solution, which is to impose their pH to the solution. Short chain phosphates such as orthophosphates and pyrophosphates are the most efficient.

Sequestering power: phosphates are able to sequestrate polyvalent cations, this will isolate them from the matrix. In general, the bigger the cations, the longer the phosphate chain is. For example: Fe^{2+} and Cu^{2+} are complex by pyrophosphates / Ca^{2+} and Mg^{2+} are complex by tripolyphosphates or polyphosphates.

Dispersing power: phosphates as polyelectrolytes are able to change the ionic charges distributions. This effect increases with the phosphates chain length. Polyphosphates are thus the most efficient.

“Water holding” capability: phosphates are able to increase the water holding capability of proteins and find its application mainly in food such as meat processing and processed cheese. This property results from the 3 previous ones. A maximum efficiency is obtained with intermediate chain length phosphates.

MAJOR FOOD APPLICATIONS

Phosphates for meat and pet food processing

The main components of meat are: proteins, water, lipids, minerals and sugar. In living muscles or directly after slaughtering, proteins fix constitution water and meat is firm and juicy. The ATP (adenosine triphosphate, or: "natural phosphate" of meat) allows proteins to keep opened. A few days after slaughtering, muscles get contracted and meat gets to be exsudative; after cooking: meat has a stringy and dry texture. At rigor mortis stage, ATP is used in biochemical reactions, local pH decreases, calcium bonds are formed, muscle proteins close and cling to each other. Water retention capability and organoleptic properties are altered. The action of the phosphates on meat proteins is as follows:

Before treatment: Environment pH = 5.5 - 6.0 Proteins structure is closed Water is not bound to proteins	After treatment: Environment pH increase Proteins structure is open Water is bound to proteins
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The use of phosphates allow to restore these properties: it improves water retention of proteins (restore juiciness and tenderness of cooked meats), but also improves texture, cohesion, homogeneity of brine meat pieces and of comminuted meat products, reduces oxidative rancidity, stabilises cured colour, makes the process easier and finally improves microbiological quality (however phosphates cannot be consider as preservatives). Pyrophosphates and tripolyphosphates are the most efficient. Longer chained phosphates are also efficient as they are quickly hydrolysed into pyrophosphates or tripolyphosphates under the action of enzymes.

Phosphates for Processed Cheese

The melting process is influenced by many parameters: chemical (as raw materials), physical (as cheese structure) and thermal (as the process itself) parameters. The emulsifying salt has then a major impact on the structure and consistency of process cheese. It is therefore very important to choose the right phosphate.

The emulsifying salt can bring three properties:

- The buffering capability (pH control) is important for consistency and taste.
- The ion exchange capability, to make the cheese melt (calcium caseinate is insoluble / sodium caseinate is soluble). Thus, only the sodium phosphates can be used for cheese processing, not the potassium phosphates.
- The creaming reaction (or casein peptization) to swell casein, which is playing the role of emulsifier.

The longer the chain is, the lower the buffering capability and the higher the ion exchange capability. Pyrophosphates have the highest creaming reaction. This property decreases with the chain length and is close to zero for orthophosphates. Citrates are very close to orthophosphates but they have a negative impact on colour (calcium citrates crystal). They are however used for their taste. Polyphosphates have an effect on process cheese stability as they have a bacteriological action (which increases with the chain length).

The phosphate to be selected depends on the type of final product: block, slices or spreadable cheese. The blends range available on the market is very large. Each product has been developed for one special application. Prayon's blends range is called KASOMEL[®].

Leavening Phosphates for the baking industry

In baking, the aim is to cause a gas release in the dough in order to make dough leaven (rise) and to obtain the wanted cake volume. In this application, phosphates are used as leavening agents; they are part of the gas releasing system. Three potential sources of CO₂ does exist:

- Fermentation: $C_6H_{12}O_6$ (sugar) + Yeast \rightarrow 2 C_2H_5OH (alcohol) + 2 $CO_2 \uparrow$
- Decomposition: NH_4HCO_3 (ammonium bicarbonate) + Heat \rightarrow NH_3 (ammoniac) + H_2O + $CO_2 \uparrow$
- Acid-base reaction: $NaHCO_3$ (sodium bicarbonate) + HX (acid) \rightarrow NaX (acid salt) + H_2O + $CO_2 \uparrow$

Using the acid-base reaction, the Carbon dioxide release (CO₂) takes place during mixing and/or cooking of the dough. The importance is to choose the right acid to control the rate of CO₂ released in order to obtain the good final result (volume, porosity,...of the cake). Different phosphates can be used such as SAPP (sodium acid pyrophosphate), SALP (sodium aluminium phosphate), MCP (monocalcium phosphate) anhydrous or monohydrate, or any combination of these.

Phosphates allow a high flexibility in the process: they give the possibility to proportion and to program the CO₂ releasing in the course of time. There are two very important parameters to

consider: the neutralisation value (NV) which is the amount (kg) of sodium bicarbonate that can be neutralised by 100 kg of phosphates and the dough rate reaction (DRR) which is the speed reaction in the dough. Phosphates react gradually because of their weak solubility. The speed of reaction is linked in with temperature.

	NV	DRR (2 minutes)
SAPP 40	72	38
SAPP 28	72	28
SAPP 22	72	22
SALP	100	22
MCP anhydrous	83	24
MCP monohydrate	80	60

Other Food Applications

◆ *French Fries*

After peeling and during the drying step, iron ions form a complex with phenolic compounds. Due to this phenomenon, potatoes turn to black. Sodium acid pyrophosphate is used to avoid the complex formation, and therefore the discoloration.

◆ *Vegetables*

Canned beans, peas and lentils skin is easily softened when using phosphates; cooking time is then reduced. This treatment helps also avoiding colour changes (see French Fries). Sodium hexametaphosphate is also used to improve and control the viscosity of tomato sauces/purées and to increase the yields of juice obtained from tomato pulp.

◆ *Beverages*

Polyphosphates are used for vitamin C stabilisation in citrus juices. Sodium hexametaphosphate is used to stabilise some "fruity drinks". Calcium and potassium phosphates are used as Ca, K, and phosphorous source in mineral supplementation (sports drinks). Phosphoric acid is also added to Cola soft drinks as acidulent.

◆ *Cereal products*

Phosphates applications in cereal products include pH adjustment, buffering, dough conditioning. Phosphates are also used as a mineral enrichment. Indeed, phosphorous cannot be synthesised by the body, thus it must be provided at adequate levels in the daily diet.

◆ *Egg Products*

Phosphates are use to improve the processing and functional properties of eggs. Their functions include complexing undesirable metal ions, buffering to optimum pH values, improving foam volume and stability, and inhibiting enzyme activity, microbiological organisms and fat oxidation.

◆ *Fats and oils*

Various phosphates are useful in the processing and the applications of fats and oils in foods. Phosphates aid their extraction in their refining, in stabilisation of fat against flavour deterioration, and in obtaining stable fat and oil emulsions. Phosphoric acid is also used for food grade vegetable oils refining.

◆ *Noodles*

Phosphates make the instant noodles more elastic and tasty. Indeed, without phosphates addition the consistency of instant noodles would be rubbery. Thus, our blends are used to accelerate gluten bonding, to improve noodles elasticity and flexibility, to improve texture and chewy properties, but also to reduce water cloudiness when cooking.

◆ *Toothpaste*

Calcium phosphates (such as Dicalcium phosphates or Calcium pyrophosphates) are used as polishing agent. They are also a source of Ca, main component of teeth. Moreover, sodium pyrophosphates are used to prevent tartar deposits and sodium tripolyphosphate as bleaching / whitening agent.

◆ *Miscellaneous*

Phosphates and/or Phosphoric acid are used in other various applications such as starch modification, aromas, gelatines, drinking water, blood treatment, yeast manufacturing, sugar processing, powder foodstuffs ...

MAJOR TECHNICAL APPLICATIONS

Phosphates in Detergent

There are two main types of detergent: household and industrial. Purified phosphoric acid is used primarily in industrial detergents, still referred to as I&I (Industrial & Institutional). Some phosphates are also used for this application. Purified phosphoric acid is used in manufacturing detergents with a pH of less than 7 (they are most effective on scale, soot, glue and dairy products). An acidic pH also effectively disinfects surfaces that have been cleaned in this way. Phosphates themselves are used mainly in alkaline formulations with a pH higher than 7 (they are most effective on fats and oil). Clearly, given the wide range of applications and contaminants encountered, very specific formulations are required according to the application (all-purpose detergents, detergents for dairies, breweries and bottling factories, bathrooms, metals, disinfectants and so on).

In terms of household cleaning, phosphate based formulations offer several advantages over 'alternative formulas'. In fact the latter generally tend to not clean effectively or require larger amounts of other ingredients, in particular surfactants. On the other hand, we should not forget that phosphates are the only recyclable component of the laundry products, they have significant environmental advantage and a guarantee of sustainable development.

Different types of phosphates are used in detergents, the main one being sodium tripolyphosphate (STPP). The various properties of the phosphates as a raw material mean they can only be replaced by complex formulations that invariably present certain drawbacks. Here are some of those properties:

• *Softening and complexing agent:*

The water used for washing contains a variable quantity of calcium and magnesium soluble salts. These salts cause deposits to build up on the object being washed, causing fabric fibres to stiffen, leaving marks on glassware and creating scale in appliances. Together with these salts, phosphates form 'complex' soluble products. The Ca and the Mg are effectively

'neutralised' in these compounds and can therefore leave no deposits on the surface being cleaned or in the appliance.

- *Synergy with surfactants*

A synergic effect results in the presence of phosphates that make surfactants more effective. This in turn makes the detergent more effective.

- *Emulsifying agent*

Phosphates are excellent emulsifiers of oil and fat, turning them into minute droplets dispersed in the detergent. They supplement the emulsifying effect of surfactants and/or sodium disilicate.

- *Dispersing agent*

Phosphates prevent mineral impurities from being re-deposited. STPP is one of the best-known dispersing agents.

- *Buffer capacity*

To make a detergent as effective as possible, it is essential that the pH of the bath remains as stable as possible throughout the washing process. However, some impurities and their degradation products are acidic. The pH of the bath can fall slightly, especially in I&I where the baths are kept for several days or even weeks. Due to their buffer (pH-controlling) capacity, phosphates neutralise this variation and maintain an optimum pH in the washing bath.

- *Alkalizing capacity*

Solutions of tripolyphosphates are slightly alkaline with a pH of approximately 10. Alkalinity helps the chemicals attack impurities by strengthening the action of other constituent ingredients of the detergent (e.g. sodium disilicate and sodium carbonate).

Metal Treatment

The use of phosphorous compounds in metal treatment dates back to the early 20th century. Cars, refrigerators, washing machines and a lot of other painted or enamelled items all have a phosphate coating between the metallic surface and the paint. This treatment is most commonly known as 'phosphatation'. When a 'reactive' metal is plunged into a phosphating solution (purified phosphoric acid and/or phosphates in solution), certain ions - such as iron - are dissolved and remain at the metal-solution interface. The acidity level at the interface is reduced and the metal phosphate salts produced, in addition to the cations (Ni^{2+} , Zn^{2+} , Mn^{2+}) already present in the solution, precipitate on the surface of the treated metals. When the process is carried out correctly, the metal surface, which naturally conducts electricity, is converted into a non-conductive surface that is more highly resistant to corrosion when exposed to electricity. A further advantage of phosphatation is an improvement in the adhesion of paint to the treated surface.

In addition, sodium and potassium orthophosphates solutions are frequently used for alkaline phosphatation thanks to their buffering capacity. Moreover, phosphatation process, the surfaces must be perfectly clean. Cleaning agents containing purified phosphoric acid and/or phosphates are used to ensure that the surface is free from grease, oil, rust, scale, glue and so on. The selection of products depends on the type of stain to be removed. For example, acidic

or neutral formulations are more effective in removing scale, while alkaline cleaning agents perform better on fatty and oily residues.

The phosphates on offer on the market have to have a very high degree of chemical purity. Indeed it is vital that there are no imperfections in the film covering the metallic surface, as any such defect would make it susceptible to local corrosion.

The magnetic metal sheet industry also uses a particular grade of phosphate, the MALP (monoaluminium phosphate). This phosphate is used in the manufacture of grain-oriented magnetic metal sheets, which themselves are used in the production of high quality transformers with a low energy loss.

Water Treatment

Hard water causes the formation of scale deposits, which result in operational costs. It can cause a lower flow rate through pipes, which in turn means increased pumping and cleaning costs. Polyphosphates can sequester the calcium and magnesium ions in soluble compounds and thereby prevent any deposits from being laid down. Depending on the water pH preference will be given to either SHMP or STPP.

While pyrophosphates and tripolyphosphates are excellent sequestering agents for ions such as Ca, Mg, etc, that make water hard, sodium polymetaphosphates (such as SHMP) can also interfere with nucleation at very low concentrations (triggering a threshold effect). This can prevent the precipitation of iron compounds (red water) and of manganese compounds (black water) when the water is exposed to oxidation in the air or in chlorine.

Phosphates are also used to reduce corrosion of water mains. With the orthophosphates, certain ions present in the water (calcium, lead, etc.) form precipitates that are sparingly soluble. These precipitates form a deposit on the pipes in the form of a protective film. This is known as anodic inhibition of corrosion. In addition to this, the oxygen present in the water oxidises the metal on the inner wall releasing metallic cations. The polyphosphates form positively charged bonds, which result in a protective film being deposited on the inner surface. This is known as cathodic inhibition of corrosion.

Older buildings are still sometimes fitted out with lead pipes. However, high concentrations of lead can pose a health risk. In order to avoid dangerously high lead content in water from the system, a small amount of orthophosphate solution or purified phosphoric acid can be added to encourage a "coating" to form on the inner surface of the lead pipes thereby preventing the lead from being released into the water.

Another vital parameter in water treatment is controlling the water pH of the water. Due to their buffering capacity, orthophosphates can actively regulate the pH.

Finally, it is worth noting that the petrochemicals and food sectors, as well as other industries that discharge water with a high BOD (Biological Oxygen Demand), purify the water biologically to reduce the 'oxygen demand'. To remain effective and to develop, the bacteria used in these processes require the nutrient P, but they also need optimum pH conditions. If the element P is missing, then the following products will be used either alone or in combination: purified phosphoric acid, monammonium phosphate (MAP), diammonium phosphate (DAP) and monopotassium phosphate (MKP).

Other Technical Applications

◆ *Ceramics, enamels and refractories*

Phosphates are used as dispersing agents and deflocculants for ceramics and enamels. The main phosphates used are disodium phosphate (DSP), tetrasodium pyrophosphate, (TSPP), sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP) and monoammonium phosphate (MAP). Purified phosphoric acid is also used in the manufacture of refractories. Ammonium phosphates and STPPs are used in the manufacture of enamels.

◆ *Porcelain*

Calcium phosphates such as DCP or TCP are used in the manufacture of high-quality porcelain. They increase the translucent effect of porcelain (Bone China).

◆ *Flame retardants*

Ammonium phosphates - MAP (monoammonium phosphate) and DAP (diammonium phosphate) - are often used as flame retardant to fireproof a variety of materials (particle board, matches, textiles, etc.) and in the manufacture of fire extinguisher powder. DAP and ammonium polyphosphates are found in products used to fight forest fires.

◆ *Paints*

Polyphosphates and in particular sodium hexametaphosphate (SHMP), are dispersing agents and can change the distribution of the ionic charges in soluble and insoluble compounds. This stabilises the emulsion, which is characterised by a reduction in viscosity. This property is particularly useful in the paint industry. Due to their chelating properties, phosphates are used in corrosion inhibition through chelation of Fe ions.

◆ *Glass*

Aluminium metaphosphate (ALMP) is used as an additive in the manufacture of special types of glass, optical fibres and as an opacifier in glass. STPP can also be used as an opacifier in the glass sector.

◆ *Antifreeze agents*

Dipotassium phosphate (DKP) is frequently used in the manufacture of antifreeze, acting as an anti-corrosion agent in car radiators and other equipment. DKP helps to keep the pH stable at around 9 thereby reducing the risk of corrosion. Purified phosphoric acid can be used in this way combined with KOH to achieve a solution of DKP *in situ*.

◆ *Polystyrene*

Tricalcium phosphate (TCP) is one of the main compounds used in the manufacture of expanded polystyrene. It acts as an anti-caking agent by coating the polymer droplets preventing them from joining together.

◆ *Yeast and fermentation*

The high quality phosphates (mainly MAP, DAP and MKP) and purified phosphoric acid means that they are used extensively as nutrients in the yeast industry as well as in a whole range of bio-industrial processes based on fermentation (e.g. manufacture of alcohol and pharmaceutical products).

◆ *Miscellaneous*

Purified phosphoric acid is the basic raw material in the manufacture of phosphates. It is also used to purify vegetable oils, in the purification of activated carbon and the production of TiO₂ and H₂O₂. Phosphates are also used in a number of other applications such as textiles, paper, glass fibre, cement, plaster, photography, drilling mud and the manufacture of titanium dioxide (TiO₂), etc

CONCLUSION

Phosphates salts are very important helpers in everyday life. They are used in food processing but also in many technical applications. Phosphorus is in all living organisms and we could not live without. A minimum intake per day is required for the proper nutrition of plants, animals and human beings. They participate to the biological energy transfer through a natural phosphate called adenosine triphosphate (ATP). On the other hand, many industries would be under serious troubles and would have a major challenge should they reformulate without using phosphate salts and for sure some currently available products would completely disappear from the market or would become anecdotal.

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