

**28.35 - Phosphinates (hypophosphites), phosphonates (phosphites) and phosphates; polyphosphates, whether or not chemically defined.**

2835.10 - Phosphinates (hypophosphites) and phosphonates (phosphites)

- Phosphates :

2835.22 - - Of mono- or disodium

2835.24 - - Of potassium

2835.25 - - Calcium hydrogenorthophosphate (" dicalcium phosphate ")

2835.26 - - Other phosphates of calcium

2835.29 - - Other

- Polyphosphates :

2835.31 - - Sodium triphosphate (sodium tripolyphosphate)

2835.39 - - Other

**(A) PHOSPHINATES (HYPOPHOSPHITES)**

Subject to the **exclusions** mentioned in the introduction to this sub-Chapter, this heading includes phosphinates (hypophosphites), metal salts of phosphinic (hypophosphorous) acid ( $H_3PO_2$ ) (heading 28.11).

These are soluble in water and decompose on heating with evolution of hydrogen phosphide which ignites spontaneously. Alkali phosphinates are reducing agents.

The most important are :

(I) **Sodium phosphinate (hypophosphite)** ( $NaPH_2O_2$ ), in white tablets or crystalline powder, hygroscopic.

(II) **Calcium phosphinate (hypophosphite)** ( $Ca(PH_2O_2)_2$ ), colourless crystals or a white powder (obtained by the action of white phosphorus on boiling milk of lime).

Both these products are used in medicine as tonics or restoratives.

(III) **Ammonium, iron or lead phosphinates (hypophosphites).**

**(B) PHOSPHONATES (PHOSPHITES)**

Subject to the **exclusions** mentioned in the introduction to this sub-Chapter, this heading includes phosphonates (phosphites), metal salts (neutral or acid) of phosphonic (phosphorous) acid ( $H_3PO_3$ ) (heading 28.11).

The most important phosphonates are those of ammonium, sodium, potassium or calcium, soluble in water and acting as reducing agents.

### (C) PHOSPHATES AND POLYPHOSPHATES

Subject to the **exclusions** mentioned in the introduction to this sub-Chapter, this heading includes metal phosphates and polyphosphates derived from the acids of heading 28.09, i.e. :

- (I) **Phosphates** - metal salts of phosphoric acid ( $H_3PO_4$ ). These are the most important and are often called "phosphates" without further qualification. The salts formed by phosphoric acid with monovalent metals may be mono-, di- or tribasic (with monovalent metals they contain one, two or three metal atoms); there are, for example, three sodium phosphates : sodium dihydrogenorthophosphate (monobasic phosphate ( $NaH_2PO_4$ )), disodium hydrogen-orthophosphate (dibasic phosphate ( $Na_2HPO_4$ )) and trisodiumorthophosphate (tribasic phosphate ( $Na_3PO_4$ )).
- (II) **Pyrophosphates** (diphosphates) - metal salts of pyrophosphoric acid ( $H_4P_2O_7$ ).
- (III) **Metaphosphates** - metal salts of metaphosphoric acids ( $HPO_3$ )<sub>n</sub>.
- (IV) **Other polyphosphates** - metal salts of polyphosphoric acids having a high degree of polymerisation.

The most important phosphates and polyphosphates are :

#### (1) Ammonium phosphates and polyphosphates.

- (a) **Triammonium orthophosphate** ( $(NH_4)_3PO_4$ ), stable in aqueous solution only.
- (b) **Ammonium polyphosphates**. There are several ammonium polyphosphates having a degree of polymerisation ranging from a few units to a few thousand.

They occur as white crystalline powders, soluble or insoluble in water; they are used in the preparation of fertilisers, in fire-proofing additives for varnish or in fire-proofing preparations.

They remain in this heading even though their degree of polymerisation is not defined.

Ammonium dihydrogenorthophosphate (monoammonium phosphate) and diammonium hydrogenorthophosphate (diammonium phosphate), whether or not pure, and intermixtures thereof, are **excluded** from this heading (**heading 31.05**).

#### (2) Sodium phosphates and polyphosphates.

- (a) **Sodium dihydrogenorthophosphate** (monobasic phosphate) ( $NaH_2PO_4 \cdot 2H_2O$ ). Colourless crystals, soluble in water, which under the action of heat lose water (pulverised phosphate) to become pyrophosphate and, finally, metaphosphate. Used in medicine, in the man-made textiles industry, as a coagulant of protein substances, in electroplating, etc.
- (b) **Disodium hydrogenorthophosphate** (dibasic phosphate) ( $Na_2HPO_4$ ), anhydrous (white powder) or crystallised (with 2, 7 or 12  $H_2O$ ). Soluble in water. Used as a size for silk (with tin chloride), for fire-proofing fabrics, wood or paper, as a textile mordant, in chrome-tanning, in the manufacture of optical glass, for glazing porcelain, in the preparation of baking powder, in the manufacture of colouring matters and soldering fluxes, in electro-plating, in medicine, etc.

(c) **Trisodium orthophosphate** (tribasic phosphate) ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ). Colourless crystals, soluble in water, releasing part of their water of crystallisation on warming. Used as a flux for dissolving metal oxides, in photography, as a detergent, for softening industrial water and descaling boilers, to clarify sugar and spirits, in tanning, in medicine, etc.

(d) **Sodium pyrophosphates** (sodium diphosphates). Tetrasodium pyrophosphate (neutral diphosphate) ( $\text{Na}_4\text{P}_2\text{O}_7$ ). Non-hygroscopic white powder, soluble in water. Used in laundering, in the preparation of detergents, of mixtures to prevent the coagulation of blood, of refrigerating products and of disinfectants, in cheese manufacture, etc.

**Disodium dihydrogenpyrophosphate** (acid diphosphate) ( $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ), which has the same appearance, is used as a flux in enamelling, for precipitating the casein from milk, and in the preparation of baking powder, of certain malted milk powders, etc.

(e) **Sodium tripolyphosphate** ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) (pentasodium tripolyphosphate also known as sodium tripolyphosphate). White crystalline powder; used as a water-softener, as an emulsifier or to preserve foodstuffs.

(f) **Sodium metaphosphates** (basic formula  $(\text{NaPO}_3)_n$ ). Two metaphosphates meeting this description are sodium cyclo-triphosphate and sodium cyclo-tetraphosphate.

(g) **Sodium polyphosphates** having a high degree of polymerisation. Some sodium polyphosphates are incorrectly called sodium metaphosphates. There are several linear sodium polyphosphates having a high degree of polymerisation ranging from a few dozen to a few hundred units. Although they generally occur as polymers having an unspecified degree of polymerisation, they remain in this heading.

These include :

The product incorrectly known as sodium hexametaphosphate (a polymeric mixture of formula  $((\text{NaPO}_3)_n)$ , also known as Graham's salt. Vitreous substance or white powder, soluble in water. In aqueous solution, this product sequesters the calcium and the magnesium contained in the water, hence its use as a water-softener. Also used in the preparation of detergents and casein glues, to emulsify essential oils, in photography, in the manufacture of processed cheese, etc.

(3) **Potassium phosphates**. The best known is potassium dihydrogenorthophosphate (monopotassium phosphate) ( $\text{KH}_2\text{PO}_4$ ). Obtained by treating phosphated chalk with orthophosphoric acid and potassium sulphate. Colourless crystals, soluble in water. Used as a yeast nutrient and as a fertiliser.

#### (4) Calcium phosphates.

(a) **Calcium hydrogenorthophosphate** ("dicalcium phosphate") ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ). Obtained by the action of an acidulated calcium chloride solution on disodium hydrogenorthophosphate. White powder, insoluble in water. Used as a fertiliser; as a mineral supplement to animal fodder, and in the manufacture of glass, medicaments, etc.

Calcium hydrogenorthophosphate containing not less than 0.2 % by weight of fluorine calculated on the dry anhydrous product is excluded (heading 31.03 or 31.05).

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- (b) **Calcium tetrahydrogenbis (orthophosphate)** (monocalcium phosphate) ( $\text{CaH}_4(\text{PO}_4)_2 \cdot 1$  or  $2 \text{ H}_2\text{O}$ ). Obtained by treating bones with sulphuric acid or hydrogen chloride. Occurs in thick solutions; releases its water of crystallisation under the action of heat. It is the only calcium phosphate soluble in water. Used in the preparation of baking powders, as a medicament, etc.
- (c) **Tricalcium bis(orthophosphate)** (neutral calcium phosphate) ( $\text{Ca}_3(\text{PO}_4)_2$ ). The heading covers precipitated calcium phosphate (i.e., ordinary calcium phosphate). Obtained by treating the tricalcium phosphate contained in bones, first with hydrochloric acid and then with sodium hydroxide, or by precipitating a solution of trisodium orthophosphate by means of calcium chloride in presence of ammonia. Amorphous white powder, odourless and insoluble in water. Used as a mordant in dyeing; to clarify syrups; for pickling metals; in the manufacture of glass or pottery; in the preparation of phosphorus and medicaments (e.g., lactophosphates, glycerophosphates), etc.

Natural calcium phosphate is **excluded (heading 25.10)**.

- (5) **Aluminium phosphate**. Artificial aluminium orthophosphate ( $\text{AlPO}_4$ ), prepared from trisodium orthophosphate and aluminium sulphate, occurs as a white, greyish or pinkish powder. Used as a flux in ceramics, for sizing silk (with tin oxide), and in the preparation of dental cements.

Natural aluminium phosphate (wavellite) is **excluded (heading 25.30)**.

- (6) **Manganese phosphate** ( $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ ). Obtained from manganous chloride and phosphoric acid. It is a purple powder which, alone or mixed with other products, constitutes Nuremberg violet, used by artists and in enamels. Associated with ammonium phosphate, it forms Burgundy violet.

- (7) **Cobalt phosphates**. Tricobalt bis (orthophosphate) ( $\text{Co}_3(\text{PO}_4)_2 \cdot 2$  or  $8 \text{ H}_2\text{O}$ ) is prepared from sodium orthophosphate and cobalt acetate. Amorphous pink powder, insoluble in water. When heated with aluminium oxide, gives Thenard's blue used in enamels. Associated with aluminium phosphate, it is used in the preparation of cobalt purple.

- (8) **Other phosphates**. These include phosphates of barium (opacifier), chromium (ceramic colours), zinc (ceramic colours, dental cements, fermentation control, medicine), iron (medicine) and copper (ceramic colours).

The heading also **excludes** certain phosphates, viz. :

- Natural calcium phosphates, apatite and natural aluminium calcium phosphates (**heading 25.10**).
- Other natural mineral phosphates of **Chapter 25 or 26**.
- Ammonium dihydrogenorthophosphate (monoammonium phosphate) and diammonium hydrogenorthophosphate (diammonium phosphate), whether or not pure (**heading 31.05**).
- Precious and semi-precious stones (**heading 71.03 or 71.05**).