GPI GLOBAL PHOSPHORUS INSTITUTE

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NON-FERTILIZER USES OF PHOSPHORUS AN OVERVIEW

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1 Introduction

Phosphorus has played an important role in human society since the implementation of agriculture. It is one of three macronutrients—potassium, phosphorus, and nitrogen—needed for plant growth and plays several irreplaceable roles in the chemistry of life, including in DNA, bones in vertebrates, and the energy cycle in cells. To serve in these roles, phosphorus is present in the form of phosphate, PO_4^{3-}, in which phosphorus is in its most oxidized state: 5+. Phosphate is also almost exclusively the form in which phosphorus is found in nature, such as in mineral deposits.

Well before the formal discovery of phosphorus, the effects of manure were noted in agriculture, primarily due to the limited availability of one of the three essential macronutrients. This was partially because phosphate has a much stronger tendency to form water-insoluble compounds than potassium or nitrogen, thus limiting its availability to plants.

In modern society, phosphorus continues to play a crucial role in agriculture as a key ingredient in modern fertilizers. The entire aim of the phosphate fertilizer industry is to increase the availability of phosphates to plants by chemical transformation of mined phosphate ore to increase its water solubility, specifically in the form of (impure) phosphoric acid, which is subsequently transformed into derivatives such as ammonium phosphates and superphosphates. Together with the equally crucial Haber–Bosch process of transforming inert atmospheric dinitrogen into plant-available compounds, the development of a method for large-scale phosphate fertilizer production has led to a spectacular increase in crop production in the 20th century. Because of fertilizer use, the earth's population increased to 7 billion people in 2020.[1-3] Without the benefits of fertilizers, only a fraction of these people could be fed.

All phosphate fertilizers are produced from mineral resources, which are mined. These mineral resources consist of layers of apatite, a calcium phosphate fluoride/hydroxide that has accumulated as a result of sedimentation from oceans on the geological timescale and sometimes as a result of volcanic action. These minerals, which are often impure, are commonly referred to as phosphate rock. Because these resources are being used at a much faster rate than they (re)accumulate, it has been feared that phosphate might become scarce in the future,[4] even though phosphorus – in the form of phosphate rock – is moderately abundant in the Earth's crust. The concern of imminent scarcity has been largely disproven, but care must be taken to use existing resources sensibly.

While the importance of this application of phosphorus cannot be overstated, this element does have other applications. Although nonfertilizer phosphorus constitutes only approximately 10% of the total phosphorus consumed annually, there are hundreds of different phosphorus applications involving many phosphorus-based chemical compounds. A significant part of this field concerns phosphates or polyphosphates, which are similar to fertilizer phosphates in a chemical sense, but a diverse field of chemistry exists based on organophosphates and on lower oxidation states of phosphorus. The field enables a huge sector of the economy well beyond its intrinsic value as chemicals.

A crucial event related to the nonagricultural use of phosphorus was the discovery by Hennig Brandt in 1669 of a highly reactive elemental form: white phosphorus. Even though Brandt's experiment can be classified as alchemy, this event marks the birth of modern chemistry, since it was the first time that an element that does not occur in elemental form in nature was synthesized. The reactive nature of white phosphorus—it burns spontaneously in air—allows the production of a vast array of non-phosphate-type compounds.

Virtually all phosphate in nature occurs in oxidation state +5. From the elemental state (oxidation state 0), other oxidation states of phosphorus can be reached: +1, +3, -1 and -3. White phosphorus is a key entry point for virtually all branches of phosphorus derived chemistry, apart from fertilizers, feed and food phosphates. It is also the form that is obtained via the heat-driven reduction of phosphate ore, a process that can be performed on a large scale. This process utilizes the same raw material used for the production of fertilizers: apatite.

Other, less reactive allotropes of phosphorus include red phosphorus, violet phosphorus, Hittorf's phosphorus and black phosphorus. These can be produced from white phosphorus via thermal and/or pressure treatment. These other allotropes are described in section 2.

White phosphorus is very reactive and consists of tetrahedral molecules containing four P atoms: P_4. The angles between the P-P bonds in this molecule are quite strained, which explains the high reactivity of the molecule. This structure prevents clean and straightforward transformations of white phosphorus to many end products in one step, because once the first P atom reacts, the three remaining P atoms in the now-opened molecule will react violently and uncontrollably with anything in the reaction mixture. Thus, transformations of white phosphorus occur via intermediates, which are called first derivatives, in a few steps to generate end products.

The key position of white phosphorus in the phosphorus value chain and its transformation via first and second derivatives into products is represented in Figure 1, with the fertilizer phosphate value chain shown for comparison.

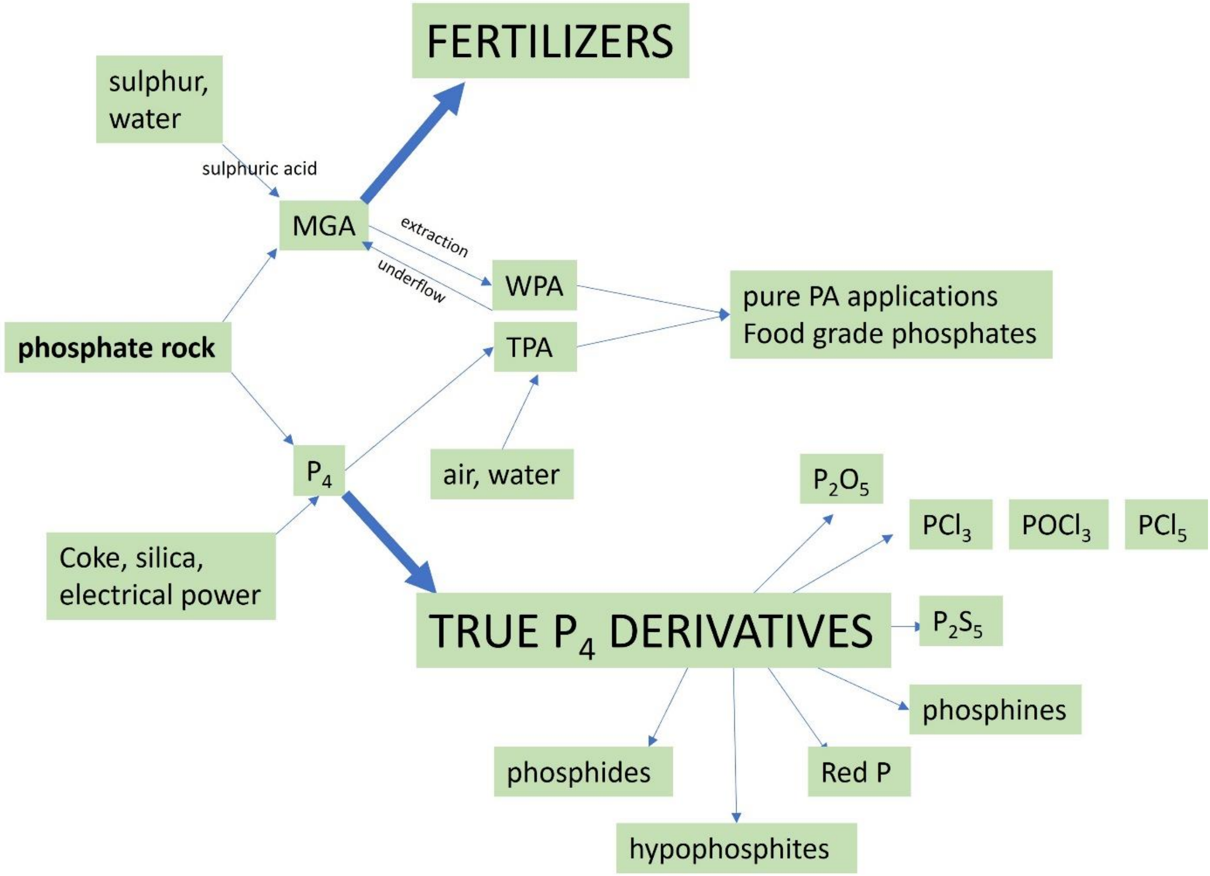


Figure 1 Phosphate rock value chains. Apatite-rich phosphate rock can be mixed with sulphuric acid (made from oxidizing sulphur in air, followed by water addition) to produce so-called merchant grade phosphoric acid (MGA, a concentrated grade). The MGA is an intermediate product in the phosphate value chain that is used in phosphate fertilizers. Varying degrees of purification of MGA give industrial and feed grade acid, with the most purified product suitable for metal treatment and food applications (food grade quality) - a high-purity grade termed wet process phosphoric acid (WPA).

The thermal processing of apatite-rich phosphate rock requires metallurgical coke, silica and electrical power to produce elemental phosphorus (P_4), known as white or yellow phosphorus. When reacted with air and water, P_4 is converted to so-called thermal phosphoric acid (TPA), a high-purity grade of phosphoric acid which has the same purity and applications as WPA. Alternatively, P_4 may undergo multi-step reactions through intermediates, designated as true P_4 derivatives, to achieve desired end products. These true P_4 first derivatives are phosphorus pentoxide (P_2O_5), phosphorus trichloride (PCl_3), phosphorus oxychloride ($POCl_3$), phosphorus pentachloride (PCl_5), phosphorus pentasulphide (P_2S_5), phosphine (PH_3), red phosphorus (polymeric chain, P_n) , hypophosphites ($H_2PO_2^-$) and phosphides (P^{3-}). True phosphorus derivatives are those products that can be made only from the element.

Phosphate rock is the ultimate source of all P-based products, for agricultural or other uses. Despite the large size of the fertilizer industry, that represents one general, though important, application, the focus of this paper is on the non-agricultural products.

The many nonagricultural uses of phosphates and polyphosphates are applications that typically use pure or purified phosphoric acid. As explained in section 3, the required purity can be reached by upgrading fertilizer-grade phosphoric acid, or by oxidation of white phosphorus and subsequent hydrolysis of the resulting phosphorus pentoxide (Figure 1). At this point, the two value chains intersect, with economics and the availability of technology and infrastructure determining which route is favored. Additionally, for chemically related polyphosphoric acid, a similar dichotomy exists; this species can be obtained via extreme water removal from phosphoric acid, or from the true P_4 derivative phosphorus pentoxide and water (section 4).

Metal phosphides, as byproducts of white phosphorus manufacture or from intentional production, constitute a minor segment with mainly applications in metallurgy.

Phosphorus pentoxide can be generated only from elemental phosphorus and serves as the entry point to produce acid phosphate esters. These materials have a wide range of applications.

Phosphorus trichloride (PCl_3) has phosphorus in its +3 oxidation state. A clear majority of phosphorus chemistry uses this compound as the key starting intermediate. The reasons for this are as follows:

- In many organophosphorus compounds, phosphorus exists in the +3 oxidation state.
- In contrast to P_4, PCl_3 contains a single P atom attached to three easily removed chloride atoms, resulting in predictable and repeatable reactivity.
- PCl_3 can be converted to phosphorus oxychloride ($POCl_3$), which serves as an entry point for obtaining organophosphates (e.g. flame retardants)
- PCl_3 is also a precursor to the chemicals phosphorous acid (H_3PO_3) , and phosphorus pentachloride (PCl_5), a key intermediate for lithium-ion battery electrolytes.

A prime example of a P^{3+} compound is glyphosate, a herbicide produced from PCl_3. Among all true P_4 derivatives, this compound has by far the largest volume and use.

Notably, in almost all PCl_3 pathways, chloride is not present in the end product, and ends up in byproducts or waste.

P sulfides are another important type of P_4 derivatives. Unlike in applications of PCl_3, in P sulfide applications, sulfur is intended to end up in the final product along with P. Typically, organo-thiophosphates are produced from P_2S_5 which are applied as insecticides and lubricant additives.

Phosphines may constitute the most diverse class of chemicals in this context, even though their volume is small. Organophosphines, for instance, are used as ligands for catalysts and play many crucial roles in (petro)chemical conversions. Phosphine oxides serve as highly selective agents in metal extraction processes in mining.

Hypophosphites constitute a minor group in terms of volume, but have important applications in nickel plating, extraction agents, and flame retardants.

In the first derivatives and many end products, a phosphorus atom is incorporated into a molecule, where it contributes significantly to the total molecular weight. A few phosphorus derivatives and their P contents are listed in Table 1.

Table 1 Phosphorus content (P %, by mass) of common substances.

Name	**Compound**	**P %**	**Uses**
White phosphorus	P_4	100	Intermediate
Red phosphorus	P_n *	100	Intermediate; true P_4 derivative
Phosphorus pentoxide	P_2O_5	43.8	Intermediate; true P_4 derivative
Phosphorus pentasulfide	P_2S_5	27.9	Intermediate; true P_4 derivative
Phosphorus trichloride	PCl_3	22.6	Intermediate; true P_4 derivative
Phosphorus oxychloride	$POCl_3$	20.2	Intermediate; true P_4 derivative
Phosphorus pentachloride	PCl_5	14.9	Intermediate; true P_4 derivative
Sodium hypophosphite	NaH_2PO_2	35.2	Metal plating agent, intermediate
Phosphoric acid, 75%	H_3PO_4	23.7	Acidulation, etching, intermediate
Sodium tripolyphosphate	$Na_5P_3O_{10}$	25.3	Detergents, food additive
Sodium acid pyrophosphate	$Na_2H_2P_2O_7$	27.7	Leavening agent in baking powders
Sodium hexametaphosphate	$NaPO_3$ (approx.)	30.3	Food additive, toothpaste ingredient
Ammonium polyphosphate	$[NH_4PO_3]_n$ *	32.0	Flame retardant, fertilizer

Glyphosate	$C_3H_8NO_5P$	18.3	Broad spectrum herbicide
ZDDP	$Zn[(S_2P(OR)_2]_2$	7.1**	Anti-wear additives in lubricants

* n denotes a long chain of varying length.

** this P concentration refers to the common variety of ZDDP where R denotes an ethyl group

In Sections 2-7 of this document, the production and uses of P_4 and its derivatives are explored in more detail.

The chemistry of phosphorus is described in detail in ref.[5]

Generally, the main reasons for the use and presence of phosphorus as part of phosphorus derivatives are as follows:

- its value as a nutrient, making it valuable in fertilizers, food, and animal feed
- its acidity (as phosphoric acid, or a solid salt with acidic properties), which can be beneficial in, for example, etching and beverages
- its ability to form flame retardants that can be incorporated into flammable materials such as fabrics or plastics; additionally, it can aid in plastic processing and stabilization
- its ability to form substances with sequestering properties, which can be used in water treatment e.g. to prevent scaling (polyphosphates, phosphonates or polyphosphates) or as selective extraction agents in mining applications
- its role as a component in crop protection agents, e.g., to stop unwanted plant growth (glyphosate) or kill insects (the P-S motif in many pesticides)
- its properties as the central atom in catalyst ligands, which can be attached to reactive metal centers; yielding catalysts used in (petro)chemical conversions

- its role as a counterion to allow lithium conductivity in batteries
- its ability to form molecules that protect surfaces from wear
- its ability (via defined derivatives) to extract water, to reduce metals in solution, or to deliver chlorine atoms to a target molecule

All but the last category involve the actual incorporation of a P atom into a functional molecule, which accounts for the vast majority of all applications. Its roles in chlorination, drying or reduction agents exploit the specific properties of the compound in question without incorporation of the P atom into the product.

A nonexhaustive summary of the main applications of each first derivative is provided in Table 2.

Table 2 A nonexhaustive summary of uses of true P_4 derivatives: phosphorus pentoxide (P_2O_5), phosphorus trichloride (PCl_3), phosphorus oxychloride ($POCl_3$), phosphorus pentachloride (PCl_5), phosphorus pentasulphide (P_2S_5), phosphines (containing PR_3), red P (amorphous elemental phosphorus, P_n), hypophosphites (NaH_2PO_2), metal phosphides (reduced P as P^{3-}) Purified phosphoric acid (H_3PO_4) is shown for comparison.

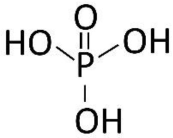
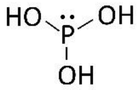
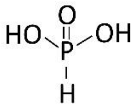
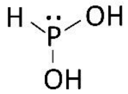
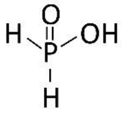
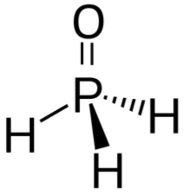
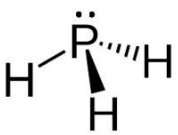
Application	**P_2O_5**	**PCl_3**	**$POCl_3$**	**PCl_5**	**P_2S_5**	**PH_3**	**Red P**	**NaH_2PO_2**	**Metal phosphides**	**Purified H_3PO_4**
Flame retardants	ammonium polyphosphate	phosphites	organo-phosphates			THPC [d]	Red P	phosphinates		
Plastic additives		phosphites	organo-phosphates							
Crop protection		glyphosate	organo-phosphates		thion insecticides	Storage fumigation			Storage fumigation	
Lubricant agents	acid organo-phosphates		organo-phosphates		ZDDP-ethyl [c]					
Water treatment	acid organo-phosphates	phosphonates	acid organo-phosphates							
Food additives			starch modification							beverages, bakery, meat, dairy
Pharmaceuticals	water removal	bisphosphonates	multiple uses	7-ACA [a]	multiple uses					
Catalysis						ligands				
Metal treatment										surface treatment
Metal extraction	acid organo-phosphates					phosphine oxides, phosphonates		phosphinates		
Li ion batteries				$LiPF_6$ [b] electrolyte	Electrolyte					Li-Fe phosphate cathode
Metallurgy									copper, bronze, steel	

[a] 7-ACA: 7-aminocephalosporanic acid ; [b] $LiPF_6$: Lithium hexafluorophosphate; [c] ZDDP-ethyl: zinc diethyl dithiophosphate ; [d] THPC: tetrakis(hydroxymethyl) phosphonium chloride.

The nomenclature of phosphorus compounds can be confusing, as a plethora of terms exist. Some of these are explained in sections 2-7.

The oxides and associated oxyacids and hydrides are systematically explained in Table 3.

Table 3 The oxidation state of phosphorus in oxides and oxyacids/hydrides.

State	Oxide	Acid/hydride	Acid common name(s)	Structure(s) of the acid(s)
+5	P_2O_5	H_3PO_4	Phosphoric acid, orthophosphoric acid	
+3	P_2O_3	H_3PO_3	Phosphonic acid, phosphorous acid	 
+1	*P_2O not proven to exist*	H_3PO_2	Hypophosphorous acid Phosphinic acid	 
-1	-	*H_3PO unstable, but organic derivatives exist*	Phosphine oxide	
-3	-	PH_3	Phosphine	

2 The element phosphorus

- White phosphorus is the parent compound of a large family of phosphorus-based chemicals.
- It is prepared in an energy-intensive process using a furnace with electrical heating.

- It is a waxy white solid that tends to burn spontaneously in air.
- A red variety of phosphorus also exists, which is used to fireproof materials.

2.1 General

As discussed in section 1, phosphorus is a moderately abundant element in the Earth's crust. It is almost exclusively found in the form of mineral deposits of calcium apatite, a form of orthophosphate. Although other phosphate-containing minerals, such as lazulite, monazite or turquoise, exist, they remain in the same chemical form, namely, orthophosphate (PO_4^{3-}) , which is the most oxidized form of phosphorus (+5). Virtually no other chemical forms of phosphorus occur naturally on Earth.

The preparation of commercially important phosphorus chemicals, such as organophosphates and compounds with different valence states of phosphorus (see section 1), starts with the elemental form. To produce elemental phosphorus, a chemical reduction reaction is used.

Elemental phosphorus is obtained by the so-called electrothermal reduction of phosphate rock. Like iron/steel manufacturing, this is performed by heating phosphate rock with a reducing agent such as coke, which causes the phosphate in the rock to be reduced to the elemental form.[6]

This route, as described in detail below, is the standard production route that has been used in industry since the late 1880s to obtain this element (Figure 2). This pathway always yields white phosphorus. Other forms (allotropes) of elemental phosphorus also exist, which are described below, and they are all prepared from the white allotrope.

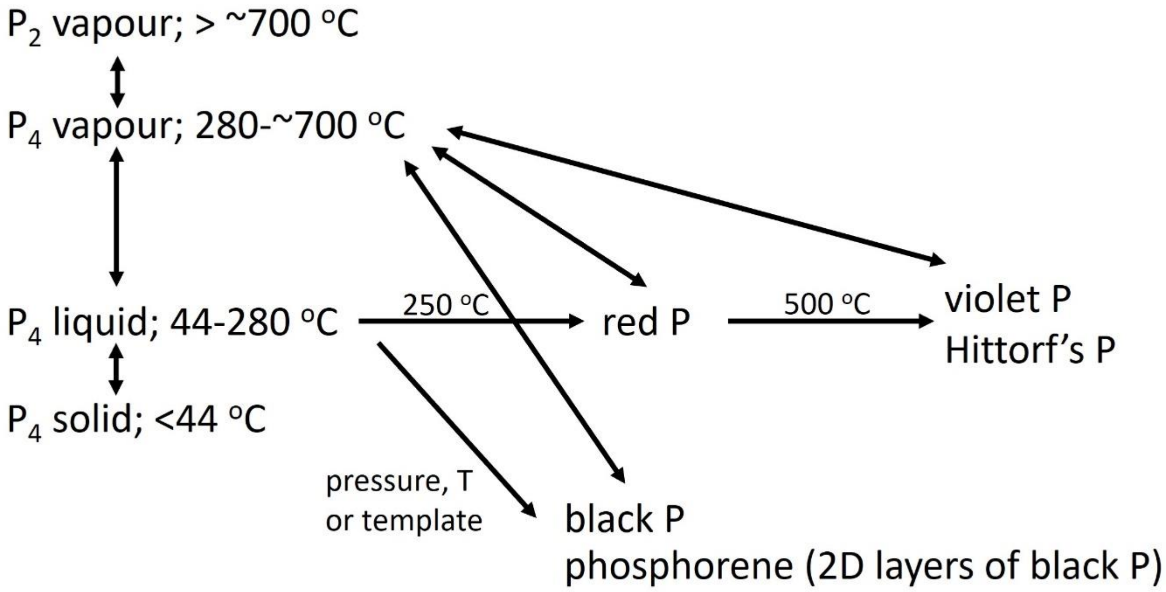


Figure 2 Allotropes of phosphorus. White phosphorus (P_4) is the form in which the element is obtained from the reduction of apatite. By applying the right conditions (temperature, pressure) under the exclusion of oxygen, white phosphorus can be converted to red phosphorus (amorphous), violet phosphorus/ Hittorf's phosphorus (rhombohedral crystals), black phosphorus (orthorhombic puckered honeycomb structure with a lattice of interlinked six-membered phosphorus rings), or phosphorene, with a two-dimensional structure similar to graphene.

White phosphorus is the parent compound for all phosphorus compounds other than phosphates, including all organophosphorus compounds.

2.2 White phosphorus

The most industrially relevant form of phosphorus is white phosphorus.

White phosphorus consists of tetrahedra of four P atoms that form the molecule P_4 (Figure 3). It is a waxy, white to yellowish solid that melts at 44 °C and boils at 280 °C. Its density at room temperature is 1.83 g/ml (approximately 1.73 when molten).

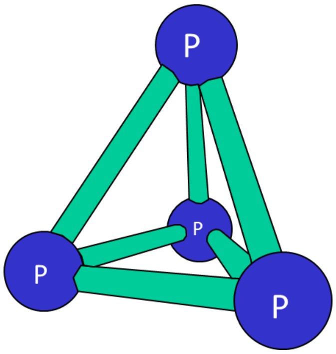


Figure 3 The P_4 molecule.

Although this form of phosphorus is naturally white/colourless, it often appears yellowish when exposed to light or due to the presence of impurities. The terms white phosphorus and yellow phosphorus are both commonly used, but refer to the same material.

A remarkable property of white phosphorus is its ability to be supercooled as a liquid. If it is kept in a smooth container, it can remain in the liquid state at temperatures well below its freezing point of 44 °C for prolonged periods. When induced to solidify, e.g., by touching it with a solid object, this liquid white phosphorus freezes exceptionally quickly—much quicker than any other known material—because of the special property that when frozen, the P_4 tetrahedra can still rotate freely within the solid form, so during freezing, the P_4 units do not need to align to form a crystal lattice.

As explained in section 1, the nature of the strained P_4 molecule causes it to be highly reactive. White phosphorus, especially when molten, burns spontaneously in air. Upon exposure to the skin, it immediately causes severe and deep burns. During burning, it emits a thick white smoke consisting of phosphorus pentoxide (see below for an application).

The solid material does not ignite directly in air, but can still ignite unexpectedly after several hours of slow oxidation in air. Cold phosphorus can oxidize slowly while emitting a pale greenish-blue light (chemiluminescence), which is the origin of its name (Greek: phos-phoros, light bearer)

In addition, white phosphorus is toxic. P_4 vapors can enter the body, e.g., via tooth cavities, causing necrosis of the jawbone, a condition called phossy jaw, which afflicted many match factory workers (processing white phosphorus) in the 19th century.[7] Phosphorus is soluble in apolar solvents, and the resulting solutions are toxic when ingested.

These properties make white phosphorus an exceptionally hazardous material to handle on laboratory and industrial scales.

During storage and transport, phosphorus is usually kept under a layer of water, which is lighter than the liquid phosphorus and floats on top. Water is also used to push liquid phosphorus out of railcars, drums and tanks, which reduces the risk of leaks that may occur in direct contact pumps. Alternatively, a blanket of an inert gas such as nitrogen is applied.

2.2.1 White phosphorus: production technology

The production of white phosphorus occurs in a so-called submerged arc furnace (Figure 4).[8,9]

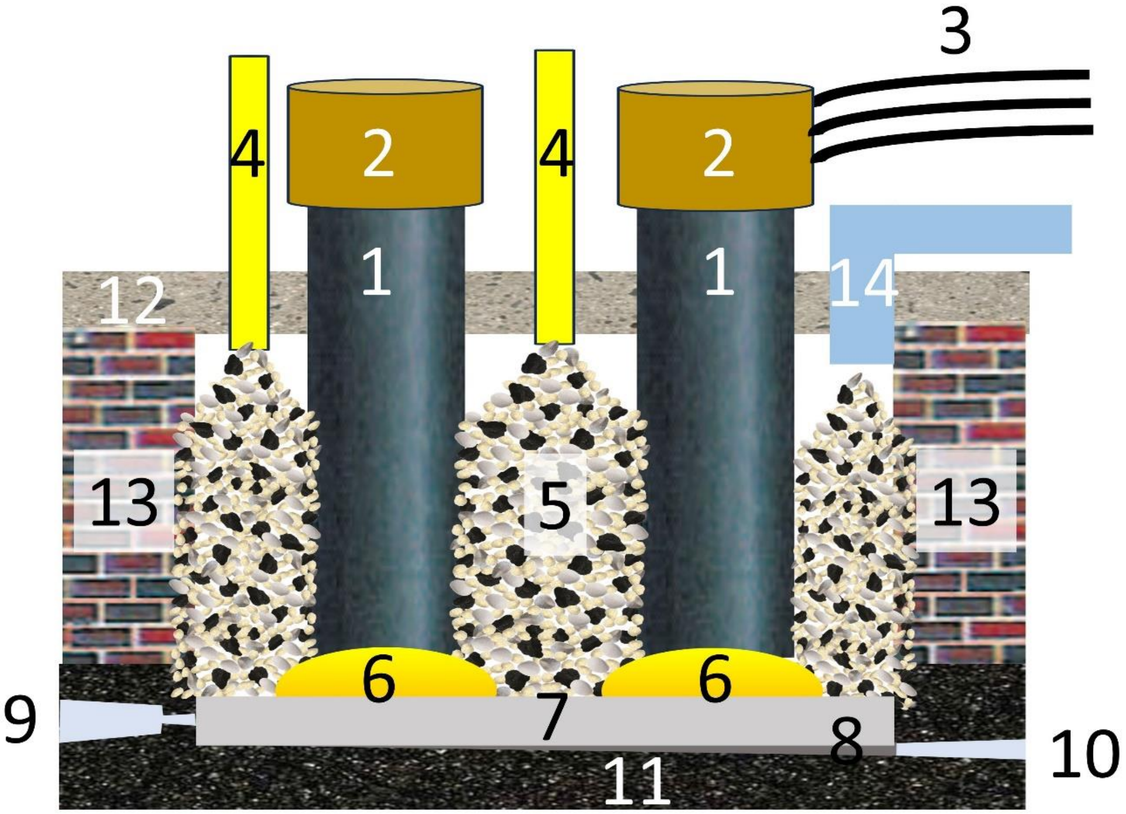


Figure 4 Electrothermal reduction of rock phosphate is done in a submerged arc furnace. Numbers in this cross section correspond to the following: 1, carbon or graphite electrodes (not all shown); 2, holding clamps and a power transfer system; 3, power lines from the transformer; 4, feed chutes (not all shown); 5, packed feed bed (phosphate rock, metallurgical coke, and silica gravel); 6, hot reaction zone; 7, silicate slag melt; 8, ferrophosphorus melt; 9, silicate slag tap hole; 10, ferrophosphorus slag tap hole; 11, carbon bottom furnace lining; 12, concrete furnace top; 13, refractory furnace walls; 14, phosphorus and carbon monoxide gas duct. Slag tapping can also be done with one combined tap hole for both slags.

In the furnace, a mixture of phosphate rock and metallurgical coke as a reducing agent is fed through the top via feed pipes (see Figure 4). In addition to rock and coke, a third component is also present, namely, silica, which is usually present in the form of ordinary gravel. Silica is needed to form a liquid slag at the bottom of the furnace, as explained below.

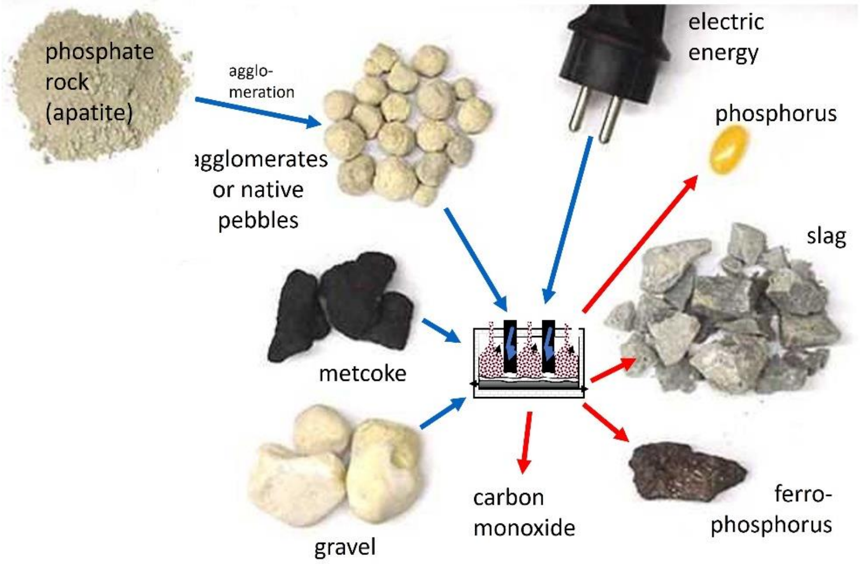


Figure 5 Reactants and products of the electrothermal production for white phosphorus in a submerged arc furnace. Phosphate rock, most commonly apatite (calcium phosphate fluoride/hydroxide) is added as 0.5–3 cm diameter particles, either from agglomeration of smaller materials or in the form of natural pebbles. Other inputs include metallurgical coke as a reducing agent, gravel (silica that reacts with calcium oxide to form a liquid slag) and electric energy to heat the feed mass. Products are elemental phosphorus (P_4), carbon monoxide, plus two slags: calcium silicate, and ferrophosphorus, an alloy of iron and phosphorus.

Electrically conductive electrodes composed of carbon or graphite are placed through the furnace top into the feed mass. Six electrodes in a hexagonal arrangement or three electrodes in a triangular arrangement are used in such furnaces. Linear electrode arrangements also existed in the past. The tops of the electrodes are connected to transformers via clamps, providing 300-700

V and thousands of amperes, to supply heat to the process by electrical resistance of the feed. A typical phosphorus furnace uses 10 to 50 MW of electrical power.

Because this process uses carbon, the electrodes are also slowly consumed. The voltage and current are controlled to minimize this consumption, but it is still noticeable. Therefore, the electrodes need to move down into the furnace to remain within the reactive zone in the feed. For this purpose, the furnace is equipped with a lifting, often hydraulic, system that allows electrode movement while keeping the power feed on. If the electrode on the furnace top is too low near the lid of the furnace, a new piece is joined to it by means of a screw thread; then, the clamps are repositioned, and the electrical power supply resumes. The position of the electrodes is also used to control the process.

As explained, the furnace feed mixture is heated by passing a large current through it between the electrodes. The contents of the furnace are not very conductive to electrical currents, so the resistance of the furnace feed causes heating to above 1500 °C as a result of electrical resistance. This heating causes the coke to reduce the phosphate rock to the elemental form. A gas consisting of P_2 and CO is formed at these temperatures, which rises through the feed (preheating the feed in the countercurrent flow and thus undergoing cooling when in contact with the incoming feed) and leaves the furnace through a duct at the top edge. Under these conditions, the coke forms carbon monoxide, not carbon dioxide; the phosphorus and carbon monoxide are emitted from the furnace as a gaseous mixture, with some dust entrained. Along the cooling trajectory, the P_2 dimerizes into P_4.

A typical white phosphorus plant is shown in Figure 6.

Figure 6 A white phosphorus plant (Vlissingen, The Netherlands), with storage tanks for P_4 in the foreground. This plant was closed in 2012.

The emitted gas contains dust, from the feed and formed in the process, which can be removed with an electrostatic precipitator that contains wires to expose the dust to an electric charge. This causes the dust to become statically charged, allowing it to stick to the wall of the precipitator with the opposite charge. In smaller furnaces, this step is often omitted.

The furnace gas is then cooled with a spray of water in a cooling tower. This causes phosphorus to condense and drop out as a liquid. There is always some remaining dust, which causes a very stable emulsion of phosphorus in water that has the appearance of gray mud. Through a series of agitation/settling stages, most of the phosphorus is recovered.

The liquid phosphorus is added to containers, such as railcars or drums, and shipped.

The remaining gas consists of carbon monoxide and can be used as a fuel, e.g., in rock pretreatment (as described below).

When the phosphate rock is reduced, the phosphate component of the rock is removed as P_4 and CO, and the remaining calcium oxide remains in the furnace. This material is a solid at operational temperatures and is an enormous challenge to remove from the bottom of the furnace. For this, silica (gravel) is added to react with the calcium oxide to form calcium silicate, which exists as a liquid compound at these temperatures. This allows continuous tapping of this material, the so-called slag, from the furnace. The slag is cooled (passively against air or by quenching with water) and used in road construction or landfills. In remote locations, this slag is usually stockpiled or used to backfill adjacent phosphate mines; in several Chinese plants, slag is used in construction or cement plants. Civil construction also used to be the main slag outlet in European plants.

All phosphate rocks contain a small amount of iron phosphate as an impurity. The iron is reduced along with phosphorus and forms a separate slag, an alloy of iron and phosphorus termed ferrophosphorus (see section 7.5). This is collected separately and sold to steelworks as a minor additive. It has a much greater density than the calcium silicate slag (7.6 g/ml vs. 2.8) and is either tapped separately from its own taphole, at the lowest point of the furnace, or separated in a liquid slag separator basin inserted into the tapped slag flow.

The white phosphorus process runs continuously, with additional feed being supplied at the top as it is consumed during the reaction.

Phosphorus production is an energy-intensive process; for each ton of P_4, 13 to 14 MWh of energy are needed. This energy consumption is comparable to that required for aluminum manufacture.

2.2.2 Rock pretreatment

The electric arc furnace is filled almost to the top with incoming feed. In this setup, an efficient heat exchange process is created in which the gas formed in the reaction zone around the electrode tips rises and is cooled, preheating the incoming feed. However, to achieve this purpose, the incoming bed needs to be coarse and porous.

Phosphate rocks are sometimes found as granules in natural deposits (Florida, Yunnan, Vietnam) but many deposits are partially composed of dust or undergo some form of enrichment, which also involves milling. When a fine powder is present in the feed, the formed product gas will not be able to escape the furnace, and the process will stop.

Therefore, in many cases, it is necessary to granulate the rock to 0.5-3 cm particles before it is fed into the furnace. This can be accomplished by various methods, such as pellet rolling in a pan or tube reactor, briquetting (pressing predefined forms in a roller press), or melting agglomeration. Such processes require a heating step to solidify the particles after (or while) they are formed. Carbon monoxide from the P_4 furnace, a low-grade fuel, can be used for this purpose. When the rock already contains coarse pebbles, carbon monoxide is used elsewhere as a fuel, flared, or (rarely) converted to methanol.

The need to pretreat the rock to form nodules requires the addition of a considerable production unit to the actual P_4 plant.

In a somewhat related process, the so-called kiln process, coke and phosphate rock are mixed and heated. This process results in P_4, which escapes the feed as gas, is immediately (re)oxidized to phosphorus pentoxide, and is subsequently converted to phosphoric acid by quenching with water. This process (one form of which is called the IHP process) is described in section 3. It does not give access to P_4.

2.2.3 Grades of white phosphorus

The furnace technology used in P_4 manufacturing has the advantage of separating almost all other elements from the rock, so the white phosphorus becomes very pure. Exceptions include the two chemically related elements, the so-called pnictides, that appear below phosphorus in the periodic table: arsenic and antimony. Even though the levels of these compounds are quite low in phosphate rock, arsenic is present in noticeable amounts in the product, as AsP_3. Its concentration in the product is governed by the nature of the phosphate rock. Commercial P_4 contains 50 to 250 mg/kg As, which can be a nuisance in follow-up processing and applications. There are very limited options to remove it before or during the production of P_4. Derivative chemistry may allow arsenic removal during an additional step, but this is not always possible (see sections 4, 5 and 6 on P oxides, chlorides, and sulfides). Antimony is much less abundant than arsenic in phosphate rock but can be present at levels as high as 20 mg/kg in the product and may also interfere with some applications of derivatives.

Another relevant impurity is tar. In older furnaces, carbon electrodes are formed in situ from a tarry material. This releases some tar into the product, which in certain cases, restricts its use. As in the case of arsenic, this is particularly relevant where further processing does not offer any opportunities for removal.

Finally, the incomplete removal of dust during condensation and mud treatment may result in the presence of solids in the prepared phosphorus, which usually must meet a specified limit, e.g., <0.1% by weight.

According to the above discussion, there are no defined grades for P_4, but differences do exist depending on the rock used in the process and the type of electrodes used.

2.2.4 Applications

As explained in the introduction, white phosphorus is the key parent compound for many applications in chemistry. Its uses as such are quite limited. One significant application is in incendiary and smoke grenades. When incendiary grenades are dropped, phosphorus is released and catches fire spontaneously, setting fire to its surroundings. Burning phosphorus is very difficult to extinguish, so this is an effective method for setting fires in a military context. When phosphorus burns, it generates an impressive amount of thick, white smoke that is very effective at blocking sightlines in a battlefield; hence, P_4 is useful for establishing smokescreens.

Both of the abovementioned uses are negligible among the total P_4 applications in terms of volume.

In addition, white phosphorus is used in a highly diluted form in homeopathic formulations.[10]

An obsolete application is rat poison, in which P_4 is applied as a solution in ethanol.[11]

2.3 Red phosphorus

Red phosphorus is a dark reddish-violet powder that, unlike white phosphorus, does not react readily with air (Figure 7). It consists of long chains of P atoms, which is a different arrangement of P atoms than the tetrahedral structure in white phosphorus.

Figure 7 Red phosphorus

Ultrafine red phosphorus tends to be flammable/explosive in air.

Other than white phosphorus, red phosphorus is the only allotrope of phosphorus with industrial relevance.

Red phosphorus is produced by heating white phosphorus to approximately 250-280 °C, just below its boiling point, in a stirred reaction tank. This treatment converts white phosphorus to the red form in a few hours to days. When the reaction is near-complete, the remaining traces of white phosphorus are removed by washing with water or a caustic soda solution. The powder is then dried and drummed for sale, or mixed into formulations (see below).

Red phosphorus has the following uses:

- Pyrotechnics
- Flame retardants
- Matchboxes

In pyrotechnics, red phosphorus is mixed with a metal powder such as magnesium. This mixture is stable, but upon ignition, it emits a bright white display of sparks. The applications of this material include fireworks and flash grenades.

The largest application of red phosphorus is as a flame retardant. The powdered product is usually mixed with other ingredients to form so-called masterbatches. Red phosphorus is encapsulated to reduce its flammability and mixed with other ingredients to create a flame retardancy additive formulation. The use of such masterbatches has allowed the range of applications to expand beyond the original application in nylon.

Masterbatches are usually produced immediately following red P synthesis. This allows the processing of still-wet red P, which avoids the need to supply drying energy and circumvents the flammability hazards of the fine material.

The flame retardancy of red phosphorus is quite high, given its 100% P content, but it is not always suitable for applications. Discrete red P particles may not always blend well with plastic formulations. More importantly, the colour of the material means that it can be applied only to red, brown or dark gray/black plastics. These include such as polyamide-type materials (nylon), polyethylene, polystyrene, etc.

A minor application of red P is in the striking surface of matchboxes.

2.4 Violet and Hittorf's phosphorus

Violet and Hittorf's phosphorus are allotropes that are somewhat related to red P in terms of structure but have no industrial significance.

2.5 Black phosphorus

This allotrope of phosphorus is an air-stable black powder that resembles graphite in its appearance and properties (it is conductive). A long-term topic of interest in laboratory research, this allotrope of phosphorus has been attracting attention as a potential sensor material when prepared in the form of nanosheets or quantum dots. Its synthesis involved extreme pressure and heating until recently, when a relatively mild synthesis based on a similarly structured seed crystal was proposed.[12] Starting from red phosphorus, gold, tin metal, and tin iodide, a gold-tin-phosphorus compound is formed with a similar structure, onto which black phosphorus can be grown selectively. An alternative method involves reducing PCl_5 with aluminum metal in a molten salt bed of aluminum chloride.[13] Large-scale production is expected to allow other applications currently served by graphite, such as lithium-ion battery anodes, to be developed. Single-layered black phosphorus is known as graphene. Its twodimensional structure imparts conductivity that may prove to be useful in electronics (transistors) or as anode for lithium ion batteries, as a potential replacement for graphite. Its synthesis is a challenge beyond laboratory scale, where it may be produced by microcleavage of black phosphorus crystals with scotch tape.

3 Phosphoric acid and phosphates for food, feed and technical applications

- Pure phosphoric acid can be prepared by purifying fertilizer-grade phosphoric acid, or by adding air and water to white phosphorus.
- It is used in metal etching and in cola-type beverages.
- It is a raw material for sodium, potassium and calcium phosphates, which are used in food processing, including meat, fish, cheese, bakery, and pet food.
- It is also used as a raw material to prepare other derivatives for several other applications, such as batteries and toothpaste additives.

- It can also be used to prepare high-purity special fertilizers.

3.1 Introduction and technologies

The products described in section 3, such as feed phosphates, are all derived from phosphoric acid (H_3PO_4). As described in the introduction, phosphoric acid (PA) is generated from phosphate rock (essentially calcium phosphate) and sulfuric acid. The PA obtained in this way is quite impure because the trace metals and anions in the phosphate rock dissolve into the acid. This grade of PA is termed merchant-grade acid (MGA). It is usually supplied as a concentrated solution in water and is obtained by concentration via water evaporation at the end of the process, which takes place under more diluted conditions. It contains 52-55% P_2O_5 (an industry standard of expressing strength; see section 4 on P_2O_5), which corresponds to 75-80% H_3PO_4. The remainder of the solution is water, plus about 5% impurities.

MGA contains major impurities—fluoride, sulfate, iron, magnesium, aluminum and calcium—present at concentrations of 0.1-5% (w/w) and smaller but significant amounts of arsenic, cadmium, nickel, chromium, uranium, and many more trace elements, typically present in the tens of mg/kg range.

The impurity profile is determined by the nature of the phosphate deposit being used. The concentrations of these elements can vary substantially. Generally, the majority of phosphate rocks are of sedimentary origin (having been deposited from oceans in the geological past), with a minority being of igneous (magmatic/volcanic) origin. The latter tend to have higher levels of phosphate and lower contents of impurities (especially some minor elements such as Cd).

In fertilizers, these elements do not play a major role but limit the strength of the MGA that can be obtained by thickening, especially because dissolved magnesium increases the viscosity of the acid, thus limiting its processability, and the phosphate content of the fertilizers produced from it, because the impurities dilute the end product. However, a certain level of impurities is needed to facilitate fertilizer granulation. Cadmium, a toxic element, is subject to limitations in e.g the EU and limits fertilizer applications of certain MGA types.

For more sophisticated applications of PA and its salts, these impurities need to be removed. For instance, the presence of iron or magnesium in phosphate salts leads to the formation of scales and sludges when they are dissolved in water, which is often required during application. Food applications are affected by the toxicity of arsenic, fluoride, uranium, and cadmium (see Table 4). PA itself, when used as an etching agent, also needs to be purer than MGA to avoid unwanted corrosion of the metals being treated, e.g., by any remaining sulfuric or hydrofluoric acid.

Table 4 Typical food grade specifications for wet process phosphoric acid.

The permissible concentration of each impurity varies across industries and geographies.

Impurity (anion/ trace metal)	Concentration (mg / kg)
Arsenic	1–3
Chloride	200
Fluoride	10
Nitrate	5
Sulphate	100–1500
Heavy metals as lead*	10
Colour (APHA)**	20

* the combined amount of heavy metals typically including lead, cadmium, and zinc, calculated as lead

** Colour is expressed on the American Public Health Association (APHA) colour scale, from 0 (distilled white water) to 500 (distinctly yellow water), with greater values indicating more impurities in the liquid.

MGA can be purified to achieve much greater purity. The standard technique for this purpose is solvent extraction, in which an organic solvent such as methyl isobutyl ketone (MIBK) or tributyl phosphate is combined with MGA. The solvent does not mix with the MGA. If the two liquids are vigorously agitated, creating a large contact surface, a large part of the PA migrates from the watery phase to the organic solvent, but impurities do so to a lesser extent. The intensive mixing tank has an outlet, and the phases are allowed to separate in the next compartment. The loaded solvent then comes into contact with an underflow of clean acid (bled out of the final stage) to remove additional impurities, and this step is repeated multiple times. In the final step, the acid is extracted with demineralized water (Figure 8). The number of steps defines the purity of the product, which is a much-purified PA. This process allows the selection of a higher or lower degree of purification, but higher purity comes at the expense of more steps and/or lower yields and larger recycling streams.

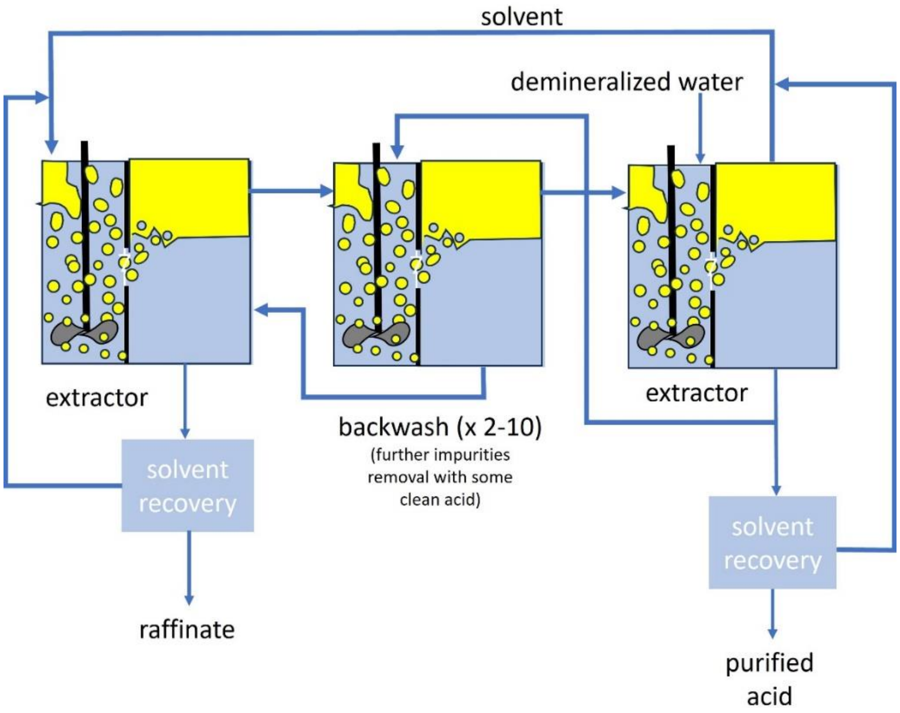


Figure 8 Purification of wet process phosphoric acid through the solvent extraction process - one intermediate stage is shown.

The underflow, called raffinate, is PA with virtually all the impurities and is normally fed to a larger fertilizer stream at the same site (typically 25 to 33% of the input PA). Both the raffinate and the product need to be stripped from the remaining solvent to prevent losses (usually solvents are somewhat expensive materials) and to keep the product pure.

This process is applied to medium diluted systems (25-40% P_2O_5); thus, a concentration step by heating is normally needed at the end, yielding a commercial grade of 75-85% H_3PO_4.

A minor route to obtaining purified PA involves the use of hydrochloric acid instead of sulfuric acid. This process does not benefit from the insolubility of calcium sulfate as in the sulfuric acid route; instead, PA and calcium chloride both remain in the solution. PA can be extracted from this mixture as a purified stream directly during the main reaction step, giving a purified phosphoric acid. Calcium chloride remains in the underflow of the extraction and can be discharged to the sea or dried to provide road deicing salt.

In most extraction technologies, the impurities are collected in the raffinate, which needs to be fed back into a larger fertilizer operation to eliminate it and valorize its high phosphate content. Alternatively, further extraction and treatment with more sulfuric acid may lead to a concentrated, relatively phosphate-poor waste stream ("total exhaustion process"), which is disposed of in a landfill.

Each MGA is unique, and no solvent extraction plant is identical to the others, although they follow the same principle. The machines used can be mixer-settlers or mixing columns.[14]

Fluoride, arsenic and sulfate are not amenable to this type of purification and need separate removal steps.

Fluoride is usually removed by steam stripping prior to the extraction process. It forms volatile compounds that are driven out of the acid with the steam. The vapors can be condensed into a fluoride-rich liquid containing fluorosilicic acid, which can be used, e.g., in aluminum manufacture, as a fluoride source to generate AlF_3 (cryolite), or to generate commercial fluorosilicic acid.

Arsenic, which is chemically similar to phosphorus, remains unchanged in the pure PA product and is subsequently removed in a separate step by sulfide precipitation. Unlike phosphate, arsenate can be reduced and precipitated to give arsenic trisulfide, a golden yellow solid that is removed by filtration. Antimony is also similar to phosphorus, just like arsenic, but cannot be removed as efficiently in this way. Normally, antimony levels are quite low in MGA and are not a concern.

Cadmium removal from MGA can be achieved together with arsenic removal by precipitation with hydrogen sulfide but is less efficient than arsenic removal. Residual Cd concentrations of 15 mg/kg may persist.[14] Cadmium removal from MGA remains a technical and economical challenge, but it is removed with other impurities during solvent purification.

Excess sulfate may be removed from MGA by the addition of calcium hydroxide prior to the extraction stage. Removal of sulfate from purified acid may require precipitation by barium, a more effective method of sulfate removal, to achieve low levels.

It is possible to extract a stream of PA product halfway and/or dispense with arsenic removal if technical applications such as metal etching are targeted, with less demanding specifications.

The PA obtained in this way is termed wet process purified acid (WPA or WPPA). Impurities are typically present at concentrations less than 50 mg/kg (major MGA impurities) and often less than 10 mg/kg or <1 mg/kg in the case of trace elements.

This process is not particularly environmentally unfriendly. Concentration by water evaporation and defluorination may result in the emission of some fluorides if the emission gas is not properly scrubbed, but otherwise, little emission or effluent occurs.

Alternatively, in direct competition with PA, it is possible to burn and hydrolyze P_4 to PA, which is subsequently termed thermal phosphoric acid (TPA). The advantage of this route is that all impurities except arsenic and antimony are removed during the P_4 process. Like in the WPA process, arsenic and, to a lesser extent, antimony can be removed. Sulfide treatment leads to TPA with a purity typically in the single-digit mg/kg range or even lower.

The route via P_4 is energy intensive and usually somewhat expensive. But local circumstances may dictate other outcomes. The production of P_4 for true derivatives (oxides, chlorides and sulfides) and for TPA as additional outlet is often practiced.

The preparation of TPA is uncomplicated - white phosphorus is burned in air to form phosphorus pentoxide (allowing energy recovery as steam), which is present as a fine mist and is absorbed into water in an absorption tower to yield 75-85% PA. In contrast, the WPA route is capex intensive and involves the disposal of a byproduct or waste.

Both types of acid are in direct competition for most applications. TPA is slightly purer and is a better starting point for accessing the highest purity grades of PA used in electronics (see below).

Alternative purification technologies include crystallization and membrane separation. Like the WPA process, these result in a purified acid, and an acid stream (underflow) collects impurities, both of which are approximately equal in volume. These methods are not as effective as solvent extraction in terms of the degree of purification per step. They are not performed on a commercial scale, except for crystallization to prepare ultrapure PA (see below).

A largely obsolete technology uses MGA as a feedstock, which is then neutralized with sodium hydroxide or carbonate to achieve the Na/P ratio needed for sodium (poly)phosphate salt production, in the form of a sodium mono/dihydrogen solution. As a consequence, most impurities precipitate and are filtered off. With some additional steps, this approach can produce feedstock for the production of near-food grade salts in a spray tower or rotary kiln.

The sections below describe the applications of such purified or pure PA alone and its sodium (Na), potassium (K), ammonium (NH_4), and calcium (Ca) salts (excluding animal feed applications, which are discussed in a separate section).

A related process is the so-called kiln process, P rock is heated in a rotary kiln with a reducing agent such as petcoke (coke derived from petrochemical operations), which causes local reduction of the rock to the elemental form (P_4). This product leaves the solid bed in the kiln as a gas and is immediately (re)oxidized to P_2O_5 in the air above the bed. This fine mist is drawn off and comes into contact with water to form a concentrated PA solution. The volatile metals cadmium (Cd), zinc (Zn) and lead (Pb) join the product, as do arsenic and antimony, and necessitate a purification step. Even though this process has been proposed for the preparation of fertilizer-grade acid, it holds some potential for higher-end applications. It has been under development under the name IHP since 1982 but has not experienced a commercial breakthrough. Its byproduct is calcium oxide, which has potential for use in construction applications.

3.2 Phosphoric acid properties and uses

Pure PA is a colourless, somewhat viscous liquid. As explained above, it is supplied as a highly concentrated solution, e.g., 75, 80 or 85%, in water. It is nontoxic but quite corrosive and harmful via, e.g., eye contact. It is transported in bulk liquid containers or, less frequently, intermediate bulk containers or drums.

Its main applications are described in the text below and in Figures 9 and 10. It is used in a variety of end uses. In addition, PA is widely applied as a raw material for the preparation of high-purity phosphate salts (section 3.3).

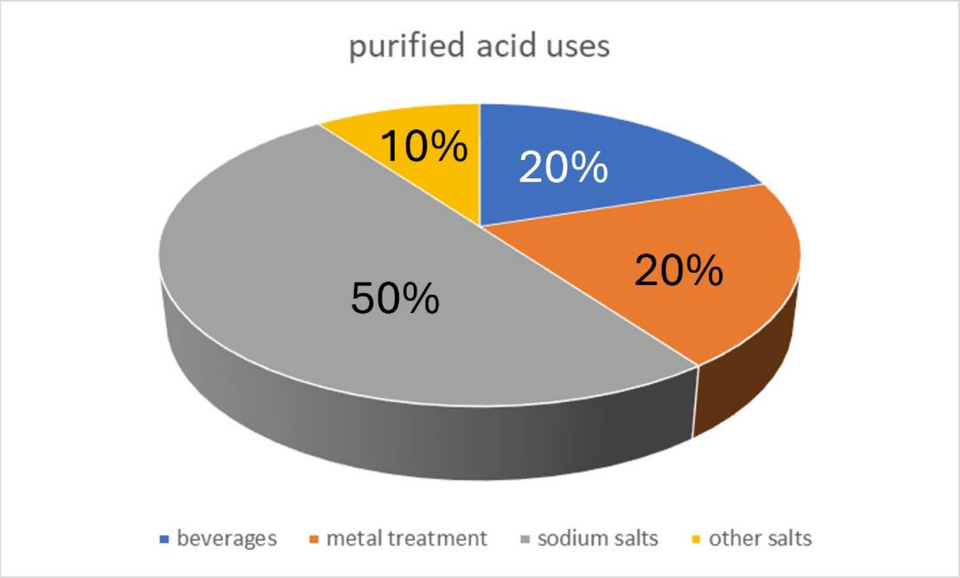


Figure 9 Purified phosphoric acid uses. It may be combined with sodium and other salts to produce phosphoric acid salts, or it may be used directly in the food and beverage industry (primarily in beverages) and for metal treatment such as etching.

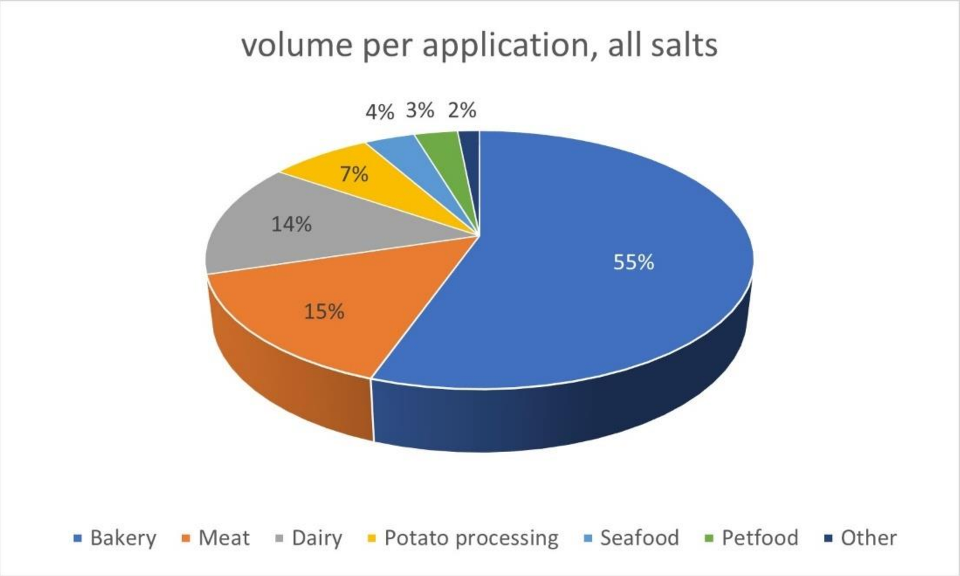


Figure 10 Typical European split over applications; all food-grade phosphates.

3.2.1 Direct applications of pure phosphoric acid

Purified phosphoric acid is applied in metal treatment, e.g., on car body steel to add a protective coating or to brighten aluminum surfaces. This is a major application of pure PA, accounting for a quarter of its total volume produced worldwide. Purity is important; for example, even trace amounts of sulfuric acid and hydrofluoric acid cannot be present, unless these acids are required for the application (e.g., for aluminium brightening, a mixture of phosphoric and sulfuric acids is used).

Pure PA is also used in soft drinks, such as cola beverages, because it adds tartness to these otherwise quite sweet-tasting drinks. Such applications require food grade standards, with limits set on heavy metals (lead, mercury, cadmium), arsenic, and fluoride.

Food-grade PA is the starting point for a large range of salts used in food applications. In addition, several applications in cleaners and detergents exist.

3.2.2 Electronic-grade PA

Crystallization can be used as an additional step starting from pure PA to achieve ultrahigh-purity PA for electronics applications. In this approach, concentrated PA is cooled until it reaches saturation, after which crystals of H_3PO_4 separate (several varieties exist). These crystals are removed with, e.g., a centrifuge and lightly washed with pure water. Most impurities tend to be rejected when crystals form, so these impurities remain in the mother liquor. When the crystals are redissolved in pure water, purer PA is obtained. When enough crystallization cycles are performed in series, acids with an impurity level of <0.1 and eventually <0.01 mg/kg are obtained. These acids, when blended with other mineral acids, are used in the etching of microelectronics (microchip production). The purity requirements are strict because the slightest impurities can disturb the ultrasmall pattern on the microchip and cause defects.

TPA, which is somewhat purer, is the preferred starting material for producing electronic-grade acid; although WPA can also be used, it requires more steps to achieve the desired purity.

3.3 Phosphate salts for food and technical applications

This important class of phosphates includes phosphates of sodium, potassium, calcium and magnesium, which are white powders that are soluble in water (except for dicalcium and tricalcium phosphate). There are no significant safety risks associated with these phosphates, except that some form alkaline solutions (for which skin and eye irritation are possible).

3.3.1 Sodium phosphates

Sodium phosphates are the most important food grade salts. There are three types of orthophosphates, two types of pyrophosphates, one tripolyphosphate, and one true polyphosphate; sodium is generally present as the cation, but sometimes potassium, calcium, or ammonium are used. Moreover, some specialty mixed phosphates exist. These salts are found both in anhydrous form and in various hydrates or lightly hydrated forms.

All sodium phosphates are produced by neutralizing PA and a sodium source (high-purity carbonate or hydroxide) to achieve the desired Na/P ratio, after which the solution is subjected to thermal treatment to obtain a dry powder in a rotary kiln or a spray tower at 250-450 °C.

These salts are specified as follows:

- MSP, monosodium phosphate (NaH_2PO_4 – 59% P_2O_5)
- DSP, disodium phosphate (Na_2HPO_4 – 50%)
- TSP, trisodium phosphate (Na_3PO_4 – 43%)
- SAPP, sodium acid pyrophosphate ($Na_2H_2P_2O_7$ – 64%)

- TSPP, tetrasodium pyrophosphate ($Na_4P_2O_7$ – 53%)
- STPP, sodium tripolyphosphate ($Na_5P_3O_{10}$ – 58%)
- SHMP, sodium hexametaphosphate (approx. $NaPO_3$ – 68-70% P_2O_5)

MSP and DSP are used as buffer agents (acidity stabilizers) and emulsifiers in meat and dairy processing.

SAPP is used in baking powders as a solid acid for chemical leavening. It is coupled with a source of carbon dioxide, usually sodium bicarbonate. Both materials are solid and unreactive when dry. The mixture is added in small quantities to baking flour. When this mixture is wetted to make a dough, the phosphate and bicarbonate start to react and release carbon dioxide gas, which creates bubbles in the dough and results in the characteristic porosity of baked goods. In this application, it is a faster alternative than yeast, which also generates carbon dioxide to create the structure of bread, but yeast reacts more slowly and requires careful temperature control to avoid damaging the organism.

The reactivity of SAPP is controlled by careful (micro)addition of impurities such as calcium or magnesium, which decrease the rate of the reaction with carbonate. This once more underpins the need to purify PA to prepare such phosphates—if SAPP is produced directly from MGA, it contains much more calcium and magnesium than desired for this application and will not react in the intended fashion.

Another equally important use of SAPP is in potato processing. Peeled and cut potatoes tend to turn black or blue when exposed to air, which is greatly enhanced by the presence of iron ions in the water used during potato processing. SAPP captures (sequesters) these ions and thus prevents this undesirable colour formation.

TSPP is used in pet food, as well as in meat and seafood processing.

STPP is used in meat and seafood processing. It is a powerful agent that helps to retain the structure and moisture of meat during processing, such as during cooking, and it has additional preservative qualities.

STPP is historically known to be a key ingredient in detergents. It has a combined role as an antiscale agent, a dust dispersing agent and a pH adjustment agent. Because of this combined functionality, it is called a detergent builder. The STPP clearly outperforms any combination of alternatives. However, in the past, used detergents were discharged into the environment via sewer systems, where they act as nutrients (after all, phosphates are also fertilizers). If such wastewater is not treated adequately, lakes, rivers and canals become overfertilized, which leads to the growth of green algae (a process called eutrophication using up all available oxygen in the water). This causes fish and invertebrates in the water to die. Even though adequate sewage treatment can remedy this side effect, phosphates were largely phased out of detergents in 1990-2015. Phosphate removal from sewage is still necessary because humans currently excrete the majority of sewage phosphate via the food chain.

SHMP is a highly polymerized phosphate with a much longer chain than those in the polyphosphates described above. It is used in cheese and dairy processing, toothpaste, and in boiler water treatment as an antiscale agent. It is prepared at higher temperatures than the other phosphates in this class in a specifically designed melting oven operating at approximately 800 °C. The melt falls onto a cooling drum, and the solidified product, a glassy coarse material, is milled to afford a white powder. Several varieties exist with medium or long polyphosphate chains.

3.3.2 Potassium phosphates

Potassium analogs of sodium salts exist, most notably M/D/TKP, TKPP and KTPP (where K replaces S in the sodium abbreviations, but the types are otherwise identical). The applications of these salts are diverse but are mostly food applications, and the choice of K analogs is based on solubility or compatibility issues, or to achieve sodium-poor foods. Production technologies are similar to those applied for sodium salts.

3.3.3 Calcium phosphates

Calcium phosphates include monocalcium phosphate (MCP) and dicalcium phosphate (DCP). Anhydrous and hydrated forms of both are commonly encountered.

Calcium phosphates are usually prepared by mixing pure PA and a source of calcium (high-purity calcium carbonate, hydroxide or oxide) in a mixing vessel equipped with a strong stirrer. The reaction between the acid and the calcium source generates enough heat to dry the reaction mixture without additional heating. The reaction product is a dry white powder, which is cooled and then stored and sold. See also the section 3.4 on feed phosphates for details about an important application of lower-purity calcium phosphates.

MCP is applied in bakery formulations as an acid component in carbon dioxide-generating formulations (for fast and controlled leavening). This same functionality is found in the sodium salt SAPP. DCP is often used as an abrasive in toothpaste, as a dihydrate (DCPD)—which corresponds to the largest application of calcium phosphate—or as an excipient (carrier/bulk mass) in pharmaceuticals (pills). Tricalcium phosphate is used as an anticaking agent in, e.g., powdered sugar.

A fine form of tricalcium phosphate is used as a dispersant in polystyrene production, which is a rare nonfood application of a food-grade product.

These phosphates can also be used as dietary sources of calcium in fortified foodstuffs and drinks.

Mono- and dicalcium phosphates are significant but minor components of the class of food-grade materials in terms of volume, but they are the leading products in the feed phosphate market (see section 3.4 related to this topic).

Calcium pyrophosphates such as calcium acid pyrophosphate, $CaH_2P_2O_7$, are minor members of this class and are used in bakeries when low sodium levels are needed.

TL tubes contain luminescent materials based on calcium apatite, a calcium phosphate. Small quantities of impurities, such as antimony and manganese, are incorporated into the crystal lattice (doping) to make the material luminescent: it emits visible light upon excitation by ultraviolet radiation.

3.3.4 Other phosphates

Food-grade ammonium phosphates are used, e.g., as yeast nutrients.

Pure monoammoniumphosphate (MAP) is used widely in specialized agricultural and horticultural applications as a liquid fertilizer (drip irrigation). It needs to be pure to avoid scale formation in the dripping system. Food-grade specifications are not mandatory, and this application allows some flexibility in the impurity profile.

Magnesium phosphates are a minor species with applications in, e.g., bakeries.

Monosodium fluorophosphate is used in toothpaste as a stable source of fluoride.

Sodium aluminum phosphates (SALPs) (a class of related salts containing sodium, aluminum oxide, and phosphate) are minor products that are especially popular in the US. The acidic compound $NaAl_3H_{14}(PO_4)_8 \cdot 4H_2O$ is an alternative to SAPP and MCP in bakeries. Alkaline compounds are used in cheese processing.

Aluminum monophosphate $Al(H_2PO_4)_3$ is a minor product used in ceramics. Aluminum metaphosphate and tripolyphosphate are also niche products.

Food-grade salts may be combined into so-called blends, physical mixtures of several powders tailor made for a specific application. Several dozen varieties of such blends exist.

3.3.5 Lithium iron phosphate

Lithium-ion batteries (LIBs) consist of four major components: an anode (usually a form of graphite), an electrolyte solution (with $LiPF_6$; see section 5.4 on PCl_5), a separator, and a cathode.

To date, lithium cobalt oxide ($LiCoO_2$, LCO), which is an established material with a high Li storage density, has mainly been used as the cathode for LIBs. However, this material also has a nonzero risk of thermal runaway reactions, leading to LIBs catching fire. This is a significant cause of severe accidents, especially in larger systems such as full electric vehicles. The life span of this material is also not impressive.

Both of these concerns are addressed by using lithium iron phosphate as the cathode material. Even though this material has a somewhat lower theoretical power density, its safety advantages make it promising to become the leading cathode technology for cars and small devices, a trend that started in China, where this technology is widely implemented. It is also less expensive to produce and does not require cobalt, the sourcing of which is controversial. In theory, LFP also has a longer lifespan than LCO.

Cathode materials, including LFP, need to be quite pure to avoid conductivity and local resistance issues. WPA and TPA are generally of sufficient purity to satisfy most LFP specifications.

LFP is expected to become a major consumer of WPA/TPA in the mid-term future, although it is expected to constitute only 2-3% of the total market for PA (all kinds, including fertilizer grade). Several phosphate mines and PA plants are being opened, aimed solely at the LFP market.[15]

3.4 Feed phosphates

3.4.1 Uses and technologies

Phosphates play an essential role in the chemistry of life. The most important use of phosphate is as a fertilizer for plant growth. However, animals (and humans) also need phosphate to grow and sustain adult life.

Animal husbandry involves raising animals for meat or dairy products. Like all vertebrates, poultry, cattle, and pigs need phosphate to grow and remain healthy, as it supports the formation of a skeleton and is used in DNA and the energy cycle.

Unlike humans, who need higher amounts of phosphate when growing but just a maintenance dose as adults, most animals grown for meat need a continuous, significant phosphate supply while growing. Once the animal nears maturity, it is slaughtered. Exceptions to this are dairy cows and broiler chickens, but these animals also need phosphate in their diet. In fact, every type of farm animal requires a different, carefully balanced feed.

Plant-based diets contain phosphate, but it is often present in a form that is indigestible: phytates or phytic acid (Figure 11). Ruminants (cows) may digest a small part, but monogastric animals (pigs, chickens) do not digest it at all.

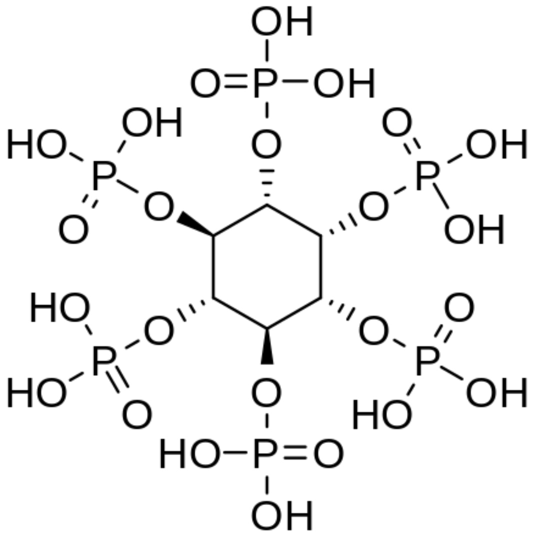


Figure 11 Phytic acid is a dihydrogen phosphate ester of inositol with six phosphate molecules, also called inositol hexaphosphate. It is the major form of organic phosphate present in the seeds and tissues of plants.

When phytic acid is not digested by an animal, nutrient deficiency and elevated phosphate levels in the animal's feces occur, which may cause environmental harm. Limiting the phosphate content of manure is a serious issue in areas with high animal husbandry farm densities.

A stated goal of animal feed producers is to increase the digestibility of phytate by adding the enzyme phytase, which helps to break down phytic acid.

In addition, digestible phosphates are added to animal feed to provide a reliable and digestible source of phosphate.

Such feed phosphates, termed inorganic feed phosphates (IFPs), are almost exclusively calcium phosphates. Traditionally, dicalcium phosphate (DCP) has dominated the market, but monocalcium phosphate (MCP) has gained popularity because it is more digestible. A mixed MCP-DCP product also exists (MDCP). Trends away from DCP – which is especially prominent in the US – are based on the digestibility (availability to the animal) of this material, which is 60-80% for DCP but 80-90% for MCP. There are two advantages to this approach: less material is needed, and the phosphate content of the manure (where the undigested part ends up) decreases.

Generally, the P_2O_5 content of these materials, which are often partially hydrated, ranges from 40 to 50%.

A more digestible form of DCP, dicalcium phosphate dihydrate, is also available, but its digestibility is not the same as that of MCP.

Technologies usually involve mixing calcite or calcium hydroxide with purified PA. If the PA is concentrated, the reaction heat eliminates the remaining water. A mixer-stirrer setup yields (M)DCP without the need for external heat input, and the process is self-drying. This type of reactor needs a heavy stirrer and engine to keep the product moving in the end when it has formed a powder.

Digestion of phosphate rock with hydrochloric acid for feed phosphates production is also observed, and is similar to the process used for hydrochloric acid to produce WPA (paragraph 3.1). DCP precipitates upon the addition of calcite and is filtered, after which a calcium chloride solution (brine) remains; this mixture can be dried to a solid form or discharged at sea. The absence of a saltwater body near the production facility may lead to closure of the plant, as the discharge of brine into fresh water has come under increased scrutiny.

Alternatively, phosphate rock is heated with a source of sodium (e.g., sodium carbonate), which removes fluoride in the form of a gas and increases the digestibility of the product. This product is called defluorinated feed phosphate (DFP - $Ca_4Na(PO_4)_3$). It tends to be inexpensive, but its digestibility is moderate. All the other impurities remain in the material. DFP is a product with a modest market share.

The abovementioned products and ammonium phosphates are also used in aquaculture, which is a growing sector.

The product, and thus the acid and the calcium source, have less stringent limits in terms of impurities than food-grade phosphates. A typical feed phosphate specification is provided in Table 5.

Table 5 Legal animal feed grade specifications for phosphates in the European Union.

Impurity (anion/ trace metal/organics)	Concentration (mg / kg)
Arsenic	10
Fluoride	2000
Cadmium	10
Lead	15
Mercury	0.1
Dioxins TEQ*	0.75 ng/kg
Dioxins + Dioxin-like PCBs TEQ	1 ng/kg
PCBs** not-dioxin-like	10 µg/kg

*TEQ: toxic equivalency values, a weighted quantity measure based on the toxicity of each member of the dioxin and dioxin-like compounds.

**PCBs: Polychlorinated biphenyls.

Dioxins are included in this list because of past issues with these substances in the food chain in Europe involving their accumulation via livestock.

As seen by comparing the fluoride and metal specifications with food-grade limits (see Table 4), this sector has less stringent specifications, especially for fluoride (10 mg/kg in food phosphates, which is 200-fold lower).

4 P_2O_5 – phosphorus pentoxide, polyphosphoric acid, and other phosphorus oxides

- P_2O_5 is a white powder obtained by burning white phosphorus.
- It is used to remove water molecules during chemical and pharmaceutical synthesis.
- It is the starting material for many phosphate-based chemicals with diverse applications.
- It is a starting material for flame retardants, but also for pharmaceuticals and vitamins
- With a small amount of water, a liquid called polyphosphoric acid is formed, which has similar functionality. The liquid form is helpful when performing reactions, e.g., during mixing.

4.1 General

This compound is a hygroscopic (water attracting) white powder that consists of P_4O_{10} molecules and has an adamantane, cage-type structure (Figure 12). The related compounds P_2S_5 / P_4S_{10} have a similar structure. Phosphorus pentoxide (P_2O_5) is the usual formula given when describing the compound and its applications, even though P_4O_{10} represents its actual molecular makeup. It contains 44% P.

Because of its ability to attract water and form a mineral acid, it is classified as a severe irritant for the skin and eyes. It is nontoxic.

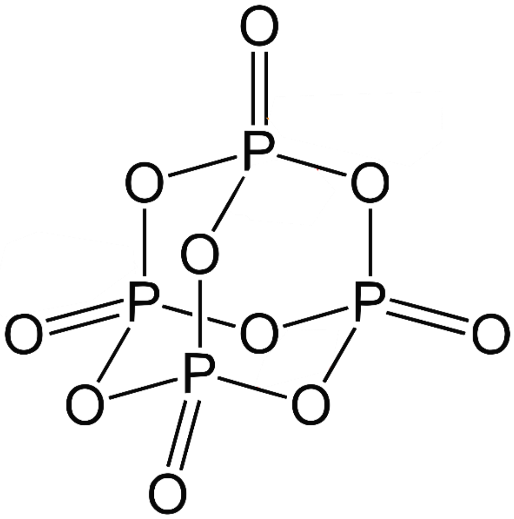


Figure 12 Phosphorus pentoxide is a P_4O_{10} molecule with an adamantane, cage-type structure.

4.2 Technology and production

The compound P_2O_5 is generated by burning white phosphorus in air, usually via a spray tower. Because this material strongly attracts water and has a high probability of creating sticky deposits in a production unit, the incoming air needs to be rigorously dried. The offgases are cooled in a cooling tower, where the product desublimes into a white powder.

P_2O_5 and P_2O_5

Confusingly, the term P_2O_5 is not just the common term for phosphorus pentoxide but also used to describe the phosphate content of many phosphates and phosphate ores, even though there is no free P_2O_5 in phosphorus fertilizers. The *compound* P_2O_5 has nothing to do with this, but it can formally be regarded as being a constituent part of such compounds – e.g., calcium orthophosphate $Ca_3(PO_4)_2$ can be regarded as being composed of the single oxides CaO and P_2O_5. These two oxides are very reactive toward water and do not occur in nature, but they form an inert mineral calcium phosphate together.

The production is straightforward, with 100% conversion and no waste or byproducts. There is very little emission if proper off gas scrubbing is implemented to remove traces of P_2O_5 mist, resulting in nearly 100% conversion. Wet scrubbing of the very fine fraction of the product that remains in the off gas can be used to produce polyphosphoric acid (PPA) as a coproduct.

Energy from incineration, which is quite exothermic, can be recovered in the form of steam by inserting a heat exchanger in the oxidation tower. This is similar to TPA production.

There is generally one grade of product, but the desublimation temperature trajectory affects the particle size and shape, which determines its flowability characteristics.

The material is nontoxic but is corrosive to the skin and reacts vigorously with water.

Unlike the method for producing phosphorus sulfides and chlorides, this production technology does not offer the opportunity to remove the arsenic contained in P_4, which remains in the product.

4.3 Applications

The product has four main uses:

- dehydration agent e.g. in pharma applications
- raw material for phosphate esters

- precursor for ammonium polyphosphate flame retardants
- precursor for polyphosphoric acid

The dehydration and phosphate esters segments can also be served by polyphosphoric acid (see below), which in terms of functionality can be seen as a liquid form of P_2O_5.

4.3.1 Dehydration agent

Phosphorus pentoxide is the most hygroscopic (water attracting) material known. When left exposed to moist air, this material starts to become sticky within minutes, after which it gradually becomes a liquid of polyphosphoric acid and then phosphoric acid. This characteristic is exploited in organic chemistry to forcibly extract water molecules from one or more reagents. This is a useful step in linking molecules to create dimers or polymers or to transform linear molecules into ring structures.

A prime example of such a ring closure process is the production of quinacridone (see the section on polyphosphoric acid below).

4.3.2 Phosphate esters

Phosphate esters are organic derivatives of phosphoric acid, H_3PO_4. These compounds share the general structure of the central phosphate unit – PO_4^{3-} – but one, two or three of the protons (hydrogen atoms) are replaced by an organic group (Figure 13). The resulting compounds are thus classified as mono- di- and triesters.

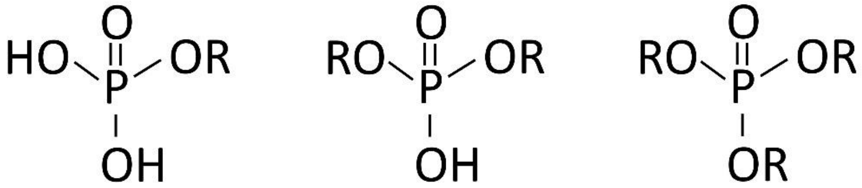


Figure 13 Structure of monoester phosphate, diester phosphate and triester phosphate. R denotes an organic functional group.

The reactivity of P_2O_5 with alcohols, a prime raw material for this class, is as follows:

3 ROH + P_2O_5 -> H_2RPO_4 + R_2HPO_4

Commonly used alcohols for this reaction are tridecanol, 2-ethyl hexanol and nonylphenol, as well as their ethoxylated varieties. The use of nonylphenol is being phased out in the EU because of (eco)toxicity concerns.

Di(2-Ethylhexyl) phosphate is often abbreviated as DEHPA and is a major product in this class. It is used as extraction agent for metals. Many medium-chain-length linear or branched alcohols are also used.

The products are so-called acid esters, which retain one or two acidic protons and thus have properties between those of phosphoric acid and purely organic triesters. Among many other properties, they have residual, mild acidity because of the remaining protons.

It is impossible to obtain triesters or exclusively mono- or diesters in this way. To form triesters, $POCl_3$ is the starting material of choice. Some triesters may be prepared from P_2O_5 and alcohols but only in small amounts: the reaction involves the concurrent release of a water molecule at the same site, which hydrolyzes P_2O_5 to form a P-OH unit. In practice, it is impossible to keep these water molecules away from the reactive P_2O_5, so mono- and diesters are formed at the same time. By carefully adjusting the reaction conditions, it is possible to shift the outcome somewhat toward the formation of diesters or monoesters by adding some water or using PPA. The nature of the alcohol used also plays a role. Purification may allow the isolation of pure mono- or diesters.

A less commonly used route to prepare triesters from P_2O_5 and ethers exists.[16] The use of ethers, especially the linear ones needed here, is generally challenging in industry because of safety issues. The most common ester produced in this way is triethyl phosphate (TEP), which is used as a catalyst in acetic anhydride production, as a versatile solvent, as a peroxide stabilizer, and as a plasticizer/flame retardant in plastics. See section 5.3, which focuses on $POCl_3$, for more information about phosphate triesters, including another route toward TEP.

In terms of applications, acid phosphate esters are likely the most diverse group of organophosphorus compounds. There is no single dominant application, and many varieties exist based on the different alcohols used. Compared with alternatives such as carboxylic acids, these materials are relatively stable and robust. Generally, they are preferred over alternatives under nonstandard conditions such as alkaline solutions or elevated temperatures.

The applications include the following:

- Antistatic agents, e.g., in the spinning of fibers
- Specific, mild acids for cleaning and polishing
- Antiscaling agents
- Corrosion inhibitors (sequestering of metals) and antioxidants in high-performance lubricants
- Curing (hardening) of resins
- Surfactants, e.g., in industrial cleaning formulations for use in extreme conditions or as mud dispersants for use in drilling

- Emulsifiers
- Flotation agents
- Dispersing and wetting agents, e.g., for use in drilling mud
- Defoamers
- Solvents
- Antiwear agents for metal working fluids
- Hydraulic oil additives
- Resin curing agents
- Extraction agents, e.g., DEHPA for uranium and other metals

Compounds in this class include the following:

di(2-ethylhexyl) phosphate (DEHPA)
amyl acid phosphate
butyl acid phosphate
isooctyl acid phosphate
octylphenyl acid phosphate
tridecyl acid phosphate

The production and use of these materials occur mainly in the industrialized world (the US, the EU, and East Asia).

4.3.3 Dehydration

A minor portion of P_2O_5 is used to extract water molecules during vitamin B6 synthesis. This is a rare case in which a P derivative is not needed for its P content. This material can also convert amides into nitriles during pharmaceutical synthesis.

4.3.4 Ammonium polyphosphate

P_2O_5 is a key ingredient in the flame-retardant ammonium polyphosphate (APP), a white solid. Actually the product class APP consists of a range of medium- and long-chain polymerized ammonium phosphates. The short-chain varieties are water soluble, whereas the long-chain varieties are water insoluble. This material is used in intumescent (char and foam forming) flame retardant formulations, e.g., for polyolefins and polyurethane. It is prepared by reacting ammonium orthophosphates with P_2O_5 and gaseous ammonia (or a precursor) at high temperatures and pressures.

4.4 Polyphosphoric acid (PPA)

This viscous, colourless liquid can be considered a liquid variety of P_2O_5, with some identical applications, especially in drying/water extraction.

> PPA and PPA
>
> Confusingly, the acronym PPA is used in industry to mean both polyphosphoric acid and purified phosphoric acid. The latter is just a pure grade of ordinary phosphoric acid. In this text, the second use of the acronym is avoided. Instead, in this document, the terms WPA (wet phosphoric acid) and TPA (thermal phosphoric acid) are used to describe essentially the same grade of pure phosphoric acid prepared via very different routes, and the term PPA is reserved for polyphosphoric acid.

Polyphosphoric acid can be regarded as a solution of phosphoric acid in a small amount of water. At any concentration above approximately 90% H_3PO_4, the individual H_3PO_4 units tend to polymerize. From a molecular point of view, PPA consists of the molecule $H_{n+2}P_nO_{3n+1}$, where $n > 1$. This molecule is composed of phosphate units that share one oxygen atom, forming a P-O-

P chain with an =O and -OH group on each P atom. These chains are polycondensated phosphoric acid, i.e., phosphoric acid groups linked together by splitting a water molecule.

Figure 14 shows the variation in the PPA chain length with concentration. These and other species occur in equilibrium with each other in polyphosphoric acid. The mean chain length increases with increasing PPA concentration.

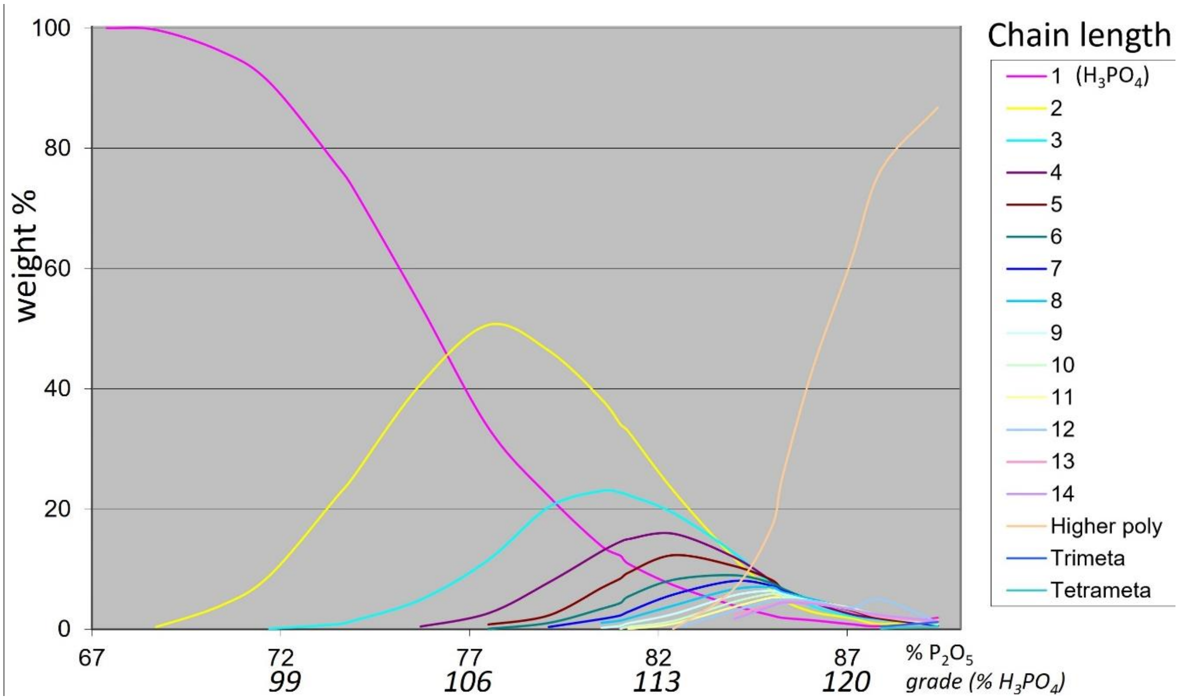


Figure 14 Polyphosphoric acid chain length varies as a function of the P_2O_5 content (% mass) and the grade number (% H_3PO_4 by mass in solution), on the x-axis. Longer chain length implies more interlinked HPO_3 units with PO_3H_2 end groups. The chain length increases when the solution contains less water.

The predominant composition of $H_4P_2O_7$ is sometimes referred to as pyrophosphoric acid.

PPA is supplied with a range of strengths, with an increasing tendency to extract water at higher grades. These characteristics are indicated by a number corresponding to the hypothetical H_3PO_4 content; e.g., grade 116 is a strongly dehydrating liquid. A number higher than 100 indicates that the sample is polycondensed and contains very little free H_3PO_4.

PPA tends to increase in viscosity with increasing strength, and some compounds are prone to crystallization at room temperature. Storage and transport require heating for some grades.

4.4.1 Technology and production

PPA can be prepared by dissolving P_2O_5 in water or ordinary phosphoric acid under vigorous stirring. The synthesis occurs with 100% yield and generates no waste.

An alternative production route is the removal of water from phosphoric acid. The obtained product becomes increasingly hygroscopic as water is removed, so further removal of water becomes increasingly difficult. Additionally, the boiling point increases dramatically. The preparation of the highest PPA grades involves heating a highly acidic liquid to 400-500 °C, which is challenging in terms of reactor materials.

In one method, heating is performed in a conductive carbon pot with a central carbon electrode. When a current passes through the liquid, it becomes hot, and water evaporates until the desired strength is reached. In practice, this process is operated at the desired strength in the crucible, with continuous PA feeding and product removal[17]

Another method involves a standard type of spray tower (Figure 15), through which hot gases, e.g., from a natural gas flame, are passed. This results in water evaporation, and the polyphosphoric acid is collected at the bottom.[18]

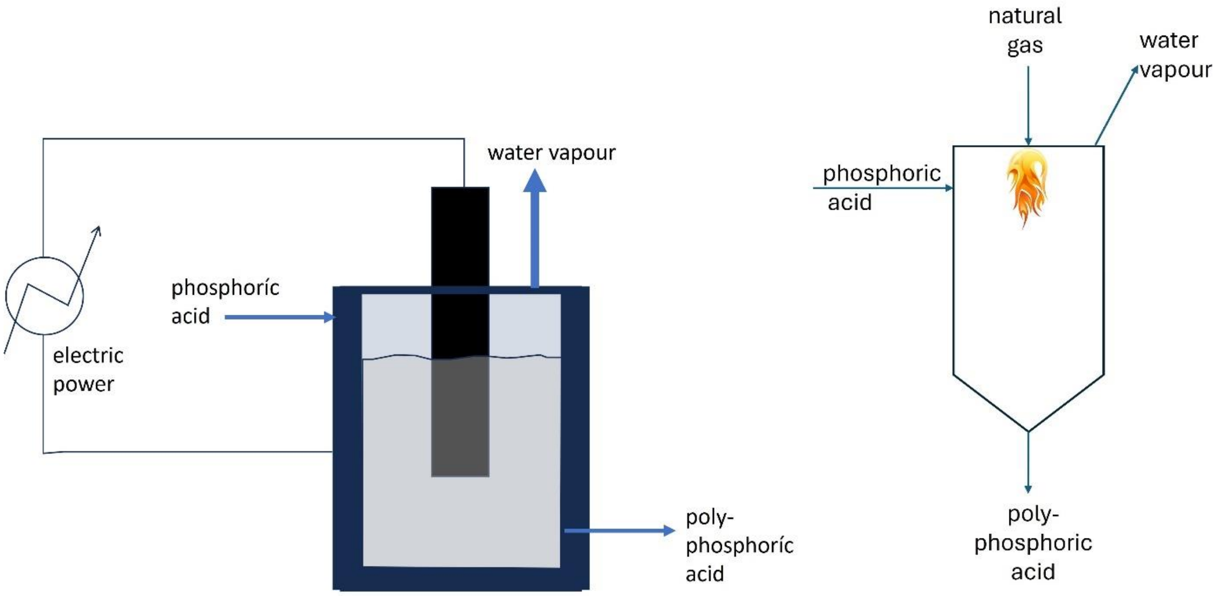


Figure 15 An electroheating crucible for PPA production and a tower concentrator. Excess water vapour is removed through a vent at the top of the equipment.

4.4.2 Applications

4.4.2.1 Polymers and dyes

Like the related P_2O_5, PPA – especially at higher grades – retains much of its water-attracting characteristics. This material can thus be used in so-called reactive baths, where PPA acts as (part of) the solvent while simultaneously extracting water from the reaction mixture, thus linking individual molecules or closing rings.

A typical application is the production of quinacridone pigments, which occur in many shades of dark yellow and from red to purple. These pigments are generated in a reactive bath of PPA[19,20] by double ring closure involving the removal of water (Figure 16).

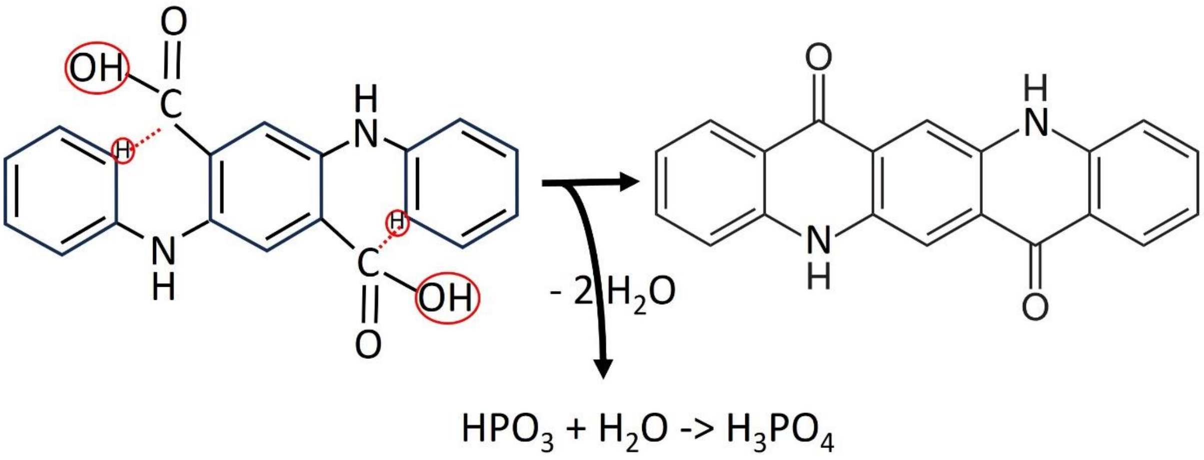


Figure 16 Quinacridone production with polyphosphoric acid starting from 2,5-dianilino-terephthalic acid. The groups in red circles are extracted – as H_2O – due to the hygroscopic nature of polyphosphoric acid. The extraction of the -OH group of the carboxyl unit and the hydrogen atom directly across the C_6 ring results in the closure of two rings in the molecule (red dotted lines; these occur after extraction of the water molecule). For clarity, the polyphosphoric acid is represented as its longest possible chain, HPO_3.

4.4.2.2 Pharmaceuticals (e.g., antidepressants)

For pharmaceutical production, PPA is often applied in ring closures (as described in the previous paragraph) by similarly extracting a water molecule from between reactive groups of a mid-sized molecule.[21] Quetiapine is an examples of such a product.

4.4.2.3 Catalysts

PPA is used to prepare solid phosphoric acid catalysts, which are used in polymerization reactions in refineries.

4.4.2.4 Fibers

Ultrastrong polyamide fibers (related to Kevlar) are sometimes prepared in a reactive bath of PPA, such as phenylene bisoxazole polymers[22]

4.4.2.5 Asphalt

PPA is also an asphalt additive, especially in the US. In areas with climates with large temperature differences, roads can experience cracks in the asphalt due to thermally induced stress. Depending on the nature of the tar used in the asphalt, adding PPA can improve the cracking resistance of the asphalt.[14]

4.5 Lower oxides of phosphorus

The oxides of lower valence states of P are not as straightforward as those of P^{5+}. The oxide of trivalent phosphorus, P_4O_6, exists but is difficult to prepare. The oxide of P^+, P_2O, has not been observed.

4.5.1 P_4O_6 - phosphorus trioxide

The oxide of trivalent phosphorus is a colourless liquid at slightly above room temperature that solidifies to a white solid at 24 °C. It has the same structure as P_4O_{10} but without the four oxygen atoms at the apices (Figure 17). It is the anhydride of phosphorous acid but cannot be produced from this acid. Phosphorous acid is discussed in the PCl_3 chapter, because it is usually generated from this compound and is present as an intermediate in many synthesis routes starting from PCl_3.

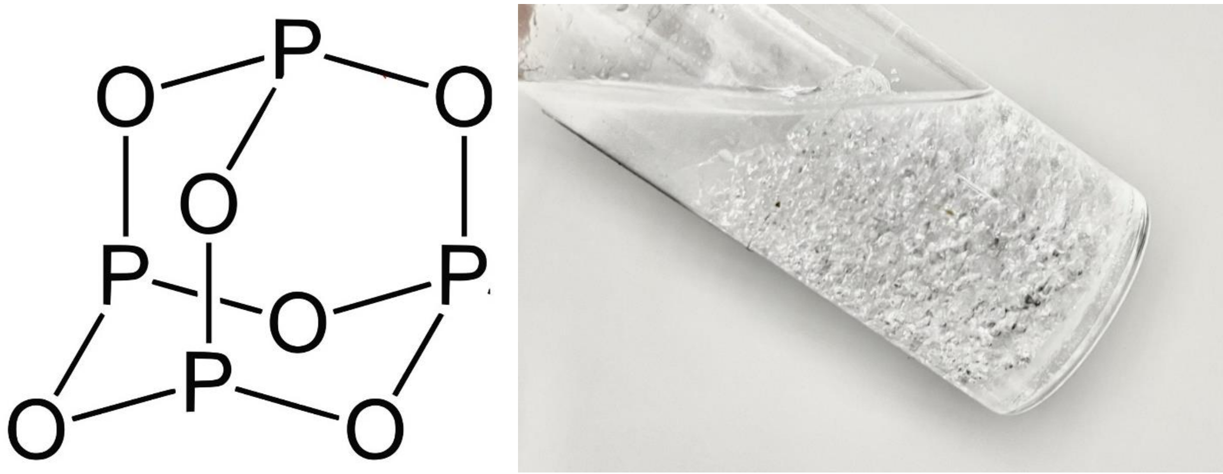


Fig 6 Phosphorus trioxide structure. The compound P_2O_5 (more precisely P_4O_{10}) has the same structure, but with four extra oxygen atoms at the phosphorus corners sticking out. Right: phosphorus trioxide solid and liquid at 23 °C.

The literature describes P_4O_6 as toxic, but this may be because residual white phosphorus is present in impure products from pilot operations. It reacts violently with water to give phosphorous acid, and tends to decompose when the reaction is not carefully controlled.

P_4O_6 can be used in the production of phosphonates, including glyphosate (essentially derivatives of phosphonic acid), but has additional anhydrite reactivity. Its production from the oxygen in air and P_4 would open a synthetic pathway to this important branch of organophosphorus compounds without the introduction and subsequent removal of chlorine atoms, as is currently the case in synthesis routes involving PCl_3. This approach could offer advantages in terms of cost and byproduct/waste formation.

However, P_4O_6 is thermally unstable and degrades into various suboxides and mixed P(III)-P(V) oxides starting at 300 °C. Given that its most promising synthesis involves burning P_4 in air under carefully controlled conditions and reaching much higher temperatures, producing this material in any reasonable yield involves rapid quenching of the reaction gases.[23] Even under optimized conditions, it is difficult to increase the yield beyond 70% without specific measures. It remains an industrialization challenge and is not prepared commercially. This material can also occur as an end product during organic synthesis.[24]

4.5.2 Lower oxides of phosphorus

The oxide PO exists as an unstable species (radical). Interestingly, it is the most abundant phosphorus-containing molecule in outer space.[25] Likewise, PO_2 is observed during some gas reactions at high temperatures.

The oxide P_2O, formally the anhydride of hypophosphorous acid (section 7.4), does not exist, although its existence has long been suspected.[26]

In laboratory manipulations with white phosphorus or PCl_3, yellow, orange, or brownish gummy substances are sometimes observed; these substances are described as poorly defined phosphorus sub(hydr)oxides (LOOPs, Lower Oxides Of Phosphorus). This remains a poorly explored area of phosphorus suboxides.

5 PCl_3 and its derivatives

5.1 General information and technology

Phosphorus trichloride (PCl_3) (Figure 18) is a colourless liquid. The possibility of selectively oxidizing and chlorinating white phosphorus to form a molecule with a single P atom in the +3 valence state, PCl_3, is the reason for the abundance of this chemical as an intermediate in organic phosphorus chemistry. It contains 22.7% P.

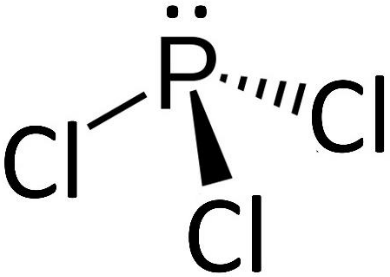


Figure 18 *Fig 1 PCl_3. The molecule has the shape of an umbrella; on the apex is a lone pair of electrons, i.e. these electrons do not take part in a chemical bond but are available for this.*

PCl_3 reacts violently with water, yielding hydrochloric acid and phosphorous acid. It is toxic and corrosive.

PCl_3 is generated by reacting P_4 with chlorine gas in a spray tower or, more commonly, a bath of PCl_3, where additional P_4 and Cl_2 are added continuously to an existing amount of PCl_3; the newly formed product boils off due to the exothermic reaction. The conversion is 100%, the reaction is uncomplicated, and the process generates very little waste. Depending on the setup, some arsenic impurities may be removed; the bath setup emits pure PCl_3 in a self-distilling fashion, leaving traces of arsenic and organics in the liquid, where it accumulates and is removed periodically.

This process results in minimal air emissions and no wastewater.

One grade of PCl_3 is commercially available. It is sold as a bulk liquid or in drums.

5.2 PCl_3 applications

PCl_3 is the single most important first derivative of P_4 in terms of volume and applications. The main derivative product classes are as follows:

- Glyphosate
- Other pesticides

- Phosphonates
- Phosphites
- Organophosphines
- Phosphorous acid
- Phosphorus oxychloride
- Phosphorus pentachloride
- Chlorination agent

The main reason for the broad use of PCl_3 is its versatile reactivity, which allows the targeted delivery of one P atom into molecules with P-C and P-O bonds and is an intermediate step in the preparation of penta- and oxychloride.

Chemical conversions of PCl_3 with organic molecules usually involve the release of chloride, often in the form of hydrochloric acid, which can be valorized as a byproduct or neutralized to form a brine that can be discharged into the sea.

The following sections describe the uses of PCl_3 by application, which also largely allows chemical classification.

5.2.1 Glyphosate

The herbicide glyphosate is the largest true derivative of white phosphorus. It is a powerful herbicide that blocks a specific pathway in plants for the production of amino acids (the shikimate pathway, involving the enzyme EPSP synthase). When plants are exposed to glyphosate, they stop growing, wither and die within a period of days to weeks. The action of glyphosate is limited to plants; its toxicity to mammals (including humans) is low (but see the considerations below).

The market for glyphosate was developed in parallel with genetically modified crops, such as cotton, soybeans, and maize, which are insensitive to glyphosate. This allows the selective extermination of weeds in a field with such crops, allowing the crops to then grow uninhibited by these weeds.

Glyphosate has recently come under scrutiny. It decays to potentially harmful derivatives in nature.[27] It – or its decay products - is suspected to be carcinogenic to humans, which has resulted in an increasing number of court cases aimed at its producers in the US,[28] even though the correlation is not considered convincing by the European Chemicals Agency.[29] Its use for consumers has been limited in the EU, and its use in agriculture is regularly up for review, with concerns raised.[30] Nevertheless, it remains a very successful herbicide with a stable market.

Glyphosate, formally known as N-phosphonomethyl glycine (Figure 19), is usually generated from PCl_3, formaldehyde, and iminodiacetic acid (IDA) in two main steps. The chemical process occurs in an aqueous medium. The first step, phosphonomethylation, occurs via a so-called Kabachnik-Fields reaction, which can also be considered a pseudo-Mannich condensation, where hydrolyzed PCl_3 (as H_3PO_3) and formaldehyde are added to the imino group in IDA to form a phosphonomethyl unit. The resulting compound is phosphonomethyl iminodiacetic acid (PMIDA) (Figure 19). This solid is isolated before the next processing step and can be easily transported. It is an important intermediate with considerable world trade.

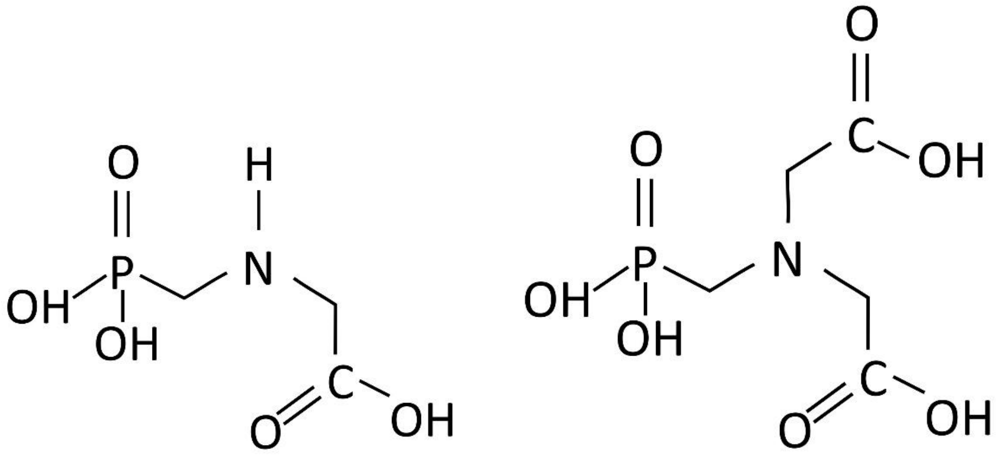


Figure 19 Molecular structures of glyphosate (N-phosphonomethyl glycine) and its chemical precursor, phosphonomethyl iminodiacetic acid (PMIDA).

The production of PMIDA is given in the reaction below:

$PCl_3 + R_2NH + CH_2O + 2\ H_2O \rightarrow H_2PO_3\text{-}CH_2\text{-}NR_2 + 3\ HCl$ (where R denotes $CH_2\text{-}COOH$)

Notably, there are no Cl atoms in the reaction; PCl_3 is hydrolyzed in situ to phosphorous acid by the water formed during the Mannich reaction, and additional water is dosed during the process. The released hydrochloric acid helps maintain the acidic conditions that support the reaction. The removal of HCl often involves the use of an amine, such as triethylamine. HCl forms an important byproduct that can be used in steel pickling or other reactions requiring acidity, or it can be neutralized to a sodium salt and discharged.

This reaction is also used in the production of many phosphonates (section 5.2.2); glyphosate is a phosphonate.

PMIDA needs to lose one of its CH_2-COOH groups to generate glyphosate. This is achieved via oxidation (decarboxylation) on, e.g., a copper catalyst.

Another pathway involves glycine, which has an advantage over IDA as a starting material: there is no need for decarboxylation as a second step. However, glycine is more susceptible to reaction with formaldehyde without the additional coupling of a phosphonate group, leading to the formation of byproducts that require additional workup.

The reaction is

$PCl_3 + RNH_2 + CH_2O + 2\ H_2O \rightarrow H_2PO_3\text{-}CH_2\text{-}NHR + 3\ HCl$ (where R denotes CH_2-COOH)

Glyphosate is usually applied as an isopropylamine salt in solutions of varying strength. Other cations are also used. The formulations often incorporate surfactants or wetting agents to increase glyphosate retention on leaf surfaces and the adsorption of the active ingredient through the leaf cuticle.

5.2.2 Phosphonates

Phosphonate are P^{3+} chemicals based on the motif shown in Figure 20. These compounds contain one P=O bond, one O-C bond, and two P-O-C bonds.

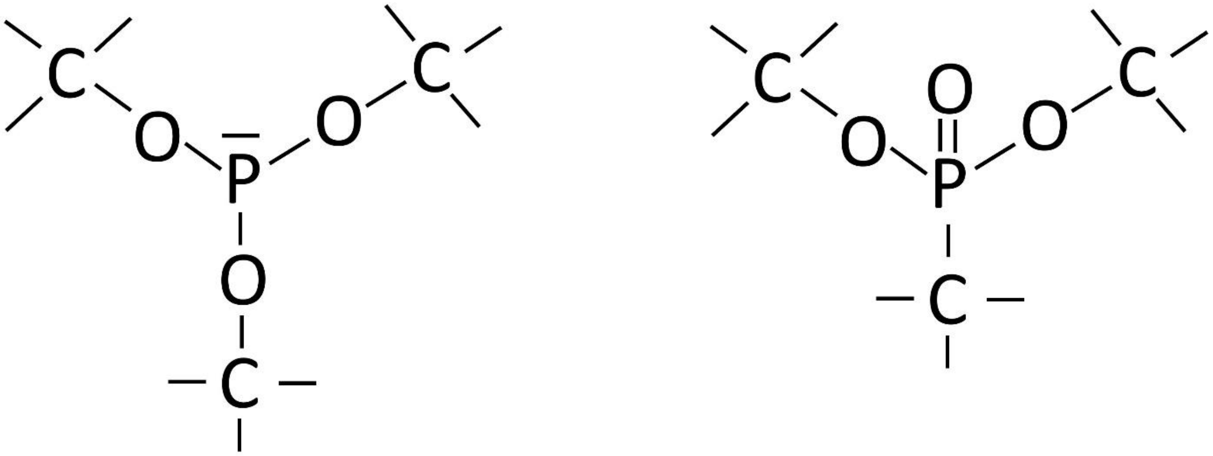


Figure 20 Trimethyl phosphite (left) and dimethyl methyl phosphonate (right). Both molecules can be described by the formula $C_3H_9O_3P$ but the arrangement is different (i.e. they are isomers).

Phosphonates may be produced by the Michaelis–Arbuzov reaction, starting from phosphites:

P(OR’)3 + R”X -> PR”(O)(OR’)$_2$ + R’X

where X denotes a halogen and R’ and R” are organic groups. Phosphites can also undergo internal rearrangement to form phosphonates by heating.

Many other industrial synthesis approaches exist, the most important of which will be highlighted here.

Phosphonates are used to capture metal ions (sequestration/chelation), which is useful in applications such as the following:

- Detergents: phosphonates keep Ca^{2+} and Mg^{2+} ions in solution and thus prevent the formation of a scale on fabrics, etc.
- Boiler and cooler water: phosphonates prevent scaling (same mode of action)
- Oilfields: phosphonates prevent scale formation with the $Ba^{2+}/Sr^{2+}/Ca^{2+}$ ions that clog oil wells

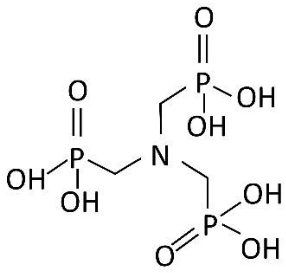
- Desalination by reverse osmosis (i.e., conversion of seawater to fresh water): phosphonates prevent blockage of the applied membranes

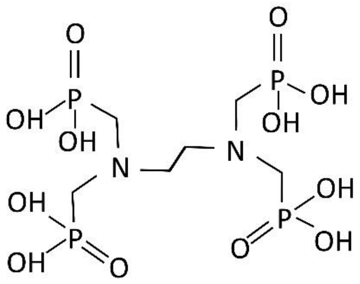
All of these applications rely on the same mode of action.

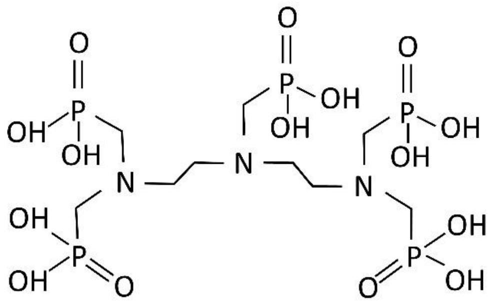
These functions can also be performed by carboxylic acids, but these compounds are less effective and less robust against extreme conditions, such as high or low pH and high temperatures.

Three types of phosphonates are commonly encountered (see also Figure 21):

- aminophosphonates: ATMP, ATMP, D(E)TPMP, HMDTMP, EDTMP (chemically related to glyphosate)
- 1-hydroxyethylene-1,1-diphosphonic acid (HEDP), or etidronic acid
- 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC)







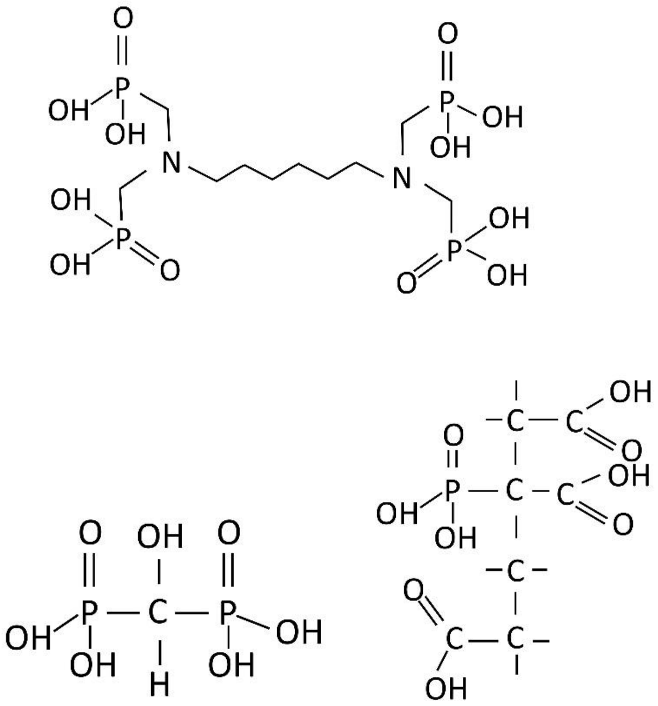


Figure 21 Four commonly used aminophosphonates: ATMP, EDTMP, DTPMPA, HMDTMP; and two common non-aminophosphonates, HEDP and PBTC (left to right, top to bottom)

Aminophosphonates are an important class of industrially relevant phosphonates. Chemicals in this class resemble glyphosate and are produced in a similar way. These compounds can be regarded as more robust variations of carboxyl analogs; e.g., ATMP is the phosphono analog of nitrilotriacetic acid (NTA).

Aminophosphonates are often used in the form of sodium or potassium salts, or partially neutralized forms, due to their limited solubility in acid form.

Longer aminophosphonates, such as DTPMP, are used in more specialized applications, such as the prevention of barium scaling in industrial and oilfield applications, and can be used under more extreme conditions, such as highly alkaline or hot environments.

Specific applications of this class of compounds include lubricant oil and hydraulic fluid additives.

HEDP, a bisphosphonate, is widely used in not only antiscaling formulations but also cosmetics, industrial cleaners, and osteoporosis drugs; in the case of osteoporosis drugs, it is commonly known by its alternative name, etidronic acid. It is produced from acetic acid and PCl_3 in an aqueous environment. Other bisphosphonates, such as zoledronic acid and risedronic acid, are also used in osteoporosis treatment.

PBTC, shown in Fig. 21, is produced from dimethyl phosphite and dimethyl maleate or their ethyl analogs[60]. It exhibits stability beyond that of most amino-based phosphonates.

PBTC constitutes a major use of phosphites. Some minor applications of phosphites involve the conversion of the corresponding phosphite, e.g., trimethyl phosphite to dimethyl methyl phosphonate, a flame retardant. A mixed methyl resorcinol-based polymeric version of this motif also exists.

As described, aminophosphonates are produced via a protocol much like the first step of glyphosate manufacture (section 5.2.1). PBTC, as mentioned above, obtains its P from the intermediate dimethyl phosphite. HEDP is produced from acetic acid and PCl_3.

5.2.3 Phosphites

Like phosphonates, these compounds are based on P^{3+} chemistry and correspond to the motif $P(OR)_3$ with an organic group (R) or hydrogen. See also Figure 20.

The reaction of PCl_3 with the appropriate alcohol leads to trialkyl phosphites.

$PCl_3 + 3\ ROH \rightarrow (RO)_3P + 3\ HCl$ (R = an organic group)

The mono- and dialkyl/aryl phosphites $ROP(OH)_2$ and $(RO)_2POH$ can also be obtained from such reactions, with parallel formation of organochlorides (RCl). The nature of the alcohol and the presence or absence of HCl determine the outcome (mono-/di-/triesters dominating).[5]

Asymmetric phosphites (with different R groups) can be obtained by replacing one R group with another type.

Phosphite applications include the following:

- Plasticizers
- Antioxidants
- Flame retardants
- Reaction intermediates

Often, these first three functions are combined to some extent, with compounds being added to a plastic for one purpose also serving to some extent in the other two functions.

An example of an industrially relevant compound is tris(2,4-di-tert-butylphenyl) phosphite, which is used as a stabilizer and antioxidant in plastics. Many other phosphites exist, such as triphenyl phosphite, trimethyl phosphite and triethyl phosphite. Tris(nonylphenyl) phosphite (TNPP) is another important compound in this class, although nonylphenyl compounds have received increased scrutiny because of concerns about their toxicity.[31] Many varieties of phosphites exist, usually with long-chain and/or branched organic groups serving as substituents.

During the processing of plastics at elevated temperatures, the plastics tend to decompose and form yellowish-brown decay products. To prevent this, phosphites are added as antioxidants. Often, more compounds are used in antioxidative formulations, resulting in synergistic effects between the constituents.

Trialkyl phosphites, the most important type in terms of volume, are used as plasticizers, with a secondary application as flame retardants. Dialkyl phosphites – which make use of the reactive P-H bonds – are used in the synthesis of derivatives such as PBTC and in hydraulic oils, e.g. in cars and airplanes.

5.2.4 Phosphorous acid (H_3PO_3)

This compound, also known as phosphonic acid, is a solid at room temperature but is often encountered as a 60-70% solution in water. It is usually traded as a solid. It can replace PCl_3 as a traded chemical in water-based chemistries such as in making phosphonates or glyphosate.

It is produced by reacting PCl_3 with water, yielding phosphorous acid and hydrochloric acid.

This compound exists in two forms (tautomers, different arrangements of the same formula, in equilibrium), not unlike the difference between phosphites and phosphonates, but these are not in equilibrium but distinct species (Figures 20 and 22). The dominant tautomer is the phosphonate form $HP(O)(OH)_2$, in which exists in equilibrium with a small amount of the phosphite form $P(OH)_3$. Even though the formula suggests that three acidic hydrogens/protons are available for acid–base reactions, only two react as acids, the third being bound to P in a strong P-H bond in the dominant tautomer.

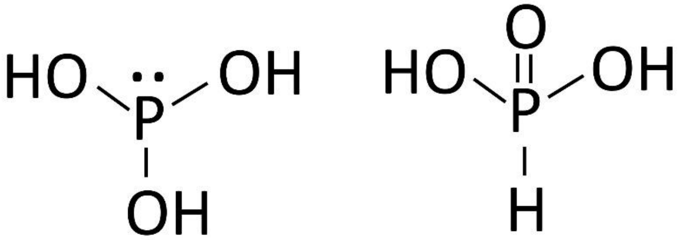


Figure 22 The two tautomers of phosphorous/phosphonic acid. These tautomers are in equilibrium, with the form shown on the right dominating.

Phosphorous acid cannot be used to produce organic triphosphites in any realistic yield because of the release of water upon reaction with alcohols, which prevents the addition of a third organic group (similar to P_2O_5). This limits the products to chiefly monosubstituted molecules, such as most phosphonates (glyphosate, aminomethyl phosphonates, PBTC or HEDP), which are prepared in aqueous media. Phosphorous acid occurs as an intermediate in many of these synthesis routes.

Inorganic derivatives of phosphorous acid, such as potassium phosphite, may be used to combat Phytophthora fungus (found on potato and tomato plants). Lead phosphite was historically important as a PVC stabilizer but has been largely banned since approximately 2000.

Phosphorous acid is the acid corresponding to phosphorus oxide P_4O_6, an uncommon material described in section 4.5.1 (phosphorus oxides).

5.2.5 Organophosphines

Although a route to prepare these compounds exists involving the intermediate PH_3 (section 7), PCl_3 also provides an entry point to these compounds and, in many cases, provides the only viable pathway.

Two related routes exist:

- To triphenyl phosphine (TPP) via a variation of the Wurtz reaction
- To trialkyl phosphines via the Grignard reaction

The Wurtz reaction uses liquid sodium to combine and dechlorinate chlorinated hydrocarbons and PCl_3:

$3\ RCl + PCl_3 + 6\ Na \rightarrow R_3P + 6\ NaCl$

where RCl is chlorobenzene in the synthesis of TPP.

The Grignard reaction involves the reaction of organohalides and magnesium metal to form organomagnesium intermediates and eventually PR_3.

Both reactions employ rather extreme and complex chemical methods and require specialized setups. Organophosphines that cannot be generated via the phosphine gas route (see section 7) need to be synthesized via the routes described above.

Triphenylphosphine is an important ingredient in the production of carotenes (vitamin A). Trialkyl and triaryl phosphines are very important catalyst ligands used in chemical conversions, e.g., in petrochemistry. This is further explained in the phosphine section 7.

5.2.6 Chlorination agents

PCl_3 may be used to chlorinate fatty acids. This is a rare chemical process in which Cl rather than P is used in the target molecule. The byproduct of such conversions is phosphorous acid.

5.2.7 Flame retardants

Most organophosphorus flame retardants are produced from $POCl_3$, but the important product 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (Figure 23) is generated from PCl_3. DOPO is a relatively new flame retardant (commercialized around 2000) with versatile applicability.[32] It is formally a phosphinate that is normally accessible only through phosphinic acid, but in this case, the unique triple-ring arrangement allows its synthesis from o-phenyl phenol and PCl_3. Itaconic acid often reacts with DOPO to generate a flame-retardant formulation, but many other variations of this motif have been explored.

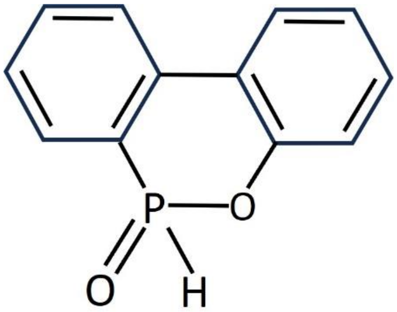


Figure 23 The flame retardant 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, referred to as DOPO, is synthesized from PCl_3 and o-phenyl phenol.

In addition, dimethyl methyl phosphonate is a minor flame retardant.

The topic of flame retardants is further explored in the $POCl_3$ section 5.3.

5.3 Phosphorus oxychloride ($POCl_3$)

5.3.1 General information and production technology

$POCl_3$, known as phosphorus oxychloride or phosphoryl chloride is a colourless liquid (Figure 24). It is produced from PCl_3 by blowing oxygen gas through it. The process and reactor (column) are quite simple, resulting 100% conversion, no waste, and minimal missions. There is one commercial grade. It contains 20.2% P. Like PCl_3, it reacts violently with water, releasing phosphoric acid and hydrochloric acid. It is toxic and corrosive.

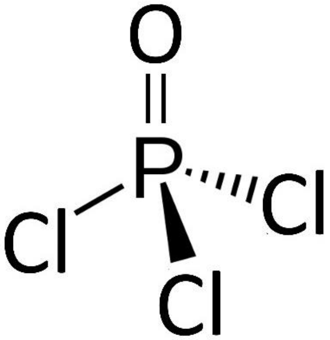


Figure 24 The phosphorus oxychloride ($POCl_3$) molecule. It is similar to PCl_3 but now the electron pair on the top has formed a bond with an oxygen atom - i.e. the PCl_3 atom has now been oxidized

$POCl_3$ can be considered a chlorinated variation of the phosphate motif. As in PCl_3, the three chloride atoms are reactive and allow the formation of P-O-C or P-C bonds, depending on the reagent. This is the entry point for organophosphate triesters, which are otherwise accessible only by reacting P_2O_5 with ethers, an uncommon process.

Most reactions with $POCl_3$ release Cl atoms in the form of chlorides, often hydrochloric acid, but some important end products also incorporate the Cl atoms (see the flame retardants section below).

The main application of $POCl_3$ is to produce organophosphate triesters, which are used as flame retardants or specialty plastic additives.

There is one grade. It is sold as a bulk liquid or in drums.

5.3.2 Applications

5.3.2.1 Flame retardants

The most important application of $POCl_3$ is as precursor for flame retardants (FR), which are additives used to fireproof combustible materials. It is typically added in the tens-of-percent to percent weight range.

Several FRs are used and work according to various mechanisms, such as the release of water (for cooling and gas dilution, e.g., aluminum hydroxide) or the release of radicals to interfere with the flame mechanism (halogenated, notably brominated FRs).[33,34] The latter have come under scrutiny due to their potential to accumulate in organisms and cause harm. FRs, including phosphorus based FRs, may also exhibit intumescent properties—they form a char-foam that serves as a barrier between the burning material and the atmosphere (see the ammonium polyphosphate section 4.3 in the P_2O_5 section 4, the aluminum diethyl phosphinate in the phosphinic acid section 7.4, the THPC product in the phosphine section 7.2, and the red phosphorus (section 2.3)).

These compounds tend to be tailored to increase their compatibility with the target material to be flameproofed; for example, for plastics, processability, and the effect on physical properties are important. It is also necessary to ensure that the FR compound does not leach out during use.

The following FRs based on $POCl_3$ are commercially important:

- Tris(2-chloro-isopropyl)phosphate (TCPP), the largest FR in this class, is prepared from propylene oxide and $POCl_3$. Note that the chlorine atoms are incorporated into the end product (see Figure 25).
- TCDPP, the 1-3-dichloro analog of TCPP, is prepared from PCl_3 and epichlorhydrine.
- TCEP, an ethyl analog made from PCl_3 and ethylene oxide, has largely been phased out due to toxicity concerns.
- Bisphenol-A-bis(diphenyl phosphate) (BDP or BADP) is prepared from $POCl_3$, bisphenol A, and phenol.
- Resorcinol bis(diphenyl phosphate) (RDP, also known as RBDP) is prepared from– $POCl_3$, phenol and resorcinol (Figure 25).
- Triphenyl phosphate and tricresyl phosphate (the latter excludes the toxic all-ortho isomer)
- Mixed butyl/propyl/phenyl phosphates
- Tri-isooctyl phosphate is used, e.g., for rubber applications.

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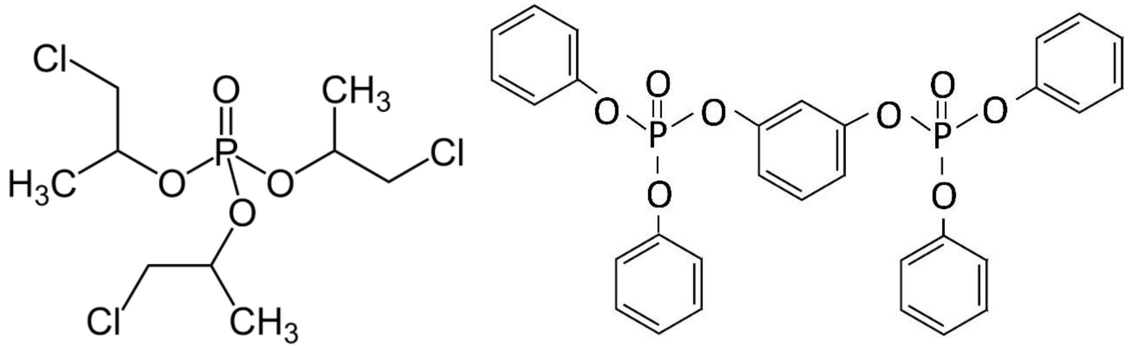

Figure 25 TCPP (left) and RDP (right) molecule structures

The first three FRs in this list exhibit several variations on the motif, all of which are collectively known as “chlorinated tris”. These organophosphorus compounds also contain chlorine and are thus not formally halogen free, although chlorine is not as heavily scrutinized as bromine in halogenated FRs. However, health concerns surrounding their use are emerging, e.g., in California.[35]

In addition to their use in plastics, phosphate esters are also used as FRs in functional fluids. This broad category includes lubricants, hydraulic fluids, and transformer oils. Phosphate triesters such as tributyl phosphate are used to flameproof specialized fluids, e.g., in aviation applications where flame retardancy is essential.

Tributyl phosphate is also used as a solvent and extraction agent (see also the pure phosphoric acid section 3).

5.3.2.2 Insecticides

Some older insecticides (e.g., dichlorvos and monocrotophos, increasingly banned) are also based on the organophosphate motif, which is generated via $POCl_3$.

5.3.2.3 Chlorination agents

Like PCl_3, $POCl_3$ is a selective chlorination agent that is used in fine chemistry and pharma. Its chlorinating action is stronger than that of PCl_3 but weaker than that of PCl_5.

5.3.2.4 Starch modification

$POCl_3$ is used to cross-link starch, improving its characteristics and, importantly, reducing its digestibility. It is therefore associated with reduced calories and increased fiber contents in foodstuffs. An example is a variety known as phosphated distarch diphosphate, E1413 in the EU food additive list.

5.4 Phosphorus pentachloride (PCl_5)

5.4.1 General and production technology

Phosphorus pentachloride (Figure 26) is a white to greenish-yellow solid. It is prepared by adding chlorine gas to PCl_3 in a type of kneader-reactor, eventually resulting in a dry solid. The PCl_5 solid is an ionic material that consists of PCl_6^- and PCl_4^+ units, but in the gas phase, it is composed of PCl_5 units. There is one single grade on the market. It contains 14.9% P. Like PCl_3, it reacts violently with water, releasing phosphoric acid and hydrochloric acid. It is prone to caking and hydrochloric acid release in moist air and is transported in tightly sealed drums.

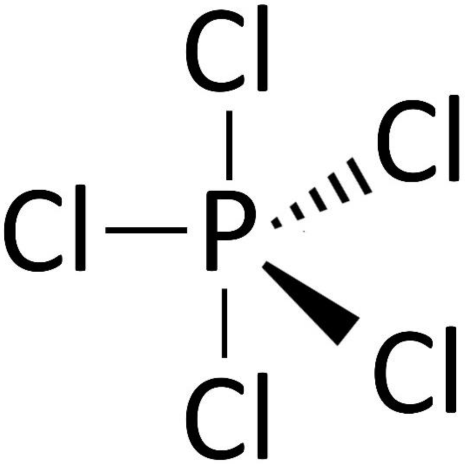

Figure 26 The phosphorus pentachloride (PCl_5) molecule. The geometry is trigonal-bipyramidal, i.e. three atoms are distributed around the P atom in a plane, and two more stick out perpendicularly to this

It has two uses:

- Chlorination in pharmaceuticals
- Intermediates for key components in lithium-ion batteries

The pharmaceutical application involves a specific chlorination step in the production of the antibiotic 7-ACA. Alternative PCl_5-free routes also exist.

Currently, it is mainly used as a precursor for the electrolyte in lithium-ion batteries. Charging and discharging a lithium-ion battery involves shuttling Li^+ ions through a liquid in the battery. This is achieved by adding a so-called electrolyte, $LiPF_6$. To prepare $LiPF_6$, PCl_5 is reacted with hydrogen fluoride and lithium fluoride. The resulting $LiPF_6$ is dissolved in a solvent. Thus, a conductive solution is obtained, which is put into the battery to allow lithium shuttling between the anode and the cathode. $LiPF_6$ is an ingredient in a well-established battery architecture and is expected to continue to be used for that role in the foreseeable future.

6 Phosphorus pentasulfide (P_2S_5)

6.1 General

Phosphorus sulfides may be considered analogs of the corresponding oxides (section 4.1). The related molecules P_4O_{10} and P_4S_{10} exhibit the same structure (Figure 12, Figure 27). However, phosphorus pentasulfide is used only in specific cases where it is necessary to incorporate a P-S motif into a molecule; thus, all its derivatives contain P and S atoms.

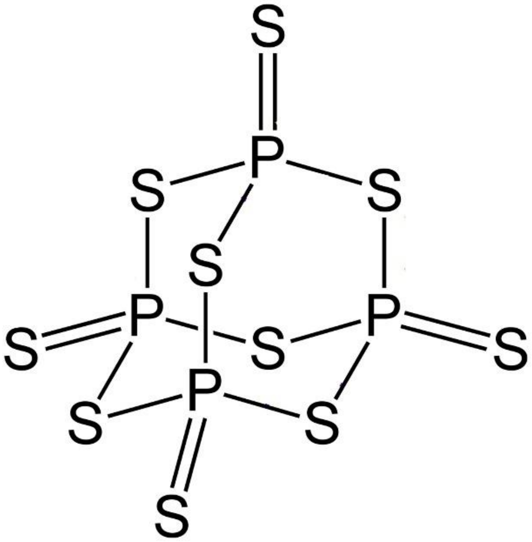

Figure 27 The phosphorus sulphide (P_4S_{10}) molecule with an adamantane, cage-type structure.

The most important P sulfide by far is phosphorus pentasulfide, a yellowish solid usually sold as flakes containing 28% P. This compound consists of P_4S_{10} molecules that have the same cage structure as P_4O_{10}. Unlike P_4O_{10}, it is possible to fine-tune the P:S ratio to achieve a lower S content. Several grades of this material exist commercially, where some of the molecules have one =S atom missing from the corners (P_4S_9). This allows the reactivity of the material to be adjusted.

Its main use is as a precursor to thion-type (P-S-based) insecticides and lubricant additives, with minor applications in flotation agents and pharmaceuticals.

P_2S_5 is a yellow solid supplied as flakes or a powder. It reacts vigorously with water, which releases the toxic gas hydrogen sulfide and (thio)phosphoric acid. It is therefore classified as toxic and corrosive. It is usually supplied in airtight drums to avoid ingress of atmospheric moisture.

A minor product is P_4S_3, which has limited use in the heads of strike-anywhere matches as a safe replacement for white phosphorus, which was previously used. This is a very minor market.

6.2 Production technology and grades

P_2S_5 is produced from white phosphorus and sulfur. Molten sulfur and phosphorus are added to a mixed reaction vessel which overflows onto a cooling drum. The solidified product is broken into flakes and bagged or drummed after screening. Optionally, the product can be distilled before cooling,[36] which removes organics and arsenic. The product is sensitive to atmospheric moisture and needs to be kept dry.

The reaction is exothermic and does not require significant energy input (other than for moving parts). The technology is relatively straightforward, and its costs are ultimately determined by those of the two inputs, white phosphorus and sulfur.

The conversion to the end product is 100%, and virtually no waste is generated. Air and water emissions are minimal if abatement measures are in place.

Several grades exist with varying flake sizes. Additionally, as mentioned, the sulfur content can vary, leading to slight variations in reactivity and hence a range of grades.

Additional quality parameters include arsenic and organics. The latter, which can be carried into the product from white phosphorus, can be important for determining the colour of derivative products.

6.3 Derived chemistry

P_2S_5 itself has limited applications.

The chemistry of sulfur is similar to that of oxygen. In many cases, thio (i.e., sulfur-containing) analogs of oxidic P compounds exist, as do many organic analogs. Here, O is replaced by S, with the rest of the molecules remaining the same. With respect to phosphates, one to four oxygens in the PO_4^{3-} unit can be replaced by sulfur, leading to thiophosphates, dithiophosphates, trithiophosphates and tetrathiophosphates. If organic groups are attached to a mixed O/S phosphate, the name indicates whether these are attached to a sulfur or an oxygen. An example is O,O-diethyl dithiophosphoric acid, where "O,O-" indicates that the ethyl groups are each attached to an oxygen atom. Incidentally, the latter is chemically favored over substitution on sulfur, and this type of compound is often encountered.

These compounds are produced by reacting P_2S_5 with alcohols; a mixed oxidic-sulfidic compound is obtained via the reaction, chiefly but not exclusively a dithiophosphate.

To describe the arrangements within a molecule, the names thiol and thion are sometimes used, where thiol indicates a P-S-H or P-S-R (R=organic) arrangement in the molecule and thion indicates the presence of a P=S bond. The latter may be found in thiophosphonates, thiophosphinates, phosphine sulfides and thiophosphates.

Most of these compounds are organophosphorus compounds. Two rare examples of inorganic P-S compounds are Nokes’ reagent and Li_3PS_4, described below.

Most of the industrially relevant organic-sulfidic P compounds contain P^{5+} and are derived from P_2S_5. The main product classes are described below.

6.3.1 Insecticides

The P-S motif is observed in a series of long-established insecticides collectively known as thion insecticides. A few examples will be highlighted.

Parathion (Figure 28) (formally ethyl parathion) has been used for decades worldwide. All insecticides in this class block the enzyme acetylcholinesterase, which is part of the nervous system functionality. Interestingly, sulfur is exchanged for oxygen upon ingestion, which yields paraoxon, a more powerful blocker of this enzyme. Direct application of this compound is considered too hazardous, so the sulfur atom can serve as a toxicity moderator**.**

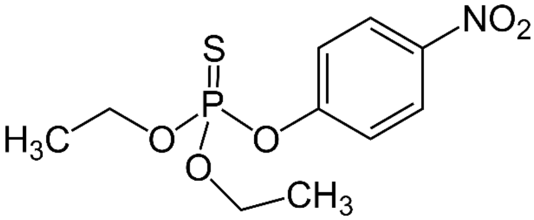

Figure 28 Parathion, an organophosphate insecticide and acaricide, is synthesized from phosphorus pentasulphide.

Because of this functionality, parathion is classified as a nerve agent. Since it has been found to act indiscriminately on insects, birds and mammals (including humans), its use was phased out in the US and Europe in the 1990s to early 2000s. However, it continues to be used elsewhere. The use of its sister compound methyl parathion, which is slightly safer for use by humans, is restricted in the US and is banned in China, Japan and the EU, but it continues to be used elsewhere.

Malathion (Figure 29) has a similar mode of action, but its conversion to a more potent agent occurs only in insects and related creatures. This compound therefore has low toxicity toward humans, as it is metabolized into less toxic compounds via a competing pathway. This advantage has led to its use as one of the most widely used organophosphorus insecticides.[37]

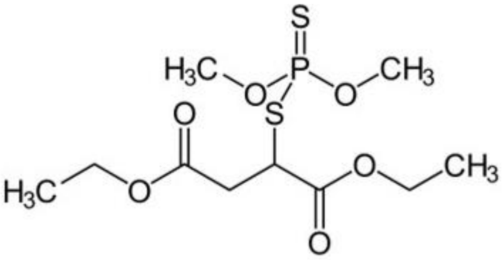

Figure 29 Malathion, an organophosphate insecticide, is synthesized from phosphorus pentasulphide.

Chlorpyrifos is a partially chlorinated variant of the parathion motif that has a similar mode of action but is less toxic; it has nevertheless been phased out in Europe in 2020.

Acephate, another thion insecticide, is moderately toxic to humans but is very effective against aphids and is widely used to control them.

Other insecticides, such as methamidophos, diazinon, dimethoate and terbufos, have undergone development similar to that of chlorpyrifos; they have lower toxicity than parathion but are nevertheless still quite toxic and are therefore being phased out in most Western countries, with the rest of the world set to follow suit at some point. Some essential uses prevent blanket bans on a few products. For instance, methamidophos continues to be used extensively in rice fields in Southeast and East Asia, but its use is restricted in China.

6.3.2 Lubricant (oil) additives

This specific class of compounds is produced from P_2S_5 and alcohols of varying chain length:

$P_2S_5 + 4\ ROH \rightarrow 2\ (RO)_2PS_2H + H_2S$

with R denoting an alkyl group such as an ethyl group. Notably, the fifth S atom is released in the form of H_2S during such reactions.

When reacted with a zinc salt, a zinc dialkyl dithiophosphate (ZDDP) ($Zn[(S_2P(OR)_2]_2$) is obtained:

$2\ (RO)_2PS_2H + ZnO \rightarrow Zn[(RO)_2PS_2]_2 + H_2O$

ZDDP is added to combustion engine lubricating oils. Upon entering the cylinder of such an engine, it forms a self-healing protective layer on the metal surface of the cylinder based on the DDP moieties released from the zinc ion. This considerably increases the lifetime of the engine by reducing wear. In addition, it exhibits antioxidant properties that prolong the lifetime of the oil.[38]

A minor amount of ZDDP (Figure 30) is used for similar functions in specialty lubricants, such as high-pressure and gearbox oils.

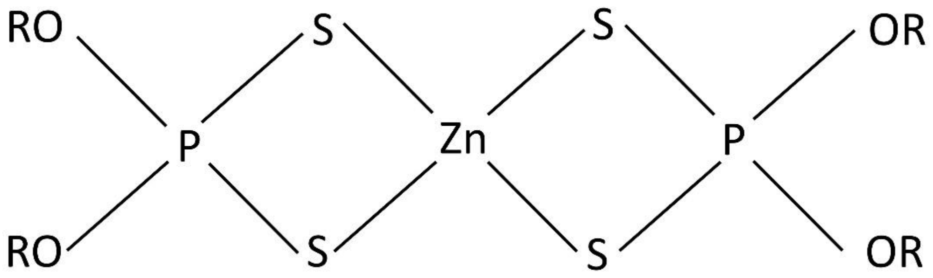

Figure 30 Zinc dialkyl dithiophosphate (ZDDP) molecule. The bond structure around the Zn atom is indicative, it retains part of its 2+ charge and the two dithiophosphate units some of their negative charge. R denotes an organic group such as ethyl.

6.3.3 Flotation agents

The most relevant application in this field is sodium dithiophosphate, also known as Nokes' reagent. It is made from sodium hydroxide and P_2S_5:

$P_2S_5 + 6\ NaOH \rightarrow 2\ Na_3PO_2S_2 + H_2S + 2\ H_2O$

This compound helps separate molybdite ores from other minerals during flotation. During flotation, finely milled ores are wetted in the presence of flotation agents and subjected to air bubbles, causing some of the minerals to leave the flotation unit via the top as froth and others to sink to the bottom. Nokes' agent strongly improves the flotation separation of molybdite (MoS_2) from accompanying minerals, such as copper sulfide, in the mined ore[6,39]

6.3.4 Li-P-S batteries

The compound Li_3PS_4, produced from P_2S_5 and Li_2S, has been proposed as a versatile solid electrolyte in lithium-ion batteries. This development may eventually lead to commercialization.[40]

6.4 Other P-S compounds – nomenclature and uses

Among compounds with lower oxidation states of phosphorus, P^{3+} compounds include thiophosphites, dithiophosphites and trithiophosphites, as well as thiophosphonates, dithiophosphonates and trithiophosphonates. However, their use is limited, with their main application as insecticide precursors. Tributyl trithiophosphite is used as a defoliant on cotton.

Sulphidic P^{+} compounds also exist, although their industrial relevance is limited. This class includes thiophosphinates and dithiophosphinates. They compounds are stronger acids than the oxidic analogs. Sodium di(isobutyl) dithiophosphinate is used as a flotation and extraction agent, for instance, in silver recovery from complex ores. Bis(2,4,4-trimethylpentyl) dithiophosphinic acid is not as selective as its oxidic analog but is used to extract heavy metals from effluents. See also chapter7.

By reacting phosphines with sulfur or sulfur-containing compounds, phosphine sulfides, which contain P-, are obtained. These are comparable to phosphine oxides. These materials are useful as extraction agents, for instance, for noble metal ions. Silver recovery from metal ores (iron, zinc, copper, nickel) is an industrially relevant use of tri-isobutyl phosphine sulfide.

A mixed chloride, $PSCl_3$, exists. This may be considered a sulfur analog of $POCl_3$ and is likewise more reactive than P_2S_5, just as $POCl_3$ is more reactive than P_2O_5. This compound is useful especially if trisubstituted organic compounds with a sulfur atom in the structure are needed. Several derivatives of $PSCl_3$ exist in which chlorine remains in the end product (Figure 31). These are called O,O-dialkylphosphorodithionochloridates. The global market for this material is a few kt/y.

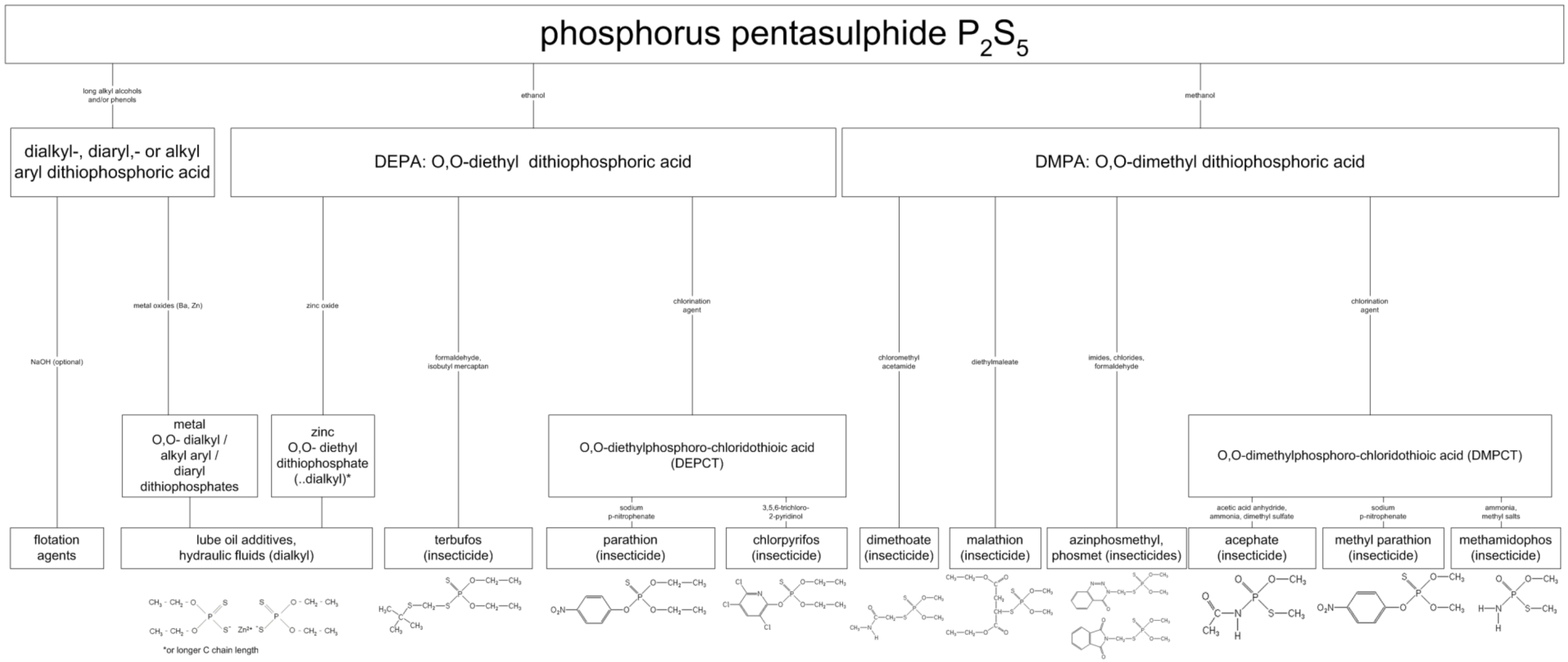

Figure 31 Some phosphorus pentasulphide, P_2S_5, *The lubricant additives box may refer to longer alkyl groups than ethyl also. Not all PS insecticides are shown.*

7 Hypophosphites, phosphines and phosphides

- Specialty chemicals produced in small quantities
- Very diverse applications
- Crucial ingredients that enable large-scale (petro)chemistry
- Other uses include depositing thin nickel layers and keeping grain silos pest free.
- Also used in flameproofing materials and to produce vitamins and drugs
- Two compounds and their uses were awarded a Nobel prize

In this chapter, three minor types of phosphorus chemistry are discussed. All of these materials are characterized by a low oxidation state of phosphorus or even contain phosphorus in a reduced form.

7.1 Phosphines

The large class of organophosphines represents a small volume of white phosphorus use, but the applications of these compounds are of immense economic importance, and the field is rich and varied.[41]

The compounds in this class can be represented by the general formula PR_3, with R representing an organic group or hydrogen.

Unlike other organic derivatives of white phosphorus, these molecules have only direct P-carbon or P-hydrogen bonds (Figure 32). The phosphorus atom has a formal charge of -3 and can therefore be regarded as reduced instead of oxidized (which is true for most other white phosphorus derivatives).

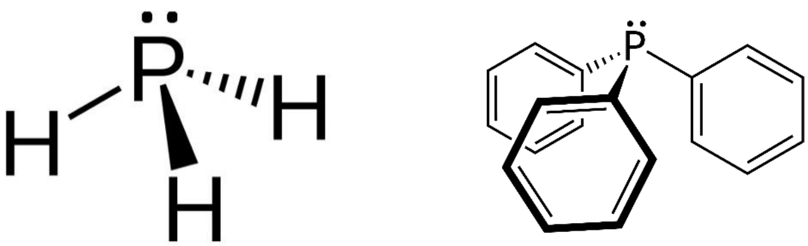

Figure 32 Phosphine molecular structure. In the left panel, phosphine PH_3. Note the structural similarity of PH_3 and PCl_3. The right panel illustrates triphenyl phosphine.

A considerable number of these compounds are produced via phosphine gas (PH_3), which is the chemical parent compound of organophosphines. Alternative approaches use organometallic chemistry to synthesize these molecules, described in section 5.2.5.

Phosphines contain two important subclasses of derivatives: phosphine oxides/phosphinates and phosphonium salts.

The term phosphane is sometimes used instead of phosphine.

7.1.1 Phosphine gas

This white phosphorus derivative is a colourless gas at room temperature. It is highly toxic. Although phosphine itself is odorless, it is often associated with a characteristic, garlicky smell caused by the presence of impurities such as diphosphine (P_2H_4).

The gas itself is flammable, and the presence of impurities such as diphosphine results in self-ignition under certain conditions. It occurs in nature as part of the ignis fatuus, a spontaneous flame that appears in marshy areas and is also known as will-o'-the-wisp. This is a very rare case of a reduced phosphorus compound in nature.

Most phosphine gas is converted to organic derivatives, but it has some direct applications. This gas is used to add very small amounts of phosphorus atoms to silicon semiconductors, a process known as doping. The phosphorus atoms are incorporated into the silicon crystals at regular intervals. Each P atom has one more electron than its silicon neighbors. This adds a specific type of conductivity (so-called n-doping) to the silicon. Likewise, boron can be used to induce the opposite p-type conductivity in silicon, as boron has one less electron than silicon. These fundamental changes in silicon conductivity are foundational in the semiconductor industry, and modern electronics critically rely on this process. For this application, the phosphine gas needs to be purified by low-temperature distillation to >99.999% purity.

Because of its toxicity, phosphine gas is used to combat pests in food storage, a process called fumigation. A typical example is the extermination of insects and rodents in grain silos. Phosphine is slowly released into a silo until all insects have been killed, after which the silo is ventilated. The gas needs to be diluted in 98% CO_2 to avoid flammability issues (phosphine is self-igniting). Metal phosphides can also be used to generate phosphine gas in situ (see Section 7.6).

Phosphine gas cannot be produced from white phosphorus with 100% conversion, which is different from most other phosphorus first derivatives. Instead, two approaches to generate this gas from white phosphorus exist, both involving a process called dismutation—the simultaneous oxidation and reduction of P atoms in a reactive mixture—both requiring the input of water.

One approach uses a hot acid medium. The addition of white phosphorus causes it to dismutate into phosphoric acid and phosphine:

$2\ P_4 + 12\ H_2O \rightarrow 5\ PH_3 + 3\ H_3PO_4$ [reaction 1]

In practice, phosphoric acid continuously forms a reactive medium (providing the necessary acidity), and the excess is purged out of the reactor. The phosphine gas leaves the reactor at the top and reacts further, with or without compression (see below).

This process starts from a mixture of red and white P, which forms under these synthesis conditions.

This process is far from atom efficient, unlike oxidation to chlorides, oxides, or sulfides; however, the cogenerated phosphoric acid has value and can be sold for technical application. It contains traces of phosphite and usually attracts the arsenic in the P_4 feed.

The other approach is carried out under alkaline conditions, in which sodium hydroxide and water act on white phosphorus:

$P_4 + 2\ NaOH + 7\ H_2O \rightarrow 2\ NaH_2PO_2 + Na_2HPO_3 + PH_3 + 3\ H_2$ (*) [reaction 2]

(*) Notably, the above reaction is approximate; there are no integer numbers here, and splits can be influenced slightly by the reaction conditions.

The main product or byproduct, depending on the conditions, is sodium hypophosphite (see section 7.4).

Phosphine generated via the acid route is purer than that generated via the hypophosphite route (Figure 33). To produce pure phosphine and derivatives, the acid route is more suitable, the hypophosphite route achieves this same main goal, but lends itself more to the generation of coproducts THPC/S salts (the products mostly suited to unpurified and unpressurized phosphine gas input).

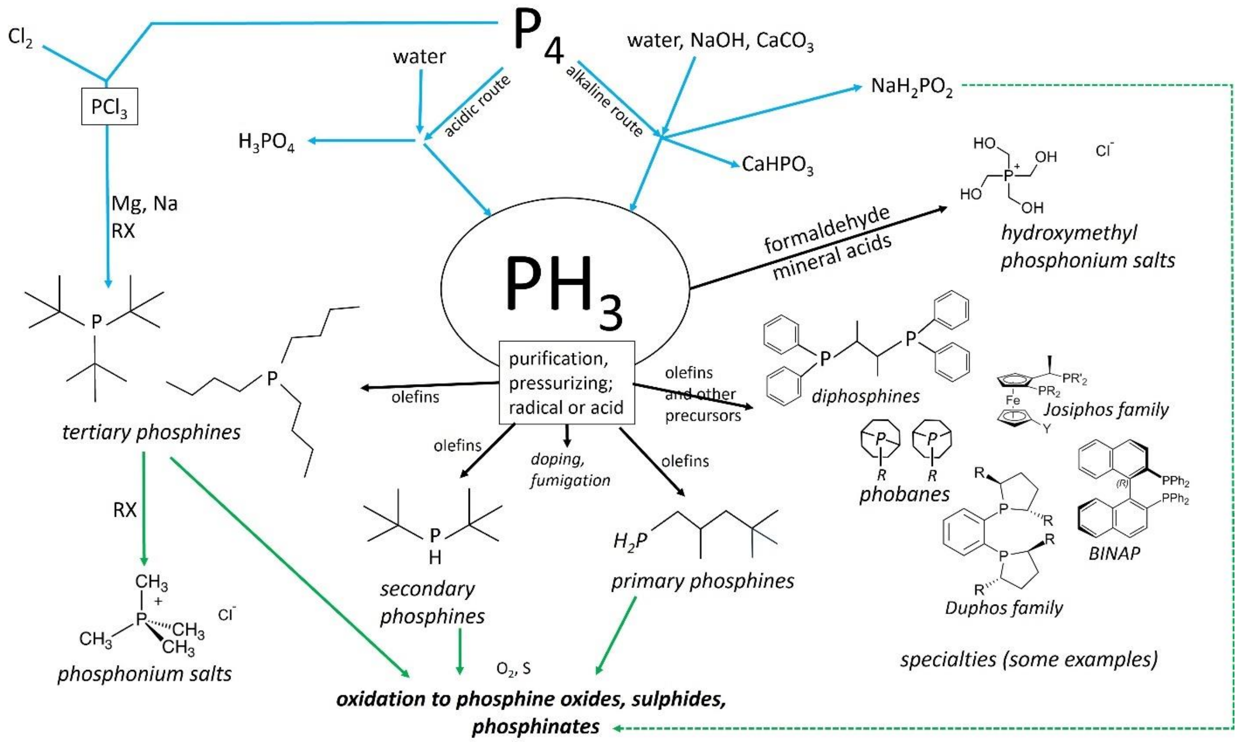

Figure 2 Phosphine routes.

Phosphine is usually generated and converted to derivatives in the same facility; only fumigation and doping phosphine are transported in gas cylinders.

7.1.2 Organophosphines

Like phosphate esters or phosphites, this class contains primary phosphines (PRH_2), secondary phosphines (PR_2H) and tertiary phosphines (PR_3).

These products are typically colourless liquids or solids, while some monophosphines are gaseous.

There are a few approaches to produce these compounds:

7.1.2.1 Via phosphine gas

Phosphine gas is reactive toward olefins (organic molecules containing a double C=C bond; alkenes). The alkene of choice is brought in contact with prepurified phosphine under pressure (which then forms a liquid) and often with some heating. The reaction proceeds via a radical mechanism (molecular fragments with uncoupled electrons) and needs a radical initiator (reaction starter). This protocol provides access to a large array of organophosphines.

An acid-catalyzed route – also starting from olefins – exists, which allows the addition of bulkier groups during the production of tertiary phosphines.

7.1.2.2 Via organometallic intermediates

If alkenes are not an option, a specialized reaction via organomagnesium compounds is used, which is a variation of the Grignard reaction. This method uses chloroalkanes, magnesium metal, and PCl_3 (to avoid phosphine gas). A more detailed description is provided in 5.2.5.

The organometallic pathway may be needed if the groups to react with the P atom do not have a suitable alkene precursor or, in the case of triphosphines, if these groups are too bulky. The presence of two large groups on the P atom may prevent the third one from reacting via the radical protocol because it does not fit easily between the existing two groups, and a stronger organometallic protocol is preferred.

A related synthesis is used to prepare triphenyl phosphine. This process uses the Wurtz reaction based on liquid sodium metal, chlorobenzene and PCl_3 (see 5.2.5)

A large variety of these compounds exist, with identical or different R groups as substituents. A full overview would exceed the scope of this text, but their applications are as follows:

- Catalyst ligands
- Vitamin and pharma synthesis
- Fine chemicals synthesis

Catalysts are chemicals that, by their presence, increase the speed of chemical reactions, often by several orders of magnitude, without being consumed. An important class of catalysts consist of a metal ion coordinated by several chemical groups (molecules) known as ligands. These ligands help tune the reactivity of the metal center and provide a shape (mold) that allows the targeted reactants to “dock” selectively on the catalyst. Phosphines form a rich, tunable library of such ligands.

These catalysts are used in many fields of organic chemistry. Important petrochemical conversions are also based on such catalysts. A typical example of a ligand used on a large scale is eicosyl phobane, which is part of a cobalt- or rhodium-based catalyst used in a petrochemical conversion called hydroformylation;[42] closely related variations of this motif have also been used.

Phobanes (Figure 34) are produced by reacting phosphine with cycloocta-1,5-diene or limonene. Many specific varieties exist.

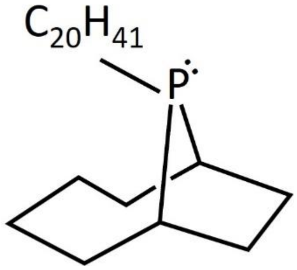

Figure 34 Eicosyl phobane, a bridged phosphine with the formal name 9-eicosyl-9-phosphabicyclo[3.3.1]nonane. The [4.2.1] arrangement is also obtained during synthesis from phosphine (PH_3) and cyclooctadiene.

Various other tertiary phosphines are applied as ligands in hydrogenation, polymerization and oligomerization reactions, with metals such as rhodium, ruthenium, palladium, nickel, chromium and titanium in the form of ions.

BINAP (Figure 35) is another example of a phosphine; it is used in stereoselective catalysis, an example of which is the production of menthol and pharmaceuticals. The development of this chemistry (Noyori asymmetric hydrogenation) was awarded a Nobel prize in 2001.

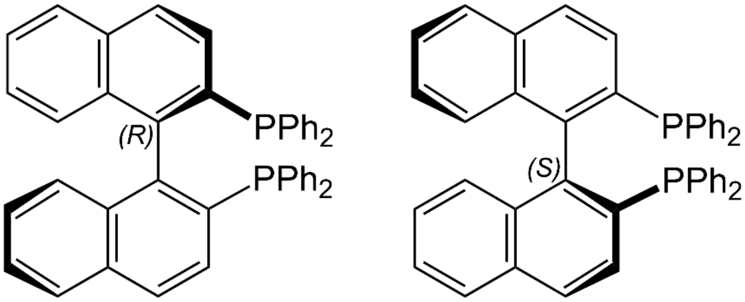

Figure 35 The phosphine (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) called BINAP; this exists as two enantiomers, which are mirror images of each other.

The Josiphos and Duphos ligand families are further important categories of these compounds.

Tributyl phosphine and trioctyl phosphine are used industrially as solvents.

Triphenyl phosphine is used on a large scale as a reactant to produce beta-carotene (vitamin A) via the Wittig reaction. The byproduct is triphenyl phosphine oxide, which poses a recycling challenge, although protocols exist for reprocessing this compound.

A somewhat exotic type of phosphine, tris(trimethylsilyl)phosphine (TMSP) (Figure 36), has recently attracted increased interest as a precursor for indium phosphide quantum dots. These materials are slated for use in high-resolution liquid displays. A new phosphine gas production plant was recently announced in Japan.[43]

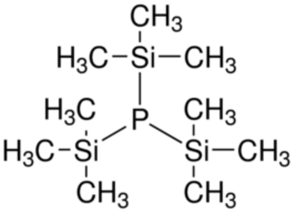

Figure 36 The novel phosphine, tris(trimethylsilyl)phosphine (TMSP) is used in quantum dots.

Although not necessarily P based, quantum dots were the subject of the 2023 Nobel prize in chemistry.

7.2 Phosphonium salts

A phosphonium salt (Figure 37), more formally a quaternary phosphonium salt, is an ionic compound containing a PR_4^+ cation (positively charged) based on the phosphine motif. The corresponding negative ion (anion) can be a simple ion such as chloride or sulfate or a more complex anion.

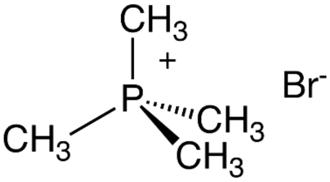

Figure 37 A phosphonium salt, tetramethylphosphonium bromide.

Phosphonium compounds can be considered a more robust variety of quaternary ammonium salts, which have the same motif but include a central nitrogen atom instead of phosphorus.

These compounds can be produced from a triphosphine and a chloroalkane or a similar compound.[44] This allows the addition of a different R group than that on the phosphine, creating asymmetric phosphonium ions. An example is tributyl tetradecyl phosphonium chloride, a biocide for industrial water treatment and for use in the oil and gas sector.

The anion can also exhibit a pattern similar to that of the cation, e.g., TFSI (bis(trifluoromethane) sulfonimide). These compounds constitute a relatively novel group of chemicals called ionic liquids. These liquids have low vapor pressure and are slated to replace volatile solvents in many chemical conversions. Industrialization has not yet occurred on a significant scale, but this may change soon.

Phosphonium salts hold some promise as specialty lubricants in electric cars. They also see application as phase transfer catalysts in reactive systems with two immiscible liquids, such as those used in the production of monoethylene glycol.

A phosphonium salt has been proposed as a proton (hydrogen ion) shuttle in the direct production of green ammonia by electrochemistry.[45] Such protocols provide a route to the crucial fertilizer precursor ammonia without emitting large amounts of carbon dioxide, as is the practice today. Ammonia is a key ingredient in fertilizers; in addition, electrification during the production of ammonia also allows the storage of hydrogen/energy. Its use as an energy carrier in the future is under consideration.[46]

All these phosphonium salts are niche and specialty chemicals.

Specific examples of phosphonium salts are, tetrakis(hydroxymethyl) phosphonium chloride and sulfate (THPC and THPS, respectively) (Figure 38). Unlike specialty salts/ionic liquids, these two compounds are produced in large quantities. Their production is much more straightforward: by passing freshly generated phosphine through hydrochloric acid or sulfuric acid in the presence of formaldehyde, these compounds form in good yield. This approach is much easier than accessing specialty phosphines and phosphonium salts; phosphine is processed at atmospheric pressure and does not require purification.

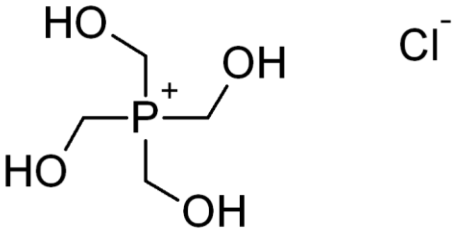

Figure The structure of the phosphonium salt tetrakis(hydroxymethyl) phosphonium chloride (THPC)

THPC is a textile (cotton) flame retardant when reacted with urea. Cotton is drenched in a THPC/urea solution and then subjected to pressure and elevated temperature in an ammonia atmosphere. This causes the THPC and urea to form long chains of alternating THPC-urea units. The product is water insoluble and crosslinked into the fabric, so the material can be washed without losing the flame retardant.

THPS is an important biocide used to control the growth of bacteria and algae in oil wells and industrial water systems.

7.3 Phosphine oxides

It is possible to selectively oxidize organophosphines to their corresponding oxides. This process results in PR_3O-type molecules.

The parent compound phosphine oxide (PH_3O) is unstable and very difficult to synthesize but was recently observed.[47]

A typical phosphine oxide is trioctyl phosphine oxide (TOPO), which is used as an extraction agent during metal mining and processing. Together with DEHPA (see the chapter on P_2O_5), this compound has been applied to extract uranium from phosphoric acid.

Phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPO, Figure 39) is used as a photoinitiator in resin curing. To prepare hard resins, a precursor is often produced in the form of a paste or liquid containing the ingredients that need to react to form the desired hard solid. A photoinitiator is an additive present in small amounts. When irradiated with light (often UV), it becomes activated, by forming a radical. This initiates a chain reaction, causing the resin precursors to react and form polymers. A well-known application is dental resins for fillings, the hardening of which is triggered by exposure to a small amount of UV light (although these materials do not commonly use BAPO).

BAPO and related compounds are produced via a rather unique protocol involving sodium organophosphide.

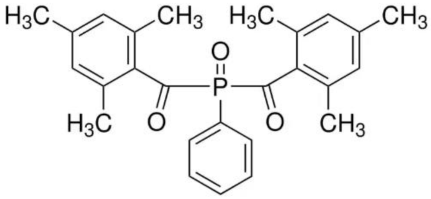

Figure 39 The BAPO motif (a photoinitiator). The C=O – P=O – C=O unit is characteristic of this group of compounds.

As explained above, triphenyl phosphine oxide is a byproduct of vitamin A production.

Specific examples of phosphine oxides are phospholanes and phospholenes, which are five-membered rings. MPO (Figure 40) is used as a catalyst for polyurethane and carbodiimides.

Others are used as special flame retardants for polyester fabrics. These compounds are prepared via the intermediate dichloromethylphosphine, a mixed phosphine–phosphorus chloride.

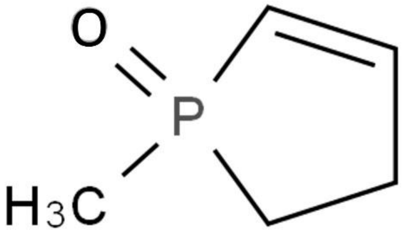

Figure 40 Five-membered cyclic phosphine oxide: 1-methyl-1-oxophospholene called MPO.

Sulfide analogs of these phosphine oxides also exist (see 6.4).

One further oxidation step of these compounds results in the production of organophosphinates, which are described in the next chapter.

7.4 Hypophosphites

Hypophosphites and hypophosphorous acids constitute a class of P compounds in which the P atom has a formal charge of +1, in contrast to phosphites/phosphonates with a charge of +3 and phosphates with a charge of +5.

Like phosphorous/phosphonic acid, the acid H_3PO_2 exists in two forms in equilibrium (tautomers): hypophosphorous acid $H_2P(O)(OH)$ and phosphinic acid $HP(OH)_2$ (Figure 41). As in the case of H_3PO_3, the hypophosphorous form dominates. Since two protons are directly bound to the P atom, the resulting compound is a monoprotic acid, meaning that only one of the three hydrogens serves an acidic function.

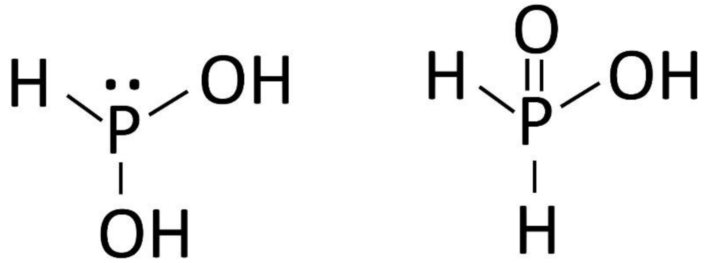

Figure 41 Phosphinic acid (left) and hypophosphorous acid (right). These tautomers are in equilibrium, with the hypophosphorous acid form dominating.

Hypophosphorous acid and its salts are colourless solids. The acid is usually sold as a 60% solution in water. It decomposes into phosphites and phosphine upon heating above 100 °C. Hypophosphites are nontoxic.

An industrially relevant production route for producing hypophosphites involves heating white phosphorus in a sodium hydroxide solution (Figure 33, alkaline route, see 7.7.1). This yields the sodium salt NaH_2PO_2 rather than the acid. The sodium salt, a white solid, is used as a reducing agent and the starting material for derivative chemistry. The acid H_3PO_2 is generated from the sodium salt by adding a stronger mineral acid, such as sulfuric acid.

Depending on local needs, phosphine or hypophosphite is the main product. The usual approach is to produce hypophosphite while valorizing the cogenerated phosphine into THPC/S.

Unlike that of most white phosphorus derivatives, this production route involves the formation of waste or the low-value coproduct calcium phosphite ($CaHPO_3$). Lime is added to the product of the reaction to separate phosphite from hypophosphite. This compound can be valorized as a low-grade fertilizer component, or it is landfilled.

The main uses of sodium hypophosphite/hypophosphites are as follows:

- Reduction agent in, e.g., metal plating
- Flame retardant precursors

The most important use of sodium hypophosphite is in electroless nickel plating. In general, layers of metals can be deposited onto surfaces by applying an electrical current to the relevant object in a solution of a salt of the appropriate metal (plating). However, if nonconductive materials or complex shapes are to be plated, a different mode of action is needed. Sodium hypophosphite is very effective at reducing nickel from solutions of nickel sulfate onto a surface. This process produces a smooth, hard layer of nickel on the surface. The complex shapes can be covered by a uniform layer of nickel metal. A typical application is nickel plating of computer hard disk drives.

The second most important application is in flame retardants. This application involves other hypophosphite salts, such as calcium or zinc hypophosphite, but the most important class is the aluminum salts of diethyl phosphinic acid (DEPAL) (Figure 42). These are applied in resins and circuit boards.

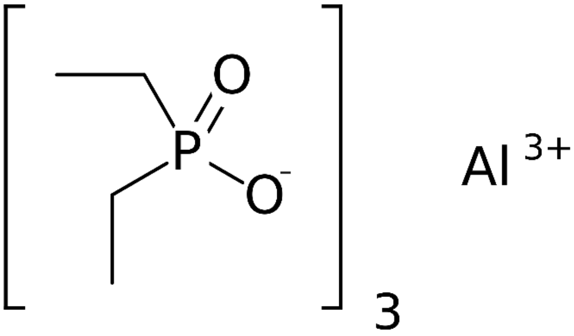

Figure 42 The hypophosphite DEPAL is an aluminum salt of diethyl phosphinic acid used as a flame retardant.

To produce these compounds, a protocol similar to that used for phosphines is applied: an olefin (unsaturated hydrocarbon, e.g., ethene) is activated via a radical mechanism to add to the hypophosphite. The produced sodium dialkyl hypophosphite is then converted to the aluminum salt. Similar compounds (organic phosphinic acids) can also be accessed by the double oxidation of organophosphines (section 7.3).

Calcium hypophosphite is also used as a flame retardant in combination with other compounds.

Both compounds are part of the broader family of P-based halogen-free flame retardants.

The acid H_3PO_2 is a niche product. Its defined salts are applied as specialty antioxidants, reducing agents, colour stabilizers, and antioxidants.

Specialty extraction agents based on this motif, e.g., bis(2,4,4-trimethylpentyl) phosphinic acid (made via PH_3), are important extraction agents allowing the separation of cobalt and nickel during mining. These metals often occur together and are otherwise difficult to separate.

Several more such chemicals based on the hypophosphite or thiohypophosphite motif exist.

The flame retardant DOPO is prepared from PCl_3 but is formally a hypophosphite.

The herbicide glufosinate, which bears some analogy to glyphosate, is formally a phosphinate produced from PCl_3.

7.5 Metal phosphides

Metal phosphides are binary, inorganic compounds of a metal and a reduced form of phosphorus.

There are two types of these compounds:

- Metallic (alloy) or semiconductor-type phosphides
- Salt-type phosphides

Alloy-type phosphides mainly include to ferrophosphorus, an alloy of Fe and P. Even though it is composed of formally discrete compounds (FeP, Fe_2P and Fe_3P), it is, in practice, a mixture of these. The material has a grayish metallic appearance. It is a byproduct of white phosphorus production and originates from iron impurities in the feedstock. Its main market is the production of specialty steels, to which it is added in small quantities. It exists with several quality levels, which vary according to the P content (between 20% and 27%).

Another compound in this class is cuprophosphorus, also known as copper phosphide, which has an approximate composition of Cu_3P and a metal-like nature with a grayish to yellowish appearance. It is prepared by contacting white phosphorus with molten copper in a crucible. It is a component of phosphor bronze, a type of bronze known for its toughness and hardness. It is also a minor additive for the aluminum industry.

These metallic phosphides are virtually unreactive toward air and water. Even though they contain elemental phosphorus, they show no tendency to oxidize or form phosphine gas with water.

The other class of phosphides is the salt type; these are nonmetallic powders. Like cuprophosphorus, all of these compounds are prepared by mixing and heating the appropriate metal with white phosphorus.

These phosphides are highly reactive toward moisture, even moist air, and release phosphine gas upon contact, making them highly hazardous to handle. This phosphine-generating property is exploited in the application of aluminum phosphide (AlP) for fumigation (see also the section on phosphine); pellets of AlP are put in a porous container and then placed in a grain silo, where phosphine gas is slowly generated from the pellets. This kills any insects or rodents in the stored grain.

AlP is also an ingredient of a class of niche photovoltaic materials, such as aluminum-gallium-indium phosphide (AlGaInP). This class also includes indium phosphides and ternary combinations of In/Al/Ga phosphides. InP is part of a new high-quality liquid display system prepared via the phosphine TMSP (see the section on phosphines). In 2023, the Nobel prize for chemistry was awarded for research on quantum dots, although not necessarily P based. Indium phosphide is also a niche semiconductor material for high-power, high-frequency applications.

Magnesium phosphide (Mg_3P_2), calcium phosphide (Ca_3P_2), and zinc phosphide (Zn_3P_2) are also used in fumigation.

New developments in phosphorus chemistry

Phosphorus was the first element to be artificially produced by humans. It is therefore not surprising that the basic chemistry of phosphorus has been well explored. Most of the phosphorus-based chemicals we use in our daily lives have been known for decades, sometimes more than a century.

These compounds have been around for so long that their markets have been consolidated. For instance, ZDDP lubricant additives (6.3.2) have been around since the 1940s and have closely followed the success of combustion engine cars. Their full potential was realized only after more demanding combustion engines were developed in the 1950s. Glyphosate herbicide (5.2.1) saw a breakthrough in the 1970s and has seen market expansion to a peak in the decades following that. It is sold together with glyphosate resistant crops, forming a package, with both components depending on each other. Phosphorus-based flame retardants have been developed since the 1960s, with phosphinates as the latest addition in the early 2000s. Perhaps the latest market addition of a significant phosphorus-based chemical is $LiPF_6$ (5.4.1), a crucial electrolyte in lithium-ion batteries.

These examples share a common trait: the underlying chemistry has been known for a long time, but their particular properties make them extremely suited for their current roles after they were selected for use in the relevant application. They are part of a wider technology package – for instance, the ingredients of a lithium-ion battery have been carefully chosen to work together in the best way (compatibility). This means the use of such chemicals has become ingrained in our technological society, and they will be abandoned only if something better is developed (for the chemical or the system it is part of) or if their current use comes under scrutiny, e.g., because of environmental concerns.

Noting that the chemistry of the field is well explored, new developments can be expected in two possible scenarios:

- Discovering a new function of an existing chemical
- Discovering a new material with useful properties

With ever increasing knowledge and two centuries of research behind us, the chances of discovering a truly new functionality for a well-established material are not very high. Even so, in some fields, there is a need for new functionalities. The world is being electrified, and we need improved batteries beyond current systems (higher capacities, increased safety). Existing phosphorus chemicals play a role in this endeavor: lithium iron phosphate for battery cathodes (3.3.5) and possibly new electrolytes based on lithium tetrathiosulphate (6.3.4). Both compounds have been known for a long time as laboratory chemicals but could now take center stage in electrifying our society.

An example of a new material is indium phosphide-based quantum dots (7.6). Even though the chemical itself has been known since 1910 and its functionality as semiconductor has been known since the 1960s, its properties as nanoparticles are markedly different from those of the bulk material, opening a new and potentially large application in displays. If the material has optimal performance and compatibility, it may undergo development as described for the established phosphorus-based chemicals.

Black phosphorus is a different example of the second category. Its existence has been known since 1914, but because its synthesis required extreme pressures, its properties were not intensively studied, as any practical applications were out of reach. Since its synthesis was considerably simplified recently, it has become available in larger quantities and at more affordable prices. This has triggered a new round of investigations that have led to potential applications at some scale. In this sense, it can be considered a new material because of its improved availability.

8 Phosphorus sustainability

Phosphorus is an element, so it cannot be destroyed. This means that all the phosphate/phosphorus we mine and use goes somewhere.

Unsurprisingly, this chiefly concerns the main use of phosphorus in our world: fertilizers.

Phosphorus sustainability is a vast subject, but this chapter aims to present some relevant information in the context of the nonagricultural uses of phosphorus.

In brief, in the phosphate value chain, a few major nodes appear where the efficiency of phosphorus use can be improved.

In mining systems, more efficient mining and beneficiation can help with the valorization of phosphate deposits. Technologies using low-grade phosphate rocks may allow access to lower-grade deposits and mine tailings. This is, of course, often accompanied by increased cost.

Phosphate fertilizing practices may benefit from precision fertilizers and rethinking the current, water-soluble-based system. Agronomy is a crucial part of phosphorus stewardship.

Phosphate in fertilizers typically ends up at two main end points: fields/runoff to water bodies and the food system. Improved fertilizer application practices are therefore expected to not only help reduce P losses (e.g., ending up fixed in soils) but also prevent losses to surface water, where eutrophication can occur.

In addition to phosphates ending up in our food via crops or meat, feed phosphates end up in manure and slaughter waste, which are byproducts of the food system.

Various opportunities exist to close the phosphorus loop (Figure 43). Phosphate in food byproducts can be recycled by composting. Manure, which represents a large phosphate stream, is already recycled, even though this process is unbalanced and oversupplied in some regions.

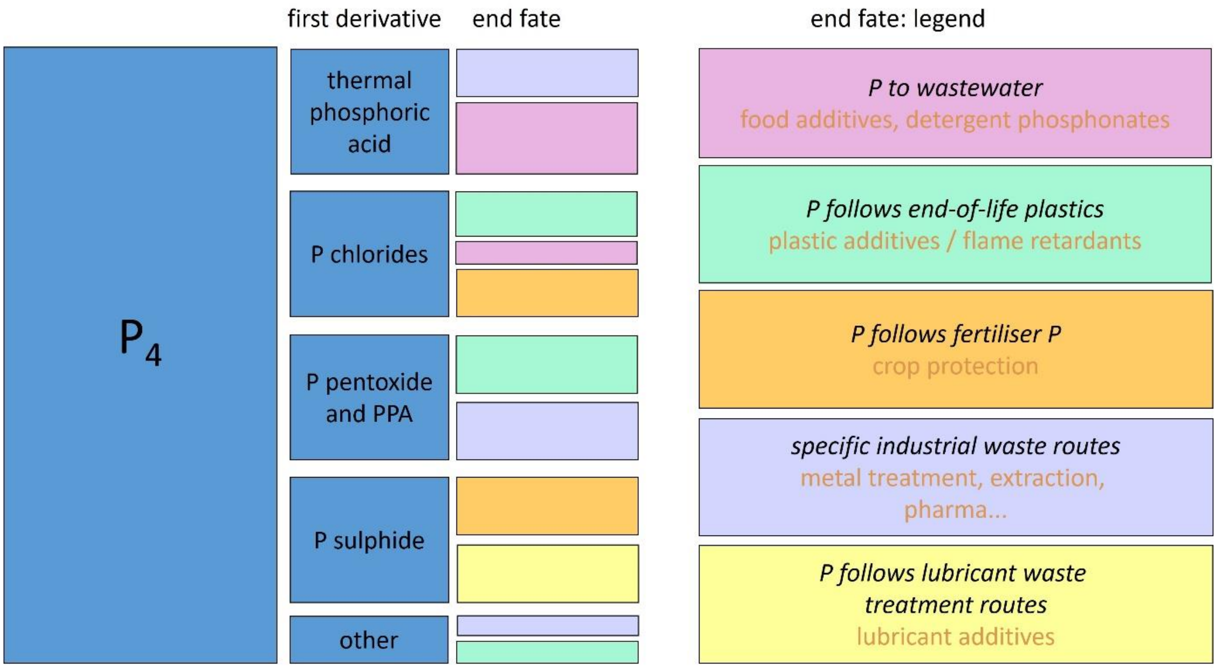

Figure 43 Main environmental fates of true P_4 derivatives

Slaughter waste is another important entry point for phosphorus recycling.

Phosphates that end up in the human food chain are collected in sewage systems. This approach offers a prime recycling option via sewage sludge, or sewage sludge ash, obtained after incineration of this sludge. Many technologies have been proposed to recycle such phosphates.[48]

With nonfertilizer applications at a fraction of the total use of phosphorus, it is obvious that any recovery of spent phosphorus in this section is minor compared to the food-feed-fertilizer system described above.

However, it is possible to determine where the phosphorus in P_4 derivatives ends up after it has been used (see Figure 43).

Not all these sectors offer a viable recycling protocol. It is therefore safe to assume that phosphorus recycling in the true derivatives sector is not based on internal cycles within that subsystem but rather by attaching to the broader food-feed-agriculture phosphorus system.

White phosphorus, which is at the center of this report, can be produced from other materials in addition to phosphate rock.

The following attempts have been or are being made to recycle phosphate into P_4:

- In 2007-2012, Thermphos International, a producer of white phosphorus based on phosphate rock, successfully recycled 60 kt of sewage ash, meat and bone meal ash, and struvite into white phosphorus, replacing phosphate rock. This company went bankrupt for unrelated reasons in 2013, preventing further development of this route. Technical limitations existed for iron, zinc and copper levels in sewage ashes, which were the main source of recycled phosphate in this project.
- The EU subsidized Recophos project in Leoben, Austria,[49] aimed to prepare P_4 from sewage sludge ash. This process faced challenges associated with the formation of ferrophosphorus, which is an issue given the iron-rich ash used in the process. It was not developed further until recently, although there has been interest from industry.[50]
- A variation on Recophos, but based on sewage sludge rather than ash, is being developed: Flashphos,[51] also with industrial backing. A goal of this project is to study whether the issue of excessive ferrophosphorus byproduct can be avoided in view of the high iron content of sewage sludge used as a feedstock.
- A relatively new process is the aluminothermal reduction of sewage ash and other materials to white phosphorus.[52]
- Research has been devoted to recovering P_4 from steel slags, which may contain approximately 4% P_2O_5. These processes suffer from co-reduction of abundantly available iron oxides, leading to the formation of ferrophosphorus and low to moderate P_4 yields.[53,54]

- Electrolysis of phosphate rock in calcium chloride[55] or in a sodium metaphosphate melt[56] has been proposed. These processes hold promise for reducing the energy use of P_4 production (typically by 25-30% in theory) but need thorough development. For a route starting from sodium phosphates/phosphoric acid, the preceding value chain to (pure) phosphoric acid also needs to be considered for comparison. These processes were preceded by literature from half a century ago.[57] There was also a patent from 1960[58] for a metaphosphate-based electrochemical P_4 production process, which has not led to industrial development.
- Thermal processes starting from phosphoric acid and carbon have been proposed [see, e.g.,[59]]. These materials do not produce slag (which results in energy loss in the classical process); however, for a true comparison, the preceding route leading from phosphate rock to phosphoric acid, including the generation of phosphogypsum, needs to be considered as well.

Conflict of interest

The author declares no competing financial interests.

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