Kirk-Othmer Encyclopedia of Chemical Technology.

PHOSPHINE AND ITS DERIVATIVES

Although phosphine [7803-51-2] was discovered over 200 years ago in 1783 by the French chemist Gingembre, derivatives of this toxic and pyrophoric gas were not manufactured on an industrial scale until the mid- to late 1970s. Commercial production was only possible after the development of practical, economic processes for phosphine manufacture which were patented in 1961 (1) and 1962 (2). This article describes both of these processes briefly but more focus is given to the preparation of a number of novel phosphine derivatives used in a wide variety of important commercial applications, for example, as flame retardants (qv), flotation collectors, biocides, solvent extraction reagents, phase-transfer catalysts, and uv photoinitiators.

1. Manufacture of Phosphine

Two processes have been used to manufacture gaseous phosphine on a large scale. These are commonly known as the alkaline (1) and acid processes (2).

In the alkaline process, an aqueous solution of sodium hydroxide is allowed to react with molten, yellow phosphorus. A long-chain alcohol is used as a dispersant (3). The reaction to produce phosphine may be represented by equation 1.

$$P_4 + 3\ NaOH + 3\ H_2O \xrightarrow{80^\circ C} 3NaH_2PO_2 + PH_3 \qquad (1)$$

However, hydrogen is formed in two side reactions, ie, by the decomposition of some sodium hypophosphite (eq. 2) and by the direct reaction of phosphorus with sodium hydroxide (eq. 3).

$$NaH_2PO_2 + 2\ NaOH \longrightarrow 2\ H_2 + Na_3PO_4 \qquad (2)$$

$$P_4 + 4\ NaOH + 4\ H_2O \longrightarrow 4\ NaH_2PO_2 + 2\ H_2 \qquad (3)$$

The presence of approximately 60% hydrogen in the gas is a disadvantage because the preparation of many phosphine derivatives involves the high pressure reaction of phosphine with, for example, olefins. However, claims have been made that careful control of the reaction conditions can prevent the production of hydrogen and that 95% pure phosphine can be generated (4, 5). Additionally, the stoichiometric yield of phosphine based on phosphorus usage is 25%, but in practice yields of 30% are obtained (3). It is probable, therefore, that equations 1–3 do not represent all of the reaction chemistry. This process, based on the patent, has been operated by Hoechst AG in Germany since the late 1970s.

In the acid process, yellow phosphorus is converted to a mixture of yellow and red by heating to almost 300°C for several hours. The mixture is subsequently treated with steam at 280°C to produce phosphine (eq. 4).

$$2\ P_4 + 12\ H_2O \xrightarrow[280^\circ C]{H^+} 5\ PH_3 + 3\ H_3PO_4 \qquad (4)$$

The reaction is acid catalyzed by the by-product phosphoric acid. Only red phosphorus reacts. Unreacted yellow phosphorus is separated and recycled.

The acid process has three advantages over the alkaline process, ie, (*1*) higher yield of phosphine (60 vs 25%); (*2*) more pure gas for use in subsequent reactions (95 vs 40%); and (*3*) by-product phosphoric acid is relatively valuable and can be sold into a number of markets, eg, in the manufacture of fertilizers and flame retardants. There is no ready outlet for the mixture of phosphites produced via the alkaline route and additional processing by oxidative spray drying is needed to produce phosphates for sale (3).

The principal disadvantage of the acid process is the higher capital cost involved; mainly because of more processing steps and the corrosivity of hot, concentrated phosphoric acid which requires a reactor built from dense graphite.

The acid process has been operated since 1970 by Cytec Canada Inc. (Niagara Falls, Canada) and since 1980 by Albright and Wilson Ltd. (Oldbury, England). Many of the details of the process are considered to be proprietary because of its specialized nature. Nippon Chemicals has also been producing phosphine, probably by the acid process, in Japan since the early to mid-1980s. Typical properties of phosphine are given in Table 1.

2. Health and Safety Factors

2.1. Toxicity

Lethality is the primary hazard of phosphine exposure. Phosphine may be fatal if inhaled, swallowed, or absorbed through skin. All phosphine-related effects seen at sublethal inhalation exposure concentrations are relatively small and completely reversible. The symptoms of sublethal phosphine inhalation exposure include headache, weakness, fatigue, dizziness, and tightness of the chest. Convulsions may be observed prior to death in response to high levels of phosphine inhalation. Some data are given in Table 2.

The potential mutagenicity of phosphine has been examined by exposing bacteria, tissue culture cells, and animals to phosphine, then examining these organisms for signs of genetic mutation. The majority of these studies have indicated that phosphine is not mutagenic but some of the studies have indicated that phosphine may be a weak mutagen. There is not sufficient evidence to indicate that phosphine is either an animal or human carcinogen.

2.2. Safety

The pyrophoric and toxic nature of phosphine requires the adoption of special precautions to ensure safety during manufacture on a commercial scale. Of particular note are the provisions of flame retardant, protective clothing for operating personnel, and strategically located breathing-air stations equipped with in-line respirators. Additionally, the facility operated by Cytec Canada Inc. is equipped with two special phosphine detectors, manufactured by HNU Systems Inc. (Newton, Massachusetts), to protect operators from overexposure. In a cycle which lasts only 12 minutes, each detector automatically collects and analyzes air samples from 10 remote sampling points located in key areas of the plant. The instruments automatically activate audio and visual alarms if the local phosphine concentration exceeds its TLV (0.3 ppm) thus allowing remedial steps to be taken.

Table 1. Properties of Phosphine

Property	Value
appearance and odor	colorless gas with garlic odor
freezing point, °C	−133.8
boiling point, °C	−87.8
critical temperature, °C	51
critical pressure, MPa[a]	6.485
heat of fusion, kJ/mol[b]	1.13
heat of vaporization, kJ/mol[b]	14.6
heat of formation, kJ/mol[b]	9.59
index of refraction (liquid), n_D^T	1.317
solubility[c] in water, mL/100 mL H_2O	26
heat capacity (liquid), J/g	
at 0°C	2.43
at 25°C	2.76
viscosity (gas), mPa(=cP)	
at 0°C	0.01
at 100°C	0.014
viscosity (liquid), mPa(=cP)	
at −50*C*	0.1
at 25°C	0.05
surface tension (liquid), mW/m (=dyn/cm)	
at 0°C	70
at 25°C	35

[a] To convert MPa to psi, multiply by 145.
[b] To convert kJ to kcal, divide by 4.184.
[c] At 101.3 kPa (= 1 atm).

Table 2. Effect of Phosphine Exposure

Parameter	Concentration, ppmv
TLV–TWA[a]	0.3
odor threshold	1.5–3.0
transient health effects after several hours	5.0–7.0
maximum exposure for 0.5–1 h without serious effects	100–200
lowest lethal concentration (human), 5 min	1000

[a] Threshold limit value–time weighted average. Defined as the maximum time weighted average concentration to which a worker may be exposed repeatedly and without adverse effects for a normal 8 h/d, 40 h/wk period.

3. Uses

Apart from the manufacture of derivatives, there are only two known uses for phosphine itself, ie, in the preparation of semiconductors and as a fumigant.

3.1. Semiconductors

Phosphine is commonly used in the electronics industry as an *n*-type dopant for silicon semiconductors (6), and to a lesser extent for the preparation of gallium–indium–phosphide devices (7). For these end uses, high purity, electronic-grade phosphine is required; normally $\geq 99.999\%$ pure. The main impurities that occur in phosphine manufactured by the acid process are nitrogen [7727-37-9], hydrogen [1333-74-0], arsine [7784-42-1], carbon dioxide [124-38-9], oxygen [7782-44-7], methane [74-82-8], carbon monoxide [630-08-0], and water [7732-42-1].

Phosphine is purified by distillation under pressure to reduce the level of these compounds to ≤ 1 ppm by volume. The final product is sold as CYPURE (Cytec Canada Inc.) phosphine.

3.2. Fumigants

Phosphine generated *in situ* by the reaction of atmospheric moisture with pelletized calcium, aluminum, or magnesium phosphide is used as a fumigant in, for example, grain silos (8, 9). However, this technique suffers from several disadvantages. For example, the rate of phosphine generation and concentration in the atmosphere are dependent on the prevailing moisture content of the atmosphere and the reaction is sufficiently exothermic to cause fire and explosions if free water comes into contact with the pellets (9). A safer, more efficient method has been developed (9) and involves the controlled injection of a mixture containing 2% by weight phosphine in carbon dioxide into the structure to be fumigated. This is used commercially in Australia.

4. Phosphine Derivatives

Commercial phosphine derivatives are produced either by the acid-catalyzed addition of phosphine to an aldehyde or by free-radical addition to olefins, particularly α-olefins. The reactions usually take place in an autoclave under moderate pressures (≤ 4 MPa (580 psi)) and at temperatures between 60 and 100°C.

In the case of olefins, the reaction generally yields a mixture of primary, secondary, and tertiary phosphines, as follows:

$$C_xH_{2x} + PH_3 \longrightarrow C_xH_{2x+1}PH_2 + (C_xH_{2x+1})_2\,PH + (C_xH_{2x+1})_3\,P \qquad (5)$$

However, the composition of the mixture can be controlled to some extent by the correct choice of olefin and reaction conditions. For example, the production of tertiary phosphines can be maximized by conducting the reaction at relatively low phosphine pressures, $\sim$1.5 MPa (200 psi), and using a 20–30% stoichiometric excess of a straight-chained olefin as in the synthesis of tributylphosphine [988-40-3] by reaction with 1-butene [106-98-9].

$$PH_3 + 3\ C_4H_8 \xrightarrow[1.5\ \text{MPa}]{90^\circ\text{C}} (C_4H_9)_3P \qquad (6)$$

In this case, yields >95% of the tertiary phosphine are obtained. Tributylphosphine is readily converted to tetraalkylphophonium salts by reaction with an alkyl halide. These compounds are used commercially as biocides and phase-transfer catalysts.

In contrast, if the olefin is more sterically hindered (branched) and/or the reaction is operated at a higher pressure (4 MPa), formation of the primary and secondary phosphines is favored as in the reaction with 2,4,4-trimethyl-1-pentene [107-39-1].

$$\begin{array}{lcccc} PH_3 + C_8H_{16} \longrightarrow & (C_8H_{17})PH_2 & + (C_8H_{17})_2PH & + (C_8H_{17})_3P & (7) \\ & 43\% & 51\% & 6\% & \end{array}$$

The mixture can be separated by distillation. The primary phosphine is recycled for use in the subsequent autoclave batch, the secondary phosphine is further derivatized to the corresponding phosphinic acid which is widely employed in the industry for the separation of cobalt from nickel by solvent extraction. With even more hindered olefins, such as cyclohexene [110-83-8], the formation of tertiary phosphines is almost nondetectable.

Other typical alkylphosphines that can be prepared through phosphine chemistry are monoisobutylphosphine [4023-52-3], trioctylphosphine [4731-53-7], monocyclohexylphosphine [822-68-4], dicyclohexylphosphine [829-84-5], and triethylphosphine [554-70-1].

4.1. Textile Flame Retardants

The first known commercial application for phosphine derivatives was as a durable textile flame retardant for cotton and cotton–polyester blends. The compounds are tetrakis(hydroxymethyl)phosphonium salts (10) which are prepared by the acid-catalyzed addition of phosphine to formaldehyde. The reaction proceeds in two stages. Initially, the intermediate tris(hydroxymethyl)phosphine [2767-80-8] is formed.

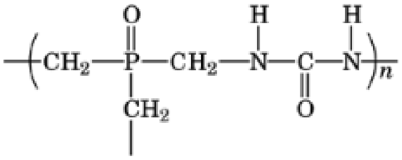
$$PH_3 + 3\ CH_2O \xrightarrow{H^+} (HOCH_2)_3P \qquad (8)$$

This compound is unstable, particularly at alkaline pH, and decomposes to release hydrogen. It is not isolated but reacts *in situ* with an additional mole of formaldehyde and a mineral acid, for example hydrogen chloride [7647-01-1], to form the phosphonium salt.

$$(HOCH_2)_3\,P + HCl + CH_2O \longrightarrow (HOCH2)_4\,P^+Cl^- \qquad (9)$$

The salt in this case is tetrakis(hydroxymethyl)phosphonium chloride [124-64-1]. The corresponding sulfate salt [55566-30-8] is also produced commercially as are urea-containing formulations of both salts. The latter formulations are actually used to flame retard the textiles (see Flame retardants for textiles).

After application to the fabric, the compounds are polymerized by reaction with gaseous ammonia (11, 12), then oxidized to phosphine oxides by reaction with hydrogen peroxide. The structure of the polymer is shown (13).



$$\left(CH_2-\underset{\underset{|}{CH_2}}{\overset{\overset{O}{\|}}{P}}-CH_2-\overset{\overset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{|}}{N} \right)_n$$

This provides a durable finish which, unlike many other flame retardants, can withstand repeated (50–100) launderings without a loss of efficiency. An added advantage is that the feel of the cloth (hand) is little effected. Principal markets are in the treatment of industrial protective clothing, military uniforms, and, in Europe, for furnishings. These products are available from Albright & Wilson Ltd. and Cytec Industries Inc.

4.2. Flotation Reagents

Only one sulfide mineral flotation collector is manufactured from phosphine, ie, the sodium salt of bis(2-methylpropyl)phosphinodithioic acid [13360-78-6]. It is available commercially from Cytec Industries Inc. as a 50% aqueous solution and is sold as AEROPHINE 3418A promoter. The compound is synthesized by reaction of 2-methyl-1-propene [115-11-7] with phosphine to form an intermediate dialkylphosphine which is subsequently treated with elemental sulfur [7704-34-9] and sodium hydroxide [1310-73-2] to form the final product (14). The reactions described in equations 10 and 11

$$2\ C_4H_8 + PH_3 \xrightarrow[80^\circ C]{3.3\ MPa} (C_4H_9)_2PH \qquad (10)$$

$$(C_4H_9)_2PH + 2\,S + NaOH \xrightarrow{60^\circ C} (C_4H_9)_2SNa + H_2O \qquad (11)$$

are carried out in an autoclave and a glass-lined kettle, respectively. The primary phosphine formed during the autoclave reaction is removed from the autoclave liquor by distillation and is recycled for use in the next autoclave batch. The tertiary phosphine reacts with sulfur in equation 12 to produce tris(2-methylpropyl)phosphine sulfide [3982-87-4], a solid which is separated from the product using a centrifuge.

$$(C_4H_9)_3\,P + S \longrightarrow (C_4H_9)_3\,P\,(S) \qquad (12)$$

AEROPHINE 3418A promoter is widely used in North and South America, Australia, Europe, and Asia for the recovery of copper, lead, and zinc sulfide minerals (see Flotation). Advantages in comparison to other collectors (15) are said to be improved selectivity and recoveries in the treatment of complex ores, higher recoveries of associated precious metals, and a stable grade–recovery relationship which is particularly important to the efficient operation of automated circuits. Additionally, AEROPHINE 3418A is stable and, unlike xanthates (qv), does not form hazardous decomposition products such as carbon disulfide. It is also available blended with other collectors to enhance performance characteristics.

4.3. Phase-Transfer Catalysts

The use of phase-transfer catalysts to improve kinetics and yields in heterogeneous reactions has been growing rapidly since the 1960s. The five to ten commercial processes in use in 1970 had risen to 550 (16) by 1989. The principal areas of application are in the preparation of polymers, accounting for 50% of catalyst consumption, followed by pharmaceuticals (20%) and agricultural chemicals (10%). Details of the chemistry and applications have been given elsewhere (17) (see Catalysis, phase-transfer). The most common phase-transfer catalysts are quaternary ammonium salts containing either alkyl or mixed alkaryl groups. However, these compounds are being displaced in some applications by the corresponding phosphonium salts mainly because of the enhanced thermal stability of the phosphorus compounds (17). Additionally, the phosphonium salts tend to be more efficient than the nitrogen-based analogues and can promote more rapid reaction kinetics (18).

Phosphonium salts are readily prepared by the reaction of tertiary phosphines with alkyl or benzylic halides, eg, the reaction of tributylphosphine [998-40-3] with 1-chlorobutane [109-69-3] to produce tetrabutylphosphonium chloride [2304-30-5].

$$(C_4H_9)_3P + C_4H_9Cl \xrightarrow{60^\circ C} (C_4H_9)_4P^+Cl^- \qquad (13)$$

Kinetics are slow and many hours are required for a 95% conversion of the reactants. In the case of the subject compound, there is evidence that the reaction is autocatalytic but only when approximately 30% conversion to the product has occurred (19). Reaction kinetics are heavily dependent on the species of halogen in the alkyl halide and decrease in the order $I > Br > Cl$. Tetrabutylphosphonium chloride exhibits a high solubility in a variety of solvents, for example, >80% in water, >70% in 2-propanol, and >50% in toluene at 25°C. Its analogues show similar properties. One of the latest applications for this phosphonium salt is the manufacture of readily dyeable polyester yarns (20, 21).

In addition to tetrabutylphosphonium chloride, typical phosphonium salts that can be produced include tetraoctylphosphonium bromide [23906-97-0], tetrabutylphosphonium acetate [17786-43-5] (monoacetic acid), and tetrabutylphosphonium bromide [3115-68-2]. In most cases, these compounds can be prepared with alternative counterions.

4.4. Biocides

Two phosphine derivatives are in commercial use as biocides. These are tetrakis(hydroxymethyl)phosphonium sulfate [55566-30-8] and tributyl(tetradecyl)phosphonium chloride [8741-28-8]. These compounds are sold by Albright and Wilson Ltd. and FMC, respectively. The preparation of the hydroxymethylphosphonium salt has been discussed (see Flame retardants). Synthesis of the tetraalkylphosphonium chloride follows the reaction described in equation 13 except that 1-chlorotetradecane [2425-54-9] is employed in place of 1-chlorobutane.

Various patents (22–24) have been issued claiming the use of tetrakis(hydroxymethyl)phosphonium sulfate in, for example, water treating, pharmaceuticals (qv), and in the oil industry where this compound shows exceptional activity toward the sulfate-reducing bacteria that are a primary cause of hydrogen sulfide formation and consequent problems associated with souring and corrosion (25).

Tributyl(tetradecyl)phosphonium chloride was developed specifically (26, 27) as a broad-spectrum biocide for the control of biological fouling in cooling water systems where it is particularly effective (see Industrial antimicrobial agents).

4.5. Ultraviolet Photoinitiators

Photoinitiators are used in increasing volume for a multitude of applications. The most important of these are in the formulation of uv-curable inks and in the production of coatings on vinyl flooring, wood, and electronics components (28, 29). The most common types of photoinitiators are phenone derivatives, for example, acetophenones and benzophenones (30).

However, Ciba-Geigy has introduced (31, 32) a type of phosphine-based photoinitiator. In general, the compound can be described as a bis(acyl)phosphine oxide and is prepared by the reaction of a monoalkylphosphine with a substituted benzoyl chloride (33). The composition of the first commercial product is proprietary.

However, advantages in comparison with conventional photoinitiators, including monoacylphosphine oxides, lie in the ability to prepare thicker coatings that have improved scratch resistance and do not yellow with age. The compound is self-bleaching. Pigmented coatings can also be prepared. This enables formulators, for the first time, to prepare white, uv-cured coatings. Initial areas of application are for furniture coatings and white screen inks.

4.6. Solvent Extraction Reagents

Solvent extraction is a solution purification process that is used extensively in the metallurgical and chemical industries. Both inorganic (34, 35) and organic (36) solutes are recovered. The large commercial uses of phosphine derivatives in this area involve the separation of cobalt [7440-48-4] from nickel [7440-02-0] and the recovery of acetic acid [61-19-7] and uranium [7440-61-1].

4.6.1. Uranium Recovery From Wet-Process Phosphoric Acid

In the mid- to late 1960s, work at the Oak Ridge National Laboratory (37, 38) led to the invention of a process to recover the low concentrations (100–200 mg/L) of uranium [7440-61-1], which occur naturally in the wet-process phosphoric acid [7664-38-2] used to make fertilizers (qv). Key to the development of this process was the discovery of the synergic interaction between the bis(2-ethylhexyl) ester of phosphoric acid [298-07-7] (D2EHPA) and trioctylphosphine oxide [78-50-2] (TOPO) in extracting U^{6+} (37). D2EHPA is prepared by conventional organophosphorus chemistry and TOPO is readily manufactured by the reaction of phosphine with octene [25377-83-7] to form intermediate trioctylphosphine [4731-53-7] which is subsequently oxidized to TOPO with hydrogen peroxide [7722-84-1] as outlined in equations 14 and 15. TOPO is a white, waxy solid with a melting point of approximately 50°C.

$$3\ C_8H_{16} + PH_3 \xrightarrow[1.5\ \text{MPa}]{90^\circ\text{C}} (C_8H_{17})_3P \qquad (14)$$

$$(C_8H_{17})_3P + H_2O_2 \xrightarrow{75^\circ\text{C}} (C_8H_{17})_3P(O) + H_2O \qquad (15)$$

Following further development (38), a two-cycle process has been adopted by industry. In the first concentration cycle, the clarified feed acid containing 100–200 mg/L U_3O_8 [1334-59-8] is oxidized, for example, with hydrogen peroxide or sodium chlorate [7775-09-9] to ensure that uranium is in its 6+ valence state; U^{4+} is not extracted. Uranium is extracted with a solvent composed of 0.5 *M* D2EHPA and 0.125 *M* TOPO dissolved in an aliphatic hydrocarbon diluent.

Uranium is subsequently stripped reductively from the loaded solvent using a bleed stream of the raffinate acid to which ferrous iron has been added to reduce uranium to its nonextractable, quadravalent state. Raffinate is acid from which uranium has already been extracted. By controlling the organic-to-aqueous volume phase ratios in the extraction and stripping circuits, uranium is concentrated by a factor of approximately 70.

Raffinate acid from the first cycle, containing approximately 7 to 14 g/L U_3O_8 is then reoxidized and re-extracted in the second, purification cycle using a solvent containing 0.3 *M* D2EHPA and 0.075 *M* TOPO. The loaded solvent is washed with iron-free acid to remove iron and then with water to remove extracted and entrained acid. The solvent is stripped with ammonium carbonate [506-87-6] to yield ammonium uranyl tricarbonate [18077-77-5] which is subsequently calcined to U_3O_8 (yellow cake). The stripped solvent is regenerated with mineral acid before recycling (39).

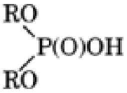
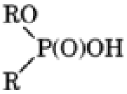
Beginning in approximately 1975, both IMC and Freeport Minerals operated large uranium recovery plants in the United States using this technology. Several plants continue to run but a number have been closed because of the depressed uranium prices that resulted when uranium from the former Soviet Union flooded Western markets. A relatively small plant is operated by Prayon in Belgium (40). TOPO is available from Cytec Industries Inc. as CYANEX 921 extractant. D2EHPA is available from Albright & Wilson Ltd. and is also sold by Daihachi as DP-8R.

4.6.2. Acetic Acid Recovery

Sulfite wood pulping operations produce dilute, aqueous effluents containing 10–20 g/L acetic acid. In some cases, 2-furancarboxaldehyde [98-01-1], more commonly known as furfural, can also be present at lower concentrations ($\sim$1 g/L) (41). Lenzing (Austria) recovers both of these by-products by solvent extraction with TOPO. Although few data concerning the plant have been published (41, 42), it is known (43) that the solvent is 30% TOPO in undecane [1120-21-4]. The extraction column is operated at 50°C and the aqueous-to-organic volume phase ratio (A/O) is 1. The loaded solvent is distilled to strip the extracted species, first to remove most of the water for recycle, then to strip an azeotrope of water, acetic acid, and furural. The azeotrope is further distilled to yield pure acetic acid and furfural. Both compounds are sold. The plant has been operating successfully since 1983 and supplies approximately 50% of Austria's demand for food-grade acetic acid.

In a similar application, Cape Industries has announced its intention to commission a solvent extraction plant to recover acetic acid from an effluent generated at its dimethyl terephthalate [120-61-6] facility (Wilmington, North Carolina) (44, 45). The plant was commissioned in February 1995. In this case, the solvent will be CYANEX 923 extractant [100786-00-3]. CYANEX 923 is also a phosphine oxide, but unlike TOPO is a liquid and can be used without a diluent (46, 47). This has the benefit of reducing plant size, capital, and operating costs.

Table 3. Organophosphorus Extractants for Co–Ni Separation[a]

Extractant[b] type	Structure	Commercial homologue, R =	Co–Ni[c] separation factor
phosphoric acid (D2EHPA)	 $(RO)_2P(O)OH$	2-ethylhexyl	14
phosphonic acid (PC-88A)	 $(RO)(R)P(O)OH$	2-ethylhexyl	280
phosphinic acid (CYANEX 272)	 $R_2P(O)OH$	2,4,4-trimethylpentyl	7000

[a] Conditions: temperature = $25C$; equilibrium pH = 4; A/O = 1.

[b] $0.1\ M$ extractant in MSB 210.

[c] Each metal ion concentration $2.5 \times 10^{-2}\ M$.

4.6.3. Cobalt–Nickel Separation

The bis(2,4,4-trimethylpentyl)phosphinic acid [83411-71-6] became commercially available during the early 1980s (48, 49). It is sold by Cytec Industries Inc. as CYANEX 272 extractant and was developed specifically to selectively extract cobalt from weakly acidic, nickeliferous solutions. It is a member of one of three groups of organophosphorus extractants that have been examined for cobalt–nickel separation. These are derivatives of phosphoric (50), phosphonic (51), and phosphinic (52) acids. CYANEX 272 has two significant advantages over its competing reagents. The first is superior cobalt–nickel selectivity, as illustrated by the results of some batch equilibrium tests shown (52) in Table 3.

The benefits of high selectivity lie in the ability to produce high purity cobalt in a limited number of stages. This minimizes capital and operating costs. It is particularly important when the solution in question contains low concentrations of cobalt. For example, solutions derived from laterite deposits may only contain 0.5–2 g/L Co but 90–100 g/L Ni.

The second principal advantage is that CYANEX 272 is the only one of the three above-mentioned compounds that extracts cobalt in preference to calcium (52). This property can minimize or eliminate the solvent losses that are associated with calcium extraction and the subsequent precipitation of gypsum cruds in the scrubbing or stripping circuits. This is illustrated in Figure 1 where calcium extraction is shown as a function of pH for the three subject reagents.

The first commercial plant to use CYANEX 272 became operational in 1985. An additional three plants were constructed between 1985 and 1989. Of the four, one is in South America and three in Europe. An additional three plants have been built; two in Europe (1994) and one in North America (1995). Approximately 50% of the Western world's cobalt is processed using CYANEX 272. Both high purity salts and electrolytic cobalt metal are recovered from solutions ranging in composition from 30 g/L each of cobalt and nickel to 0.2 g/L Co, 95 g/L Ni. Operating companies usually regard use of CYANEX 272 as confidential for competitive reasons and identities cannot be disclosed. CYANEX 272 is being evaluated on the pilot-plant scale in many additional projects involving the recovery of cobalt and other metals.

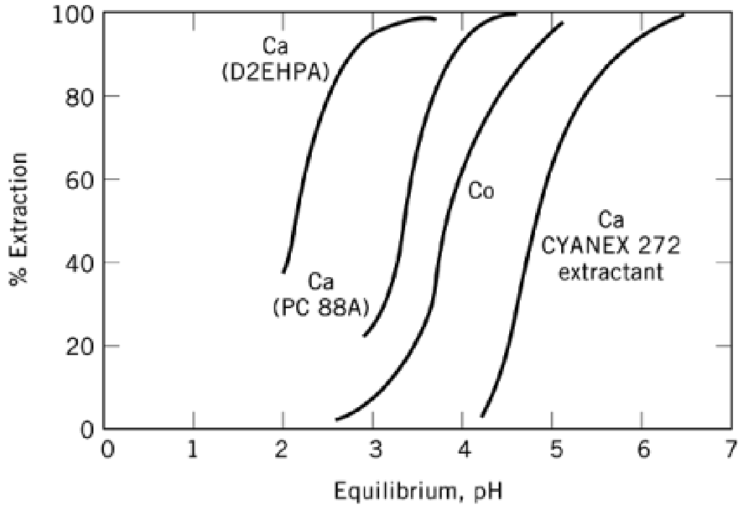


Fig. 1. Cobalt–calcium selectivity with organophosphorus extractants. Conditions: solvent $=0.6\ M$ extractant in Kermac 470B; aqueous $=0.015\ M$ metal ion as sulfate; temperature $=50C$; and A/O $=1$.

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