Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Solvent Extraction with Organophosphines—Commercial & Potential Applications—

W. A. Rickelton[a]; R. J. Boyle[a]
[a] American Cyanamid Company Welland Technical Center, Niagara Falls, Ontario, Canada

To cite this Article Rickelton, W. A. and Boyle, R. J.(1988) 'Solvent Extraction with Organophosphines—Commercial & Potential Applications—', Separation Science and Technology, 23: 12, 1227 — 1250
To link to this Article: DOI: 10.1080/01496398808075627
URL: http://dx.doi.org/10.1080/01496398808075627

SEPARATION SCIENCE AND TECHNOLOGY, 23(12&13), pp. 1227-1250, 1988

SOLVENT EXTRACTION WITH ORGANOPHOSPHINES - COMMERCIAL & POTENTIAL APPLICATIONS -

W.A. RICKELTON and R.J. BOYLE

AMERICAN CYANAMID COMPANY
WELLAND TECHNICAL CENTER
NIAGARA FALLS, ONTARIO
CANADA L2E 6T4

ABSTRACT

Phosphine was discovered in 1783 by Gengembre but, until Cyanamid began work in 1955, very little research had been concentrated on replacing one or more of the phosphorus to hydrogen bonds by phosphorus to carbon bonds. This paper describes that part of this research which focused on creating and reducing to commercial practice new organophosphine extractants for both metals and organic solutes.

The chemistry involves the reactions of phosphine with alpha-olefins to produce di- and trialkylphosphines. These derivatives can then be oxidized or thionated to afford four different types of reagents. The phosphine oxides and sulfides which are obtained function as extractants by a solvating mechanism while the phosphinic and dithiophosphinic acids produced are cation exchange reagents. The properties and performance characteristics of each of these classes of compounds are described. A new extractant, CYANEX® 925, is introduced. Commercial, as well as potential, applications for all of these extractants are discussed.

INTRODUCTION

It is generally believed that elemental phosphorus was discovered by Arabian alchemists as early as the 12th century(1), but the discovery is usually attributed to Brandt(1) in 1669. Twenty-five years later Boyle(2) prepared phosphoric acid, but it was not until 1783 that phosphine was made by Gengembre(3).

American Cyanamid Company, hereafter Cyanamid, first began synthetic work with phosphine in its Basic Research Department Laboratories in Stamford, CT in 1955. Although nearly 200 years had passed since Gengembre's discovery of the gas, the chemistry of phosphine and organic derivatives of phosphine in which one or more of the P-H bonds were replaced by a P-C bond had not been studied very extensively. The paucity of research with phosphine was probably due in part to its toxicity and flammability, but its obnoxious odor may also have been a factor.

Basic research resulted in the discovery of many products of commercial interest for several end uses. However, this paper focuses only on the research effort which created and reduced to practice new solvent extractants for both metals and organic solutes.

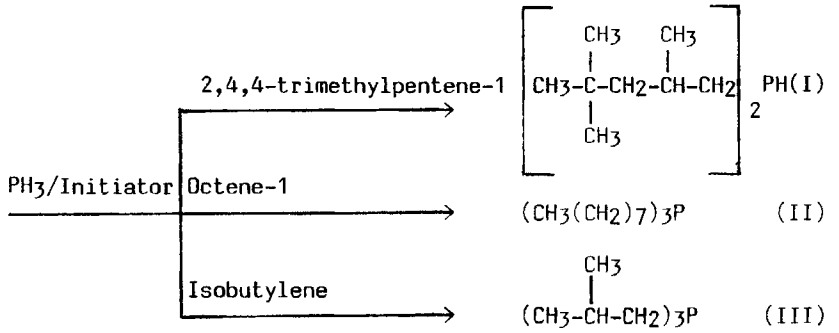
CHEMISTRY OF PHOSPHINE

Phosphine is manufactured by reacting red phosphorus with steam under pressure. The by-product phosphoric acid is sold for fertilizer manufacture.

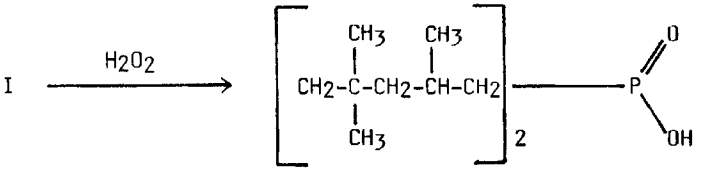
Some phosphine is upgraded to "five nine's" purity and sold as a dopant to the electronics industry. The remainder is reacted with olefins and carbonyl compounds to produce a variety of stable organophosphorus products. We are only concerned here with the derivatives obtained by the reaction of phosphine with olefins and the subsequent oxidation of these products to oxides, sulfides and acids.

Theoretically, it should be possible to react any alpha olefin with phosphine and obtain the corresponding mono, di and trialkylphosphine. But, sometimes the reaction is so fast, it is not practical to make the mono derivative; and sometimes, because of steric hindrance, it is only possible to make the dialkyl and not the trialkylphosphines.

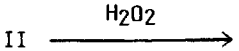
Shown below are the reactions which produce the intermediate phosphines for subsequent conversion to Cyanamid extractants.



An outstanding property of the trivalent phosphorus compounds is the ease with which they convert to the pentavalent state. When I and II are oxidized with hydrogen peroxide they produce the corresponding phosphinic acid and phosphine oxide.

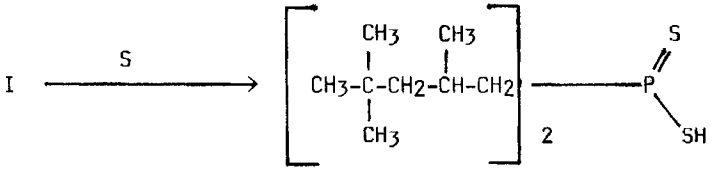


CYANEX® 272 Extractant

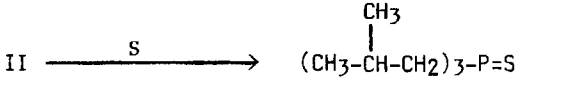


CYANEX 921 Extractant

When I and III are reacted with sulfur, the corresponding thioacid and sulfide are formed.

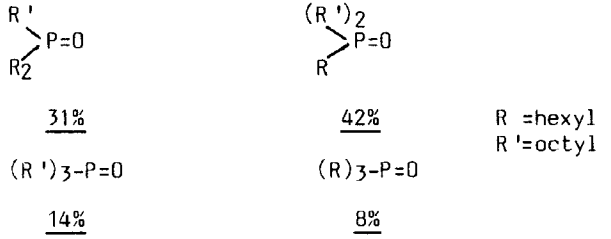


CYANEX 301 Extractant



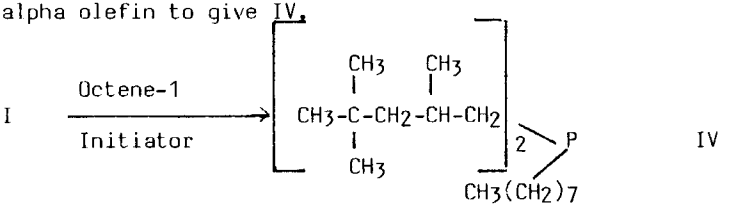
CYANEX 471X Extractant

It is also possible to react phosphine with a mixture of alpha olefins to obtain a chemical mixture of different trialkylphosphines which can be oxidized to the corresponding mixed oxides. For example, a mixture of 60% octene-1 and 40% hexene-1 will afford a mixture of trialkylphosphines which when oxidized, gives the following mixture:



This is CYANEX 923 extractant.

A mixed trialkylphosphine rather than a mixture of trialkylphosphines can be made by reacting I with a different alpha olefin to give IV.



Oxidation of IV with peroxide produces the corresponding phosphine oxide which is the latest organophosphine extractant, CYANEX 925.

PROPERTIES AND PERFORMANCE CHARACTERISTICS

All of the cited phosphines possess the ability to complex with various metals. Phosphinic and dithiophosphinic acids are compound formers which extract cations, whereas phosphine oxides and sulfides are solvating agents.

In general, phosphine oxides, like CYANEX 921, have high extraction coefficients for many metals and organic solutes but very low selectivity. On the other hand, alkylphosphine sulfides, like CYANEX 471X, have high extraction coefficients for only a few metals but are quite selective.

Dialkylphosphinic acids, like CYANEX 272, have high extraction coefficients and selectivity for many base and ferrous metals at specific pH's and also reject calcium and magnesium. Dialkyldithiophosphinic acids, (e.g, CYANEX 301) like phosphinic acids have high extraction coefficients for many metals. Extraction occurs at a low pH and the selectivity is poor, with the exception that alkaline earths are rejected.

APPLICATIONS OF PHOSPHINE OXIDES

CYANEX 921 Extractant (TOPO)

The specific extraction characteristics of TOPO have been reported in numerous publications (4). It has been studied far more thoroughly than all other organophosphines combined and has been available commercially since the mid 1970's. Despite this, only two commercial uses exist.

Uranium Recovery From Wet Process Phosphoric Acid:

In combination with di(2-ethyhexyl)phosphoric acid, (D2EHPA), TOPO is recognized as the extractant of choice for recovering uranium from wet process phosphoric acid. This process, developed at the Oak Ridge National Laboratory (5,6,7), is based on the synergic behavior of the D2EHPA-TOPO mixture. A number of these plants have been operating in the U.S. and Europe for several years.

Acetic Acid Recovery From Sulfite Pulping Liquors:

The other commercial use of TOPO is for the recovery of acetic acid and furfural from sulfite pulping liquors. Lenzing AG, a large textile fiber producer, has successfully operated such a plant in Austria since 1983. Their process is based on the patent of Kanzler and Schedler (8).

The following new uses of TOPO have been recently disclosed.

Niobium/Tantalum Separation

In Germany, Eckert and Bauer (9) have patented a process to separate and recover niobium and tantalum from a hydrofluoric - sulfuric acid leach liquor. The advantages of TOPO in comparison with the commonly used methylisobutylketone extractant are shown to be higher stability, lower aqueous solubility, rapid phase disengagement and, particularly, the production of a higher purity niobium oxide which meets the stringent specifications for nuclear, optical and electronic applications.

Arsenic Removal From Copper Electrolytes

A European patent [10] issued to Marr et al. covers the removal of arsenic from copper electrolytes by solvent extraction. TOPO is shown to be a stronger extractant for arsenic than tributylphosphate which is now used commercially in two arsenic solvent extraction plants. This property is claimed to result in lower staging requirements and solvent inventory.

Rhenium Recovery From Spent Catalyst

A recent U.S. patent [11] issued to Cyanamid discloses the use of TOPO for the selective recovery of rhenium from sulfuric acid solutions resulting from the leaching of spent petroleum reforming catalyst.

CYANEX 923 Extractant

Carboxylic Acid Recovery[9]

Data indicate that CYANEX 923 can be used to advantage over TOPO in the recovery of acetic acid because it is a liquid with a low freezing point and is completely miscible with all commonly used diluents even at low ambient temperatures. These properties permit the preparation of concentrated stable solvents, which leads to lower staging requirements in extraction and virtually eliminates the problem of plant freeze-up during periods when the ambient temperature is low.

Phenol Recovery[9]

Phenols, like carboxylic acids, are a common component of many aqueous effluents, e.g. waste streams produced during coal liquefaction, coal gasification (steel manufacture) and in the petrochemical industry.

As with acetic acid, the potential benefit of recovering phenol by solvent extraction with CYANEX 923 is the ability to construct plants with minimal staging requirements. Since phenol is strongly extracted by phosphine oxides, the advantages of CYANEX 923 extractant over TOPO are less marked than in the case of the more weakly extracted acetic acid. The major factor in choosing between the two in phenol systems will depend upon the concentration of phenol in the effluent.

Ethanol Recovery[12][13]

CYANEX 923 extractant exhibits a separation factor in ethanol/water solutions near the maximum useful limit for recovery from continuous fermentation broths, typically containing 5%

ethanol. Higher values do not further reduce extractor size or the energy required in downstream distillation. However, when compared with other candidate ethanol extractants, the principal advantage of CYANEX 923 lies in its very low solubility in water (0.001 wt.%). In actual practice soluble losses to the raffinate are even lower than this.

Impurity Removal From Copper Electrolytes[14]

CYANEX 923, like TOPO, has been shown to be an efficient extractant for arsenic, bismuth, and to a lesser extent, antimony at the sulfuric acid concentrations normally encountered in copper electrolytes i.e. approximately 160 g/L H_2SO_4. Both reagents are comparatively weak arsenic extractants but CYANEX 923 being a liquid can be used undiluted or at a high concentration in the diluent. Thus, a more efficient extraction performance is obtainable with CYANEX 923 than with TOPO, which is not only a solid but also exhibits limited solubility in commonly used diluents.

APPLICATIONS OF PHOSPHINE SULFIDES

Unlike their phosphine oxide analogues, trialkylphosphine sulfides are soft Lewis bases. As such, they only complex readily with metals which exhibit the characteristics of soft Lewis acids [15], i.e. those metals having a large ionic radius, a low or zero oxidation state and which are easily polarized. Only a few metals in the periodic table meet these criteria, e.g. Ag^+, Hg^{2+}, Pd^{2+} and Au^{3+}.

CYANEX 471X Extractant

Silver Recovery

One potential application is the selective extraction of silver from a copper-zinc sulfate solution as illustrated by a continuous, counter-current, mini-plant test[16]. (Using Bell mixer-settlers). The experiment involved two stages of extraction and two of stripping using a commercially available sodium thiosulfate "fixer" solution as the strip feed. An advantage of using this stripping agent is that silver is readily recovered from it by either cementation or electrolysis. Additionally, the ability to recycle it after silver recovery contributes significantly to the lowering of operating costs. These conditions afforded a quantitative recovery of Ag and outstanding separation factors, ($Ag/Zn = 0.5 \times 10^6$ and $Ag/Cu = 1.5 \times 10^6$).

Platinum - Palladium Separation

A commercial use of CYANEX 471X is in the separation of Pd^{2+} from chloride solutions containing Pt^{4+}[16]. As with silver,

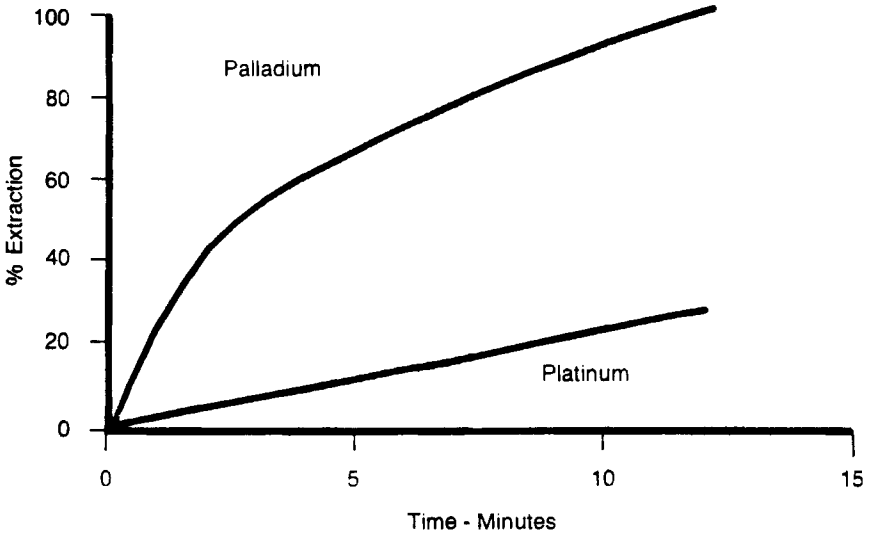


Figure 1 Kinetics of Pd (II) and Pt (IV) extraction with CYANEX® 471X extractant.

palladium extraction occurs through a solvating mechanism. Similarly, stabilized thiosulfate solutions are an effective strip feed. A study of the rate of the extraction has shown that the selective separation of these two metals is kinetically based. The results, plotted in Figure 1, were obtained at 50°C and A/O = 2 by contacting an unmodified solvent (30 g/L CYANEX 471X extractant in Varsol DX-3641 diluent) with an aqueous chloride solution containing 1 g/L Pd^{2+} and 1 g/L Pt^{6+} in 2N HCl.

Mercury Recovery

Another potential use of CYANEX 471X, investigated by Yoshimari Baba et al., is the extraction of Hg^{2+} from hydrochloric acid solution. Excellent results were reported (17). The recovery of Hg^{2+} from wastewater using CYANEX 471X is also the subject of a recent Mitsui-Cyanamid patent (18). Stripping is accomplished with aqueous thiocyanate or thiosulfate solution.

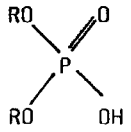
APPLICATIONS OF PHOSPHINIC ACIDS

Cobalt-Nickel Separation

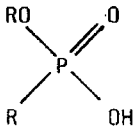
Bis (2,4,4-trimethylpentyl) phosphinic acid (CYANEX 272 extractant) is one of the three organophosphorus acids which have

been studied extensively for cobalt - nickel separation [19][20]. The other two are D2EHPA and the mono-2-ethylhexyl ester of 2-ethylhexylphosphonic acid (sold under the tradename PC-88A by Daihachi Chemical Industry, Co., Ltd.).

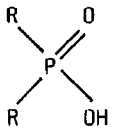
The structures of these acids are:



D2EHPA



PC-88A



CYANEX 272

where R is the appropriate alkyl group.

In cobalt-nickel separation, these structural differences have a significant impact on selectivity as illustrated by the results of some comparative shake-out tests given below[21].

Extractant	Co/Ni Separation Factor
D2EHPA	14
PC-88A	280
CYANEX 272	7000

CYANEX 272 extractant offers another important advantage in that it is the only one of the above organophosphorus acids which extracts cobalt in preference to calcium. This property can minimize or eliminate problems which are associated with calcium extraction and the subsequent precipitation of gypsum, e.g., scaling of equipment and the formation of cruds which leads to solvent losses.

Continuous counter-current tests performed at Warren Spring Laboratory[21] demonstrate the ability of CYANEX 272 extractant to efficiently recover high purity cobalt from solutions concentrated in nickel and dilute in cobalt (e.g., 99 g/L Ni and 2 g/L Co). A cobalt recovery of 99.7% was obtained together with a final cobalt: nickel ratio of 1400:1. Higher ratios (approximately 7000:1) have been achieved in a larger scale pilot plant test using a sulfate feed of similar composition (95 g/L Ni and 1.5 g/L Co.

CYANEX 272 was introduced to the marketplace in 1982 and is now being used commercially in three cobalt solvent extraction plants.

Although CYANEX 272 was designed as a cobalt extractant, given the appropriate conditions it can also be used to extract and separate several other base and ferrous metals (Figure 2).

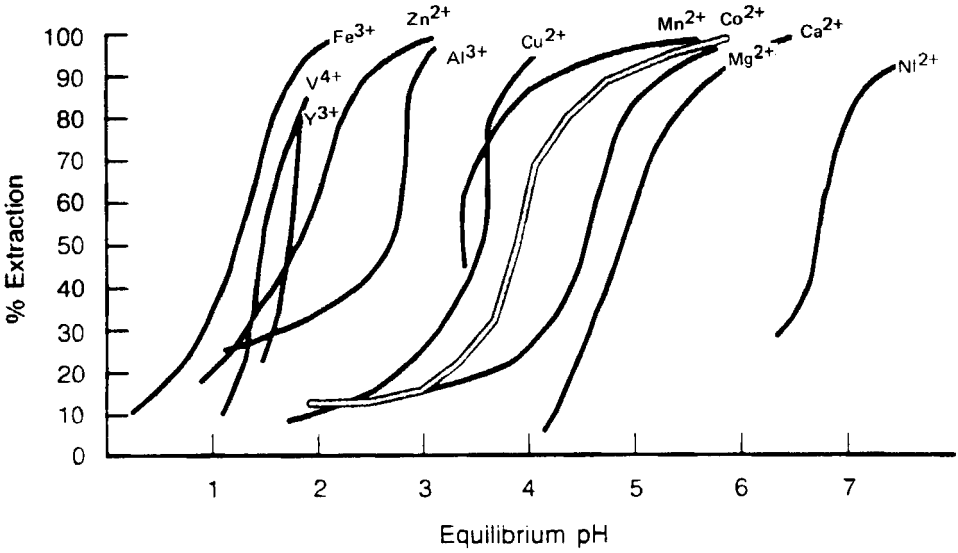


Figure 2 Extraction of metals from sulfate solution by CYANEX® 272 extractant.

Zirconium and Hafnium Recovery

Iron Ore Company of Canada [22] has filed a European Patent which claims the use of CYANEX 272 for the selective extraction of zirconium and hafnium from an aqueous sulfate solution containing titanium and other metallic impurities. Stripping is accomplished with an aqueous ammonium carbonate solution and the zirconium/hafnium is subsequently recovered by precipitation as a high purity oxide.

Gallium Recovery From Bayer Liquors

A U.S. Patent[23] has been issued to Rhone-Poulenc which claims that when an organophosphorus acid such as CYANEX 272 extractant is combined with KELEX 100, there is a substantial increase in the extraction kinetics of gallium from a Bayer process caustic solution. (KELEX 100 is a product of Schering AG).

Rare Earth Separations

A European Patent Application of Rhone-Poulenc[24] covers the use of CYANEX 272 in effecting various rare earth separations from nitrate solution.

The extraction of lanthanide metals with CYANEX 272 has also been the subject of a paper by Li and Freiser[25]. Extraction equilibria for a series of lanthanide ions is cited along with separation factors. In some instances TOPO was found to increase both the extractability and selectivity of lanthanide metals in the system.

APPLICATIONS OF DITHIOPHOSPHINIC ACIDS

Zinc-Calcium Separation at Low pH

Dialkyldithiophosphinic acids have high extraction coefficients for many metals. Extraction occurs at a low pH, which is usually an advantage but the selectivity is poor.

CYANEX 301 extractant, the sulfur analog of CYANEX 272, is such an acid and was originally developed to recover zinc from the effluent streams of viscose rayon plants. Zinc and calcium are present in these effluents in the form of their sulfate salts at a pH of between one and two. The objective is to recover the zinc and recycle it for use in the viscose process acid bath.

It is important to make a highly selectivity zinc-calcium separation because if calcium is recycled to the acid bath, gypsum forms and its precipitation has a deleterious effect on the viscose process. One further constraint is that the solvent extraction process must operate at the pH of the effluent. The low value of zinc and the comparatively dilute solutions, <1 g/L, make it uneconomical to adjust the pH.

Zinc-calcium separation can be affected by such extractants as CYANEX 272, but pH adjustment to approximately 3 is required for complete recovery. In contrast, CYANEX 301 is a stronger acid and complete zinc extraction is possible in the pH range 1-2. Additionally, this reagent exhibits a high selectivity for zinc versus calcium, (Table 1 and Figure 3). Stripping is accomplished by contacting the loaded solvent with a mineral acid, e.g. 300 g/L H_2SO_4.

Dithiophosphoric acids are also commercially available. However, acids of this type do not exhibit the high selectivity for zinc versus calcium which is associated with CYANEX 301, (Figure 4).

Heavy Metal Recovery

CYANEX 301 extractant may also be useful for removing small quantities of heavy metals from acid process streams where pH adjustment is not economical, (Table 2).

TABLE 1

ZINC-CALCIUM SEPARATION WITH CYANEX 301 AND CYANEX 272 EXTRACTANTS

Solvent: 0.6 M extractant in KERMAC 470B diluent*

Aqueous: Single metal sulfate solutions, 0.015 M in metal ion

Temperature: 50°C

pH Control: H_2SO_4 or NH_4OH as appropriate

Time: 5 minutes

CYANEX 301 EXTRACTANT				CYANEX 272 EXTRACTANT			
Zn		Ca		Zn		Ca	
% Extraction	Equil. pH	% Extraction	Equil. pH	% Extraction	Equil. pH	% Extraction	Equil. pH
99.9	0.41	0	0.62	14.6	0.90	3.4	4.15
100.0	0.91	0	1.11	24.2	1.42	20.4	4.53
100.0	1.42	0	1.50	53.3	1.88	81.7	5.38
100.0	1.67	0	2.06	87.7	2.40	99.6	6.52
100.0	1.87			99.4	3.08		
97.5	2.35						

• A product of Kerr-McGee Refining Corp.

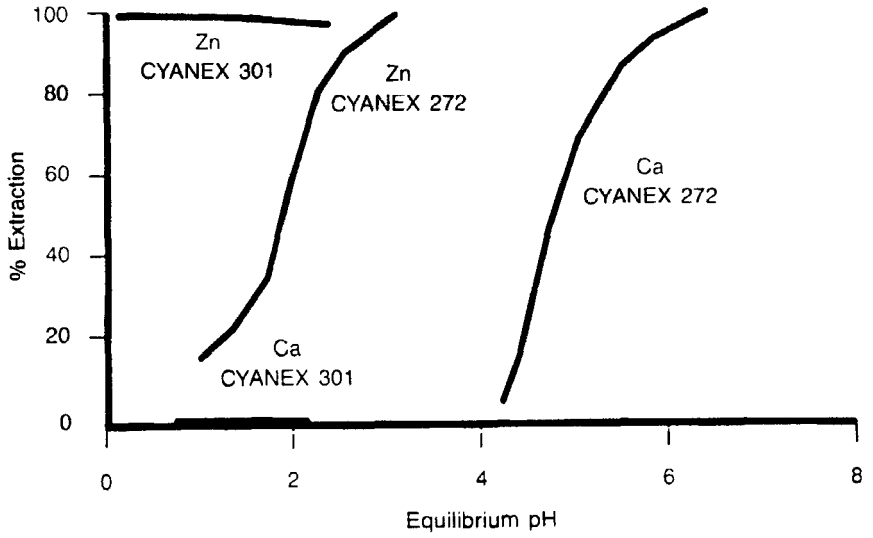


Figure 3 A comparison of the separation of Zn from Ca with CYANEX® 272 and 301 extractants.

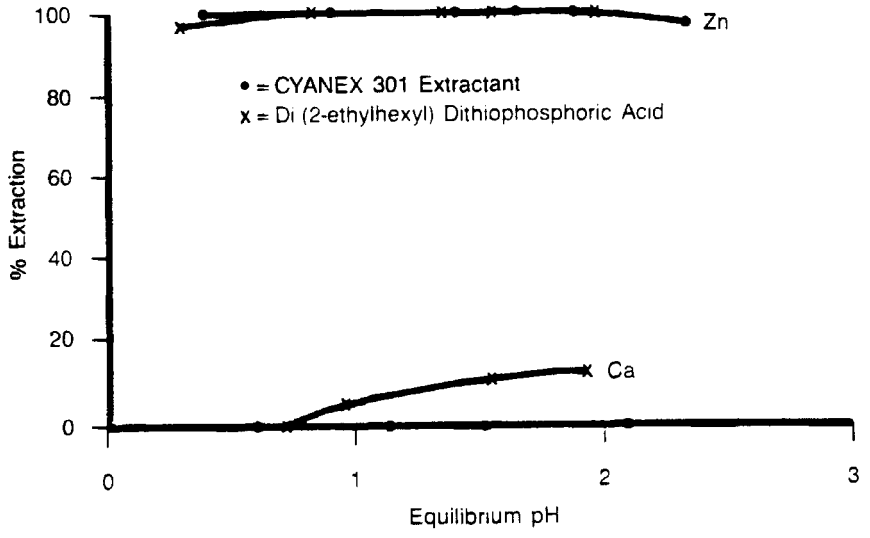


Figure 4 A comparison of the separation of zinc from calcium with a dithiophosphinic vs. a dithiophosphoric acid.

TABLE 2

EXTRACTION ISOTHERMS FOR A METAL MIXTURE CONTACTED WITH CYANEX 301 EXTRACTANT

Solvent: 160 gL extractant in toluene

Aqueous: 0.015 M Zn^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Fe^{3+} as the sulfate salts

Temperature: 50°C

Time: 5 minutes

A/O: 1 (50 mL/50 mL)

	% Extraction						
pH	Zn^{2+}	Ca^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Mg^{2+}	Fe^{3+}
0.48	100	0.8	87.6	99.1	100	0.0	37.6
0.90	100	0.6	98.2	100	100	0.0	55.2
1.55	100	0.7	99.9	100	100	0.0	97.1
2.15	100	1.1	100	100	100	0.0	99.5
2.55	100	1.0	100	100	100	0.0	100

A similar use for dithiophosphinic acids is in the removal of cadmium and other heavy metals from wet process phosphoric acid. J.R. Simplot Company recently obtained a U.S. Patent[26] for such a process using the sodium salt of diisobutyldithiophosphinic acid as the extractant. This compound is sold by Cyanamid under the tradename AEROPHINE® 3418A promoter. Its primary use is as a flotation reagent for certain copper sulfide ores which contain significant quantities of silver or gold.

CYANEX 925 EXTRACTANT

Tin Recovery

The recovery of tin from hydrochloric acid solutions with TOPO is well known. However, under these conditions other metals such as zinc and iron are also extracted. Ross and White[27,28] in the early 1960's showed that tris (2-ethylhexyl) phosphine oxide (TEHPO) was an excellent tin extractant and had the advantage of being more selective than TOPO. Despite its proven performance, TEHPO has never been made commercially. Possibly, because it is too expensive to produce even by the best synthetic route.

Cyanamid perceived that a need existed for the selective recovery of tin from leach solutions of scrap, concentrates and plating baths which may contain in addition Zn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+} and Pb^{2+}. While Cyanamid's phosphine technology did not permit the manufacture of TEHPO, a highly hindered trialkylphosphine oxide was synthesized. This was accomplished by reacting phosphine with 2,2,4-trimethylpentene-1 to form a dialkyl and then reacting this intermediate with octene-1 to form the trialkyl derivative. Subsequent oxidation with peroxide affords the desired oxide i.e. CYANEX 925 extractant.

Chain branching might be expected to make the reagent a harder Lewis base and, therefore, a stronger, less selective extractant than TOPO. However, as shown with TEHPO, the opposite is the case. CYANEX 925, due to steric effects, is in fact more selective than TOPO in the extraction of a range of metals.

By inference, one would expect that tris (2,4,4-trimethylpentyl) phosphine oxide (CYANEX 924), being even more sterically hindered that CYANEX 925, would exhibit an even greater degree of selectivity. Experiments have shown this to be the case. However, the same steric hindrance which produces this increased selectivity also has an adverse effect on the manufacturing process. The reaction kinetics are slowed to such an extent that CYANEX 924 is not an economically viable product.

TABLE 3

EFFECT OF HCl CONCENTRATION ON METAL EXTRACTION WITH CYANEX 921 EXTRACTANT

Solvent: 0.15 M extractant in Exxsol D-80 diluent*

Aqueous: Single metal chloride solutions, all 0.01 M in the metal ion in acid solutions varying from 1 to 6N HCl.

Temperature: 24°C

Time: 5 minutes

A/O: 1 (40 mL each phase)

Initial HCl Normality	Extraction Coefficients					
	Sn^{4+}	Fe^{3+}	Fe^{2+}	Zn^{2+}	Pb^{2+}	Cu^{2+}
1	**	9.8	0.099	70	1.5	1.4
2	**	330	0.51	620	1.4	1.9
3	**	1790	0.35	3100	0.79	2.8
4	**	2610	0.35	3100	0.43	4.5
5	**	5740	0.45	1600	0.24	12.5
6	**	-	0.96	690	0.11	16.2

A product of Exxon, Co., U.S.A.
Quantitative extraction observed

TABLE 4

EFFECT OF HCl CONCENTRATION ON METAL EXTRACTION WITH CYANEX 924 EXTRACTANT

Solvent: 0.15 M extractant in Exxsol D-80 diluent

Aqueous: Single metal chloride solutions, all 0.01 M in the metal ion in acid solutions varying from 1 to 6N HCl.

Temperature: 24°C

Time: 5 minutes

A/O: 1 (40 mL each phase)

Initial HCl Normality	Extraction Coefficients					
	Sn^{4+}	Fe^{3+}	Fe^{2+}	Zn^{2+}	Pb^{2+}	Cu^{2+}
1	396	0.15	0	0.60	1.4	0
2	**	2.4	0.027	1.7	0.97	0.015
3	**	92	0.098	2.7	0.36	0.021
4	**	2210	0.17	4.1	0.0064	0.069
5	**	700	0.19	11	0.0094	0.24
6	**	640	0.28	15	0.017	0.85

* Quantitative extraction observed

TABLE 5

EFFECT OF HCl CONCENTRATION ON METAL EXTRACTION WITH CYANEX 925 EXTRACTANT

Solvent: 0.15 M extractant in Exxsol D-80 diluent

Aqueous; Single metal chloride solutions, all 0.01 M in the metal ion in acid solutions varying from 1 to 6N HCl.

Temperature: 24°C

Time: 5 minutes

A/O: 1 (40 mL each phase)

Initial HCl Normality	Extraction Coefficients					
	Sn^{4+}	Fe^{3+}	Fe^{2+}	Zn^{2+}	Pb^{2+}	Cu^{2+}
1	**	0.52	0	5.9	0.98	0.006
2	**	35	0.082	20	1.4	0.016
3	**	810	0.16	68	0.46	0.120
4	**	1150	0.18	185	0.077	0.390
5	**	5000	0.22	250	0.084	0.970
6	**	3930	0.53	164	0.077	198

** Quantitative extraction observed

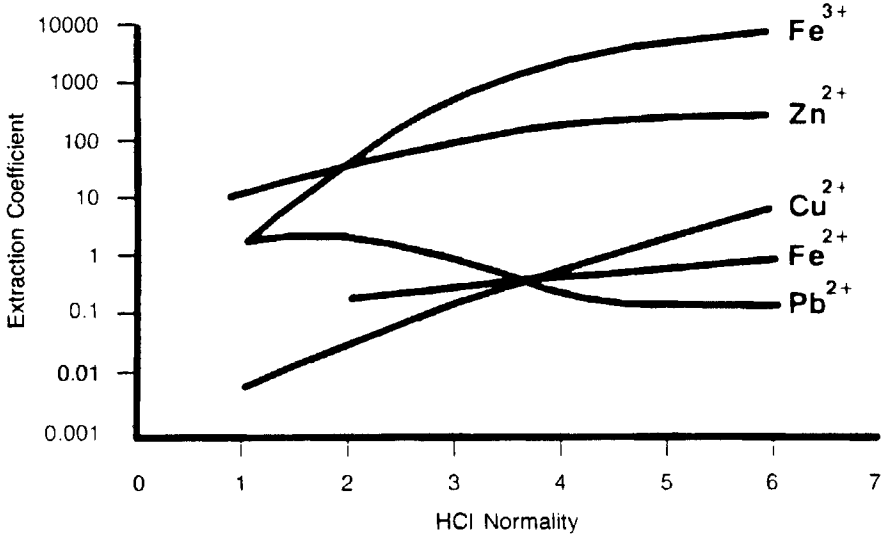


Figure 5 Metal recovery from chloride solutions with CYANEX® 925 extractant.

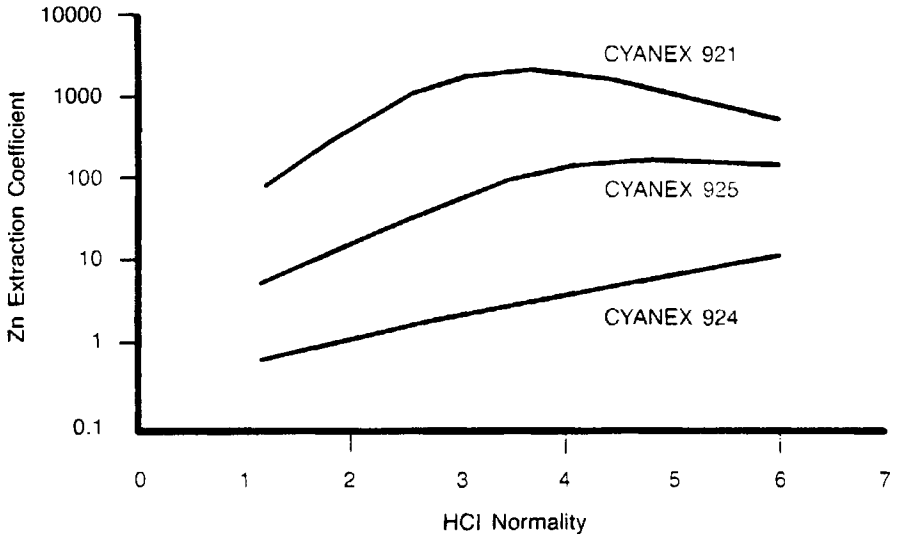


Figure 6 A comparison of Zn extraction with CYANEX® 921, 924 and 925 extractants.

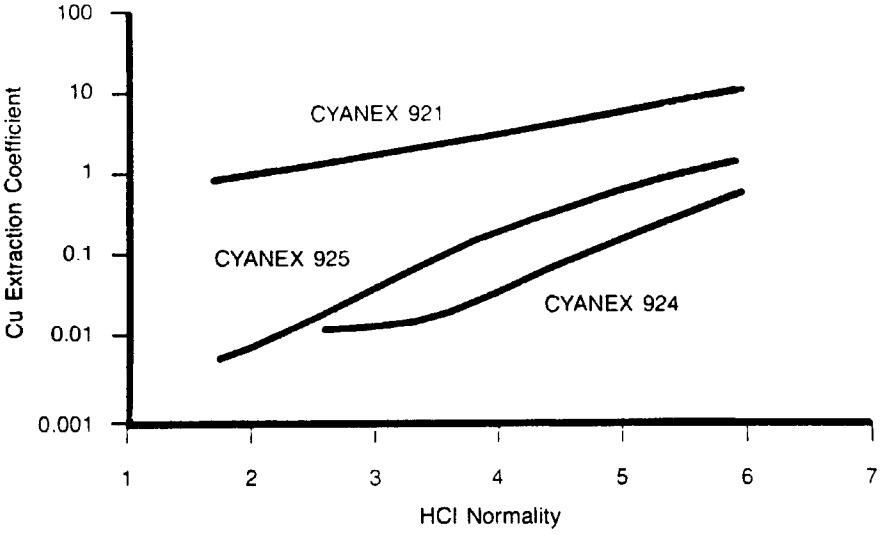


Figure 7 A comparison of Cu extraction with CYANEX® 921, 924, and 925 extractants.

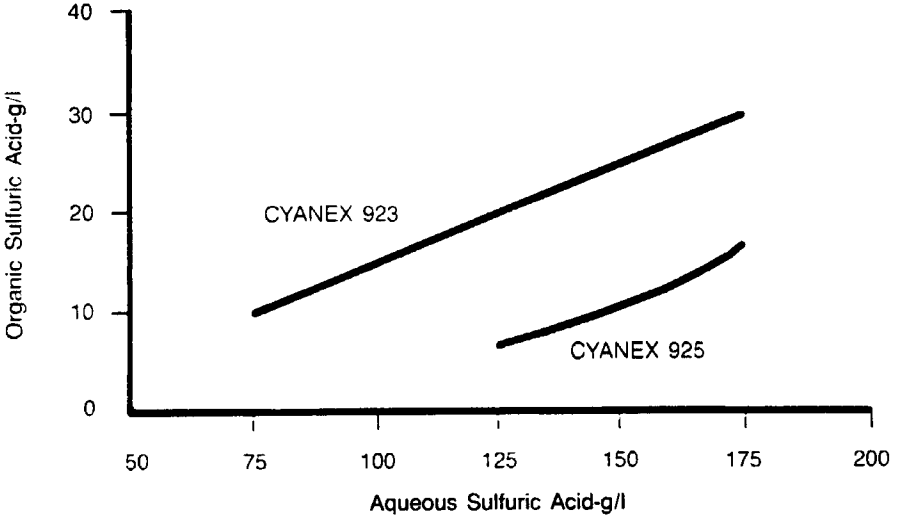


Figure 8 A comparison of H_2SO_4 extraction with CYANEX® 923 and 925 extractants.

TABLE 6

SULFURIC ACID EXTRACTION ISOTHERMS FOR CYANEX 923 AND CYANEX 925 EXTRACTANTS

Solvent: 50 v/o of each extractant in Exxsol D-80 diluent

Aqueous (g/L): 31.3 Cu^{2+}, 8.4 Ni^{2+}, 6.88 As^{5+}, 184.1 H_2SO_4 Cu and Ni as sulfates

Temperature: 50°C

Time: 5 minutes

Equilibrium H_2SO_4 Concentration (g/L)

	CYANEX 923 Extractant		CYANEX 925 Extractant	
A/O	Organic	Aqueous	Organic	Aqueous
2	30.6	168.80	17.2	175.50
1	28.1	156.00	15.0	169.10
0.5	23.4	137.30	12.0	160.20
0.2	15.8	105.00	8.52	141.50
0.1	10.6	78.40	5.83	125.80

The dependence of extraction on chain branching is illustrated by the results of some batch shake-out tests which were conducted to determine the effect of HCl normality on metal recovery from single metal chloride solutions (Tables 3, 4 and 5, Figure 5). All extractants recovered tin quantitatively under the test conditions, except for CYANEX 924 at an initial HCl normality of 1. The remaining metals were extracted in the order CYANEX 921 > CYANEX 925 < CYANEX 924 (Figures 6 and 7).

In the potential application for the selective recovery of tin, any co-extracted metals may be scrubbed from the solvent using water, a dilute acid or a reductive process (e.g. Fe^{3+}----->Fe^{2+}) and tin may be susequently stripped as a soluble stannate by the use of an alkali strip feed.

Impurity Removal From Copper Electrolytes

A further potential application is the removal of arsenic impurities from copper electrolytes which, typically, contain 150-200 g/L of free sulfuric acid. This process involves extracting arsenic, scrubbing co-extracted acid from the solvent with water at a high O/A ratio and stripping arsenic with water at a lower O/A ratio. The advantage of CYANEX 925 extractant over straight chain phosphine oxides in this application is that it extracts less sulfuric acid per unit of arsenic and the acid which is co-extracted is more readily scrubbed from the solvent. The weaker extraction of sulfuric acid by CYANEX 925 over CYANEX 923 is illustrated by the extraction isotherms shown in Figure 8. These were plotted using the data in Table 6.

SUMMARY

No attempt has been made to exhaustively review the available literature on all organophosphine derivatives which have been reported to be extractants for metals or organic solutes. We believe we have cited and discussed, albeit briefly, all of the known commercial and potentially commercial uses for this interesting group of compounds.

REFERENCES

1. Kirk-Othmer Encyclopedia of Chemical Technology, 17, John Wiley and Sons, New York, p 473, (1982).

2. Ibid, p 473

3. J.R. Partington, General and Inorganic Chemistry, McMillan and Co. Ltd., London, p 598, (1951).

4. J.C. White, and W.J. Ross, Oak Ridge National Library, Report No. 61-2-19 Series (1961).

5. F.J. Hurst, D.J. Crouse and K.B. Brown, Oak Ridge National Laboratory Report No. ORNL-TM-2522 (1969).

6. F.J. Hurst, D.J. Crouse and K.B. Brown, Ind. Eng. Chem. Process Des. Develop, Vol. II, No. 1, pp 122-128 (1972).

7. F.J. Hurst and D.J. Crouse, U.S. Patent 3,711,591 (1973).

8. W. Kantzler and J. Schedler, Austrian Patent 365080 (1980).

9. J. Eckert and J. Bauer, German Offen. 3241832 (1984).

10. R. Marr, et al., European Patent 9 106 118 A1 (1983).

11. J.H. Bright, U.S. Patent 4,599,153 (1986).

12. E.K. Watson, et al., Proceedings of ISEC 86, Vol. III, pp 775-782. Dechema, Frankfurt (1986)

13. J.H. Bright, U.S. Patent 4,544,779 (1985).

14. W.A. Rickelton and T.J. Brown, Proceeding of the 15th Annual CIM Hydrometallurgical Meeting, Vancouver, B.C. (1985).

15. R.G. Pearson, J. Am. Chem. Soc., 85, pp 3533-3538 (1963).

16. American Cyanamid Co., CYANEX® 471X Extractant Sales Brochure.

17. Y. Baba, Y. Umezaki and K. Inoue, Solvent Extr. Ion Exch., 4 (1) pp 15-26 (1986)

18. Mitsui Cyanamid KK, Japanese Patent Application 193846 (1985).

19. J.S. Preston, J.S. Afr. Inst. of Mining and Metallurgy, pp 126-132 (1983).

20. P.R. Danesi, Solvent Extr. Ion Exch., 3 (4), pp 435-452 (1985).

21. W.A. Rickelton, et al., Solvent Extr. Ion Exch., 2 (4) pp 815-838, (1984).

22. M.K. Witte and C.C. Frey, European Patent 0 154 448 (1985).

23. D. Bauer, et al., U.S. Patent 4,559,203 (1985).

24. J.L. Sabot and A. Rollat, European Patent 9 156 735 (1985).

25. K. Li and H. Freiser, Solvent Extra. Ion Exch., 4 (4) pp 739-755 (1986).

26. L.W. Bierman et al., U.S. Patent 4,511,541 (1985).

27. J.C. White and W.J. Ross, Paper No. 23, Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy (1960).

28. W.J. Ross and J.C. White, Anal. Chem., 30, pp 424-427 (1961).