SELECTIVE EXTRACTION AND SEPARATION OF Cu(II), Zn(II), Ni(II) AND Fe(III) FROM THE LEACH LIQUOR OF PRINTED CIRCUIT BOARD USING CYANEX 272 COATED MICROCAPSULES

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UNIVERSITI MALAYSIA PERLIS

2008

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0630410064

A thesis submitted

In fulfillment of the requirements for the degree of Master of Science

School of Materials Engineering

UNIVERSITI MALAYSIA PERLIS

2008

ACKNOWLEDGEMENT

I would like to express my deepest and sincere gratitude to my supervisor Dr. Md. Fazlul Bari for his kind help and continuous supervision throughout my research. Without his proper direction and guidance this thesis would not be finalized. His constructive criticism and valuable suggestion always kept this work in a right track. My sincere thanks to my both co-supervisors Professor Dr. Shamsul Baharin Jamaludin and Brigadier General Dato' Prof. Dr. Kamarudin Hussin for their valuable guidance and advice throughout the research period. My heartiest gratitude to my uncle Dr. Md. Zaidul Islam Sarker (Assoc. Prof., Universiti Putra Malaysia) who is always giving me mental support and valuable advice. My special thanks to all the academicians and technical staffs of the School of Materials Engineering for their cooperation during my study.

I would like to express my gratitude to my parents, family members and relatives for their continuous support and love from the time of my away from them. I also wish to thanks to my lab colleague Mst. Noorzahan Begum for the patience and sharing her experience.

Last but not least, my thanks go to all who have directly or indirectly helped for the completion of this thesis.

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LIST OF ABBREVIATIONS

AC	Acetic acid
Ac^-	Acetate ion
Alamine 336	Tri-octyl/decyl amine
Aliquat 336	*N*-Methyl-*N,N*-dioctyloctan-1-aminium chloride
A:O	aqueous to organic phase ratio
BTMPPA	bis (2, 2, 4-trimethylpentyl) phosphinic acid
Cyanex 272	Commercial name of bis-(2,4,4-trimethylpentyl) Phosphinic acid
Cyanex 272/PS	Cyanex 272 to Polystyrene ratio
Cyanex 301	Bis (2,4,4-trimethylpentyl) dithiophosphinic acid
Cyanex 302	Di-2,4,4,-trimethylpentyl mono-thio-phosphinic acid
Cyanex 923	Trialkyl phosphinic oxide
DTPA	Diethylene triamine pentaacetate
D2EHPA	Di (2-ethylhexyl) phosphoric acid
EDTA	Ethylene diamine tetraacetate
EHPNA	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
HA	Monomeric bis-(2,4,4-trimethylpentyl) Phosphinic acid
H_2A_2	Dimeric bis-(2,4,4-trimethylpentyl) Phosphinic acid
HA_2^-	Anion of monomeric bis-(2,4,4-trimethylpentyl) Phosphinic acid
HFSLM	Effective hollow fiber supported liquid membrane
LIX 26	Alkyl substituted 8-hydroxy- quinoline
LIX 84	5-dodecylsalicyladoxime
LIX 84I	2-hydroxy-5-nonylacetophenome oxime
LIX 973N	A mixture of 5-nonylsalicylaldoxime and 2-hydroxy-nonylacetophenone oxime
LIX 984	A mixture of 5 dodecylsalicylaldoxime and 2-hydroxy-5-nonyl-acetophenone oxime
MC	Microcapsule
MC-X	Polystyrene microcapsule coated with Cyanex 272
MC-Xs	Polystyrene microcapsules coated with Cyanex 272
mgL^{-1}	Milligram per liter
Na-Cyanex 272	Complex of Na-Cyanex 272

PCB	Printed Circuit Board
PCBs	Printed Circuit Boards
PC 88A	2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester
ppm	Parts per million
PS	Polystyrene
PS/Cyanex 272	Polystyrene to Cyanex 272 ratio
PVDF	Polyvinylidene Fluoride
PWB	Printed Wiring Board
S	Slope
S:L	Solid to liquid ratio
SLM	supported liquid membrane
S_N2	Substitution neucleophilic bimolecular reaction
SX	Solvent extraction
TOMAC	Tri-n-octylmethylammonium chloride
TOPO, B	trioctylphosphine oxide
TOPS-99	Di(2-Ethyl Hexyl) Phosphoric Acid
Versatic 10	Neodecanoic acid
% E	Percentage of extraction

ABSTRAK

PENGEKSTRAKAN DAN PERMISAHAN TERPILIH Cu(II), Zn(II), Ni(II) dan Fe(III) DARI LIKOR PELARUTLESAPAN PAPAN KEKUNCI MENGGUNAKAN MIKROKAPSUL YANG DISELAPUTI DENGAN CYANEX 272.

Tujuan utama kajian ini adalah untuk menjalankan perolehan dan pengekstrakan Cu(II) dalam kehadiran Zn(II), Fe(III) dan Ni(II) daripada larutan likor Papan Litar Tercetak (PCB) dengan menggunakan microkapsul yang disaluti dengan Cyanex 272 (MC-Xs). MC-Xs telah disediakan menggunakan kaedah penyejatan pelarut pada keadan yang berbeza dan juga keadaan optimum bagi persediaan MC-Xs telah dinilai. Pada mulanya, kelakuan penyarian cecair-cecair Cu(II) daripada medium berasid sulfat asetat oleh Cyanex 272 yang dicairkan dalam heksana telah dikaji sebagai satu fungsi terhadap keseimbangan pH, kepekatan fasa berair Cu^{2+}, SO_4^{2-} dan Ac^-, dan kepekatan Cyanex 272 dalam fasa organik. Keputusan menunjukkan bahawa prestasi pengestrakan adalah sangat bergantung pada pH, kepekatan Cyanex 272 dan kepekatan Ac^- dan dicadangkan bahawa spesies pengestrakan adalah [Cu(HA$_2$)(Ac).2HA]. Kelompok kajian perolehan dan pengekstrakan telah dijalankan daripada medium sulfat asetat untuk kedua-duanya serentak dan sistem penyarian logam tunggal menggunakan MC-Xs sebagai satu fungsi masa sentuh dan keseimbangan pH untuk penyarian serentak, dan nisbah jumlah MC-Xs, Cyanex 272 ke Polystyrene (Cyanex 272 /PS) dan PS ke Cyanex 272 (PS/Cyanex 272) dalam fasa tersebar dan Cu(II) kepekatan ion dalam fasa berair bagi penyarian logam tunggal. Dapat diperhatikan nilai pH bagi larutan suapan memainkan peranan penting untuk kejayaan pemisahan ion-ion logam. Pengambilan ion-ion logam serentak dan kecekapan pemisahan Cu(II), Zn(II), Fe(III) dan Ni(II) telah dianalisa menggunakan MC-Xs dengan turus terpadat pada nilai pH yang berbeza (2-5), menunjukkan bahawa di dalam julat pH ini, pengambilan Ni(II) adalah sifar, hampir 100% pada pH 5 untuk Zn(II) dan Fe(III). Manakala pengambilan Cu(II) adalah 26% pada pH 5. Kecekapan pemisahan Cu(II) adalah lebih tinggi daripada ion-ion logam yang lain. Tetapi, kecekapan pemisahan Zn(II) berbanding Fe(III) adalah agak rendah. Perlucutan Cu(II), Zn(II) dan Fe(III) telah dijalankan daripada MC-Xs yang penuh menggunakan kepekatan larutan asid sulfurik yang berbeza untuk nisbah cair (S:L) 1:10 menunjukkan bahawa hampir 100% perlucutan diperoleh pada larutan 0.1 M H$_2$SO$_4$ untuk Cu(II) dan Zn(II) dan 0.5 M H$_2$SO$_4$ penyelesaian untuk Fe(III). Proses perolehan dan pengekstrakan semula menunjukkan bahawa microkapsul mempunyai kestabilan cukup untuk penyarian ion-ion logam. Rekabentuk faktoran dan analisis eksperimen Yates telah dijalankan untuk penilaian kesan-kesan utama dan interaksi faktor-faktor penyarian Cu(II) dalam kehadiran Zn(II), Fe(III) dan Ni(II) menggunakan MC-Xs di dua syarat-syarat percubaan. yang berbeza. Rekabentuk faktoran dan analisis Yates dijalankan untuk menentukan keadaan optima faktor perlucutan untuk Cu(II) daripada MC-Xs yang penuh menggunakan larutan asid sulfurik. Akhirnya, satu proses yang lengkap untuk pemisahan dan pemulihan Cu(II), Zn(II), Fe(III) dan Ni(II) telah dijalankan terhadap larutan likor PCB dengan proses penyarian kelompok menggunakan MC-Xs. Proses perolehan dan pengekstrakkan semula, masing –masing menunjukkan 99.22%, 77.57% dan hampir 100% untuk Cu(II), Zn(II) dan Ni(II).

ABSTRACT

The main purpose of this study was to recover and extract Cu(II) in presence of Zn(II), Fe(III) and Ni(II) from the leach liquor of Printed Circuit Board (PCB) using polystyrene microcapsules coated with Cyanex 272 (MC-Xs). MC-Xs were prepared following the solvent evaporation method at different conditions, and optimization conditions for the preparation of MC-Xs were evaluated. At first, the liquid-liquid extraction behavior of Cu(II) from acidic sulphate-acetate medium by Cyanex 272 diluted in hexane was investigated as a function of equilibrium pH, aqueous phase concentration of Cu^{2+}, SO_4^{2-} and Ac^-, and Cyanex 272 concentration in the organic phase. Results showed that the extraction performance was highly dependent on pH, Cyanex 272 concentration and Ac^- concentration and suggested that the extracted species is $[Cu(HA_2)(Ac).2HA]$. Batch extraction studies were carried out from the sulphate-acetate medium for both simultaneously and single metal extraction system using MC-Xs as a function of contact time and equilibrium pH for simultaneous extraction, and amount of MC-Xs, Cyanex 272 to Polystyrene ratio (Cyanex 272/PS) and PS to Cyanex 272 ratio (PS/Cyanex 272) in dispersed phase and Cu(II) ion concentration in aqueous phase for the single metal extraction. It was observed that the pH value of the feed solution played an important role for successful separation of the metal ions. Simultaneous metal ions uptake and separation efficiency of Cu(II), Zn(II), Fe(III) and Ni(II) were investigated using MC-Xs with packed column at different pH (2-5), illustrating that within this pH range, Ni(II) uptake was nil, almost 100% at pH 4 for the Zn(II) and Fe(III), whereas Cu(II) uptake was 26% at pH 5. The separation efficiency of Cu(II) was higher over other metal ions. But, the separation efficiency Zn(II) over Fe(III) was quite low. Stripping of Cu(II), Zn(II) and Fe(III) was carried out from the loaded MC-Xs using different concentration of sulphuric acid solution at solid to liquid ratio (S:L) of 1:10 showing that almost 100% stripping was obtained at 0.1 M H_2SO_4 solution for the Cu(II) and Zn(II) and 0.5 M H_2SO_4 solution for the Fe(III). The regeneration experiment showed that the microcapsules have sufficient stability for the metal ions extraction. Factorial design and Yates' analysis of experiment was carried out for the optimization and evaluation of the main effects and interactions of the Cu(II) extraction factors in the presence of Zn(II), Fe(III) and Ni(II) using MC-Xs at two different experimental conditions. Factorial design and Yates' analysis was also carried out in order to determine the optimum condition of stripping factor for the stripping of Cu(II) from loaded MC-Xs using sulphuric acid solution.). Finally, A complete process for the separation and recovery of Cu(II), Zn(II), Fe(III) and Ni(II) was carried out from the leach liquor of PCB following the batch extraction process based on the batch extraction using MC-Xs. The process showed the selective recovery of 99.22%, 77.57% and almost 100% for the Cu(II), Zn(II) and Ni(II), respectively.

CHAPTER 1

INTRODUCTION

1.1 Copper, Nickel, Iron and Zinc

Copper is malleable, ductile, a good conductor of heat and electricity. Copper is used into wires or cables for power transmission, building wiring, motor and transformer wiring, wiring in commercial and consumer electronics and equipment; telecommunication cables; electronic circuitry; plumbing, heating and air conditioning tubing; roofing, flashing and other construction applications; electroplated coatings and undercoats for nickel, chrome, zinc, etc.; and miscellaneous applications. As an alloy with tin, zinc, lead, etc. (brass and bronze), it is used in extruded, rolled or cast forms in plumbing fixtures, commercial tubing, electrical contacts, automotive and machine parts, decorative hardware, coinage, ammunition, and miscellaneous consumer and commercial uses. Copper is an essential micronutrient used in animal feeds and fertilizers. The most common source of copper ore is the mineral chalcopyrite ($CuFeS_2$). Copper is widely distributed in nature as metal, in sulfides, arsenides, chlorides, carbonates and so on (Bingham, Cohrssen, & Powell, 2001b).

Nickel is silver white metal with characteristic gloss and is ductile and malleable. It is not soluble in water, but it does dissolve in dilute oxidizing acids. Almost 40% nickel production is used to manufacture stainless and heat-resistant steel grades, 21% for nonferrous alloys, and 17% for electroplating and 12% for special-purpose alloys. The remaining 10% of nickel production is used in other applications in the smelting, chemical, electric cell and ceramic industries. (Bingham, Cohrssen, & Powell, 2001a).

Iron is the silver-white solid transitional metal. It is believed to be sixth most abundant element in the universe and the fourth most abundant on earth. Iron is a metal extracted from iron ore and is almost never found in the free element state. It is the main component of steel and it is used in the production of alloys or solid solution of various metals, as well as some non metals, particularly carbon. Iron is the most used of all the metals. Its combination of low cost and high strength make it indispensable, especially in applications like automobiles, the hulls of large ships, and structural components of the building. Steel is the best known alloys of iron. (Bingham et al., 2001a).

Zinc is the relatively soft, bullish-white shiny metal. Zinc has been used for more than 2000 years, mainly to produce brass, which is a zinc-copper alloy containing largely copper and 3-45% zinc. At the end of the nineteenth century a large scale production of zinc had begun. (Bingham et al., 2001b). Zinc is used in the production of alloys, brass, and electrical apparatus. It is commonly applied as a protective coating of steel and iron products. Zinc is used in dry-cell batteries and cans and the rapeutically in human medicine, in treatment of zinc deficiency.

To sum up, copper, zinc, nickel and iron are essential metals and have wide range of applicability. There are various sources of these valuables metals. Among these, Printed circuit Board (PCB) is one of the important sources of these valuable metals.

1.2 Printed circuit board

Printed circuit boards (PCBs) is an integral part in majority of electronic system are commonly found in consumer electronics, military applications, and medical equipment

etc. PCBs are the typical and fundamental component for almost all electronic products. PCBs contain lots of base metals such as copper, iron, aluminum and tin; rare metals like tantalum, gallium, and platinum groups metals; noble metals such as gold, silver, and palladium; hazardous metals such as chromium, lead, beryllium, mercury, cadmium, zinc, nickel. PCBs also contain some toxic elements. The large quantity of recoverable materials in PCB provides a strong economic justification for material recovery and recycling. On the other hand, the toxic substance found in PCB can cause irreversible damage to the human body and environment. For instance, lead found in the PCBs accumulates in the environment and has damaging effects on human being, plants, animals and microorganisms. Improper recycling of PCB could lead to serious environmental hazard for it's containing some of toxic elements. Besides, effective recycling and recovery of materials from PCB can also conserve the exhaustible natural resource and safeguard the environment. Handling of PCB waste is a serious problem due to the toxic nature of the materials present and problems associated with the landfill. Manufacturers, government agencies, and users are now looking for environmentally responsible management of this E-waste. Besides proper disposal, economical recovery of precious and exhaustible materials is also a matter of interest.

Copper, nickel, iron and zinc have been produced from their resource using pyrometallurgical or hydrometallurgical extraction process in extractive metallurgy. Recently, hydrometallurgical extraction process are widely used to produce these metals, as hydrometallurgical extraction process has some potential advantage including lower energy consuming and lower environmental impact.

1.3 Hydrometallurgical extraction process

Hydrometallurgy is today one of the established and highly recognized parts of extractive metallurgy. It is an alternative and a relatively recent development process of pyrometallurgy. It involves the use of aqueous solutions for the recovery of metals from ores, concentrates, and recycled or residual materials.

Hydrometallurgical process utilizing an acidic medium most commonly uses sulphuric or hydrochloric acid. It is essentially concerned with methods whereby metals, metal salts and other metal compounds are produced by means of chemical reactions involving aqueous and organic solution. In recent years, hydrometallurgical process has been widely used to recover metals from various wastes for its significant advantages. Some advantages are given bellow:

   i).   Lower capital cost;
   ii).   Has the flexibility for treatment of complex ores and for the production of a variety of by-product metals.
   iii).   Less pollution than pyrometallurgy.
   iv).   Has a high chemical specificity and flexibility.
   v).   Has the possibility to recover residual reagent.

Various extraction and separation processes are involved in hydrometallurgy. Among them solvent extraction is a well known established technology being used for the production of metals from relatively concentrated feed.

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1.3.1 Solvent extraction

Solvent extraction or liquid-liquid extraction is a technique in which a solution (generally aqueous) is brought into contact with a second solvent (generally organic) essentially immiscible with the first, in order to bring about a transfer of one or more solute into the second solvent. Solvent extraction itself offers superior separation than other techniques, such as fractional crystallization and precipitation which are tedious and costly while ion exchange technique generally provides low output. Solvent extraction is used in numerous chemical industries to produce pure chemical compounds, ranging from pharmaceuticals and biomedical to heavy organics and metals, in analytical chemistry, in environmental waste purification, as well as in research (Cox & Rydberg, 1992). Though solvent extraction is very applicable but has certain limitations. The extracting solvents are limited to those that are water immiscible (for aqueous sample), emulsions tend to form when the solvent are shaken and relatively large volumes of solvents are used that generate a substantial waste disposal problem. The operations are often manually performed and may require a back extraction, this technique often the organic solvent forms emulsions with aqueous samples that are difficult to extract, and the method is not easily automated. But most of these difficulties that arise in solvent extraction can be avoided by the use of any solid phase containing an extracting reagent to contact with aqueous solution in lieu of organic solvent (Akhond, Absalan, Sheikhian, Eskandari, & Sharghi, 2006), such as supported liquid membrane (Alguacil & Alonso, 2005; Marchese, Valenzuela, Basualto, & Acosta, 2004; Sarangi & Das, 2004), solvent impregnated resin (Kabay, Arda, Saha, & Streat, 2003; Trochimczuk, Kabay, Arda, & Streat, 2004) extractant

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microcapsules (Kamio, Fujiwara, Matsumoto, Valenzuela, & Kondo, 2008; Kamio, Matsumoto, & Kondo, 2002a; Yang, Luo, & Gong, 2005b).

1.3.2 Solid phase extraction

Solid phase extraction is a technique in where an immiscible solid sorbent containing an extraction solvent is used to contact with a solution (generally aqueous) in order to bring about a transfer of one or more solutes into the solid phase. Solid phase extraction is an alternative technique of the solvent extraction. It can be continuous or batch. In solid phase batch extraction, the aqueous sample is agitated in presence of an extracting solid sorbent that is immiscible with the sample. When the sample and the solid sorbent mixture are contact in a given time, the constituents of aqueous sample may pass to the extracting solid sorbent. Then the mixture is transferred to a separator. In solid phase continuous extraction, the solid sorbent is taken in a column. The aqueous sample is passed through the column so that the constituents of aqueous sample may pass into the solid sorbent and then the effluent collected at appropriate intervals in desired fractions.

Solid phase extraction technique is not a recent use technique. It has been in use for thousands of years. Some scientists claim the first literature reference is to be found in the Bible (Riemon & Walton, 1970). McDoland (1980) points out that the term is actually applied inaccurately since the extraction is not really performed by a solid phase but by a solid surface like the organic layer of a C18 bonded silica. The modern use of solid phase extraction in the colloquial sense probably employed animal charcoal to remove pigments from chemical reaction mixtures. The term solid phase extraction was coined in 1982 by employees of the J. T. Baker chemical company.

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Solid phase extraction technique has numerous advantages including short analysis time, high separation factor, low consumption of the reagents, ease regeneration of solid phase, reusability of the adsorbant, ease of automation, and ease uses (Elci, Kartal, & Soylak, 2008; Rekha et al., 2007). Recently, this technique has been widely used for separation and preconcentration of metal ions in the field of extractive metallurgy (Absalan & Aghaei Goudi, 2004; Absalan & Mehrdjardi, 2003; Bulut et al., 2007; Duran et al., 2007; Shamsipur, Ghiasvand, Sharghi, & Naeimi, 2000). Among various types of solid phase, outstanding extraction properties can be provided by the microcapsules coated with extractant.

Microcapsules as a solid phase

Explore to search the solid phase which is most suitable for a separation/recovery process is a challenging job for a scientist. Microcapsules are micro-size polymeric particles in sphere shape which can be coated by any active functional materials. Microcapsules can be prepared using one of three methods: coacervation, physical/mechanical or polymerization method. Physical/mechanical method is divided in two methods, such as: solvent evaporation and spray-dry. Among these methods, solvent evaporation method is an easy and economical way to prepare microcapsules (Yang, Luo, & Gong, 2005a). There are several advantages of extractant microcapsules such as low costing, easy phase separation, including large specific interfacial area, minimal use of organic solvent, high selectivity, maximal solvent loading ratio, reusability and specially more stability. Nowadays, microcapsules have been used in various field for its prospective advantages (Gong, Luo, Yang, & Wu, 2006). It can also

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be applied in the wide range metal ions extraction and separation purpose by coating any effective solvent extraction reagent.

1.4 Cyanex 272 as an extractant

Cyanex 272 extractant is a well known solvent extraction reagent and extensively used in solvent extraction and related area for extraction and separation of metal ions. The active component of Cyanex 272 extractant is bis (2,4,4-trimethylpentyl) phosphinic acid. Cyanex 272 can be formed in two structural formulas, one is monomeric and another one is dimeric. Generally, it is considered as dimeric (H_2A_2) in non-polar solvents (Biswas, Habib, & Singha, 2005).The monomeric and dimeric structure of bis (2,2,4-trimythylpentyl) phosphinic acid are shown Fig. 1.1. It is a di-alkyl derivative of phosphinic acid and acts as a mono-acidic chelating agent. It is totally miscible with common aromatic and aliphatic diluents, and is extremely stable to both heat and hydrolysis (*Cytec Industries, Inc.Cyanex 272, Technical Brochures*). The presence of two P-C bonds to the structure of this reagent makes the molecule higher chemically stable and at the same time exhibit good selectivity toward certain metal ions. Another distinct feature of the reagent is that it can be easily stripped during back extraction. The Cyanex 272 extractant is an ionizable complexant that is an effective extractant for transition metals, and is used commercially for primary separation of Co and Ni. It is now employed in numerous installations throughout the world located in Europe, America, Canada and Africa. The structural formula and Physico-chemical properties of Cyanex 272 are given in Table 1.1.(*Cytec Industries, Inc.Cyanex 272, Technical Brochures*, Rickelton & Boyle, 1988).
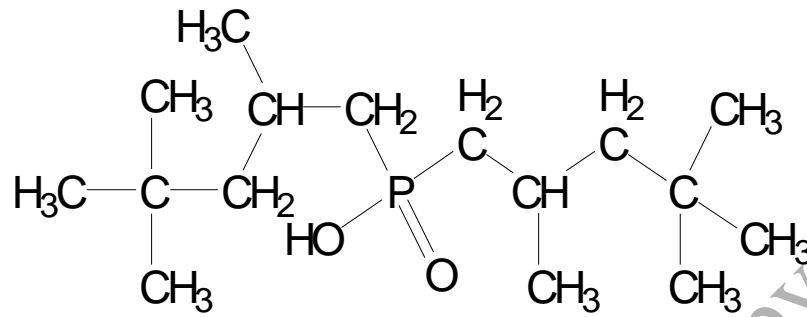
Monomer (HA)
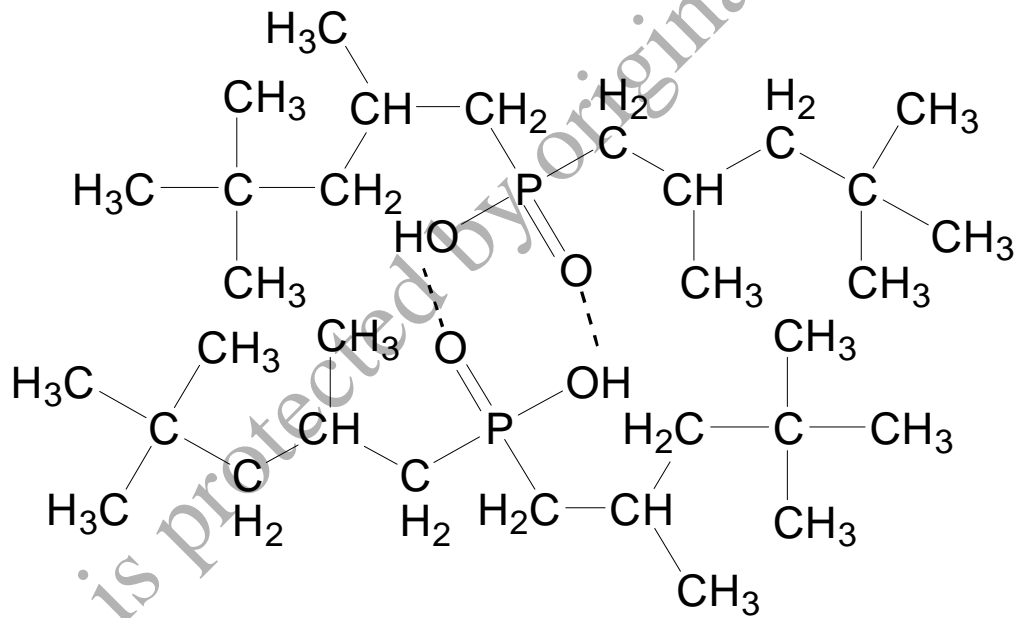
Dimer (H$_2$A$_2$)

Fig. 1.1 Monomeric and dimeric structures of Cyanex 272

Table 1.1: Physico-chemical properties of Cyanex 272 (*Cytec Industries, Inc.Cyanex 272, Technical Brochures*, Rickelton & Boyle, 1988).

		Unit
Structural formula	$$\begin{array}{c} O \\ \parallel \\ R_2P-OH \end{array}$$	
Appearance	Colorless to light amber liquid	
pK_a in H_2O	6.37	
Density	910	$kg\ m^{-3}$
Viscosity	14.2	$kg\ m^{-1}s^{-1}$
Molar mass	290	$g\ mole^{-1}$
Aqueous solubility in distilled water, at pH 2.6 pH 3.7	16 38	$mg\ L^{-1}$
Specific Gravity at 25 ^{0}C	0.92	
Boiling point	>300	^{0}C