

Sustainable Technologies for the Tin Stripping Process used in Printed Circuit Board Fabrication

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Sustainable Technologies for the Tin Stripping Process used in PCB Fabrication

1. CURRENT STRIPPING PRACTICE IN PCB MANUFACTURING

Tin is widely used throughout the printed circuit board (PCB) industry as a secondary etch resist material during the patterning of a PCB. For the sake of clarity, the basic steps of this process are now briefly described. During the manufacturing process it is necessary to convert the copper-covered surface of the partially made board into one that has defined conductor patterns (the printed circuit) enabling individual components to be assembled and interconnected. In a typical application of a standard process known as ‘pattern plating’ the board surface is covered with a photoresist layer which is exposed through a mask and developed to uncover copper areas where conductor tracks and pads are required. The panel is then made the cathode in an electroplating bath so that a metallic tin etch-resist coating is plated onto all the exposed conductive areas (i.e. all the conductors required on the final board and within the holes; see **Figure 1 a**). The deposited layer is typically in the region of 5 to 15 microns thick, depending upon the specific application. Following plating, the photoresist is stripped (**Figure 1 b**) and, after inspection, the now-exposed copper (which was covered by the photoresist) is removed with an etchant that does not attack the plated tin etch-resist (**Figures 1 c-d**). As the etchant is required to remove copper but leave the tin etch-resist in place there is a limited choice of suitable etchants that can be used. In fact, for economic production purposes, the only commonly used etchants that dissolve copper whilst not attacking the tin are the so-called ‘ammoniacal etches’. These etches are typically based on an ammonia/ammonium chloride chemistry, although ammonia/ammonium sulphate based versions are also commercially available. The sulphate based chemistry is not widely used because of its relatively low etch rate, but it does offer the advantage of enabling the dissolved copper to be recovered electrolytically and recycled in-house. Sulphuric acid/peroxide-based etch chemistries were also used in the past when etch resists were tin-lead alloys. However, they cannot be used with pure tin resists and, as the industry has almost completely moved away from tin-lead alloys, they have fallen from use in this application.

After the copper etching stage the board surface has clearly defined copper conductors, which still have a protective tin coating on them. Although there are some alternative methods, it is widespread practice then to remove the tin with a proprietary etchant to expose the underlying copper. The most commonly used stripping solutions are based on concentrated nitric acid, and these often contain other proprietary additives which help to dissolve the tin-copper intermetallic which forms at the interface between the plated copper and the tin etch-resist. Other additives are used to protect the underlying copper once it is exposed, and these tend to be based on triazole and imidazole type molecules. The typical components and functions of a tin stripping solution are as follows:

- (1) Nitric acid (or occasionally methane sulphonic acid) – this strips the majority of the tin from the PCB
- (2) An iron salt such as ferric nitrate or ferric chloride – this enhances the

- performance of the above acid and provides sufficient oxidising capability to dissolve the copper-tin intermetallic
- (3) An inhibitor – this helps protect the underlying copper surface from appreciable attack by the etch
 - (4) A copper anti-tarnish agent – this prevents oxidation prior to subsequent solder mask application etc.

Although many tin stripping operations use a single-stage chemistry containing all of the above ingredients in one package, there are also processes in which a two-stage chemical process is used. In this latter case the first chemical stage is used to remove the tin and, once the underlying tin-copper intermetallic layer has been reached, the reaction stops. In this way, any problems with variations in tin-plating thickness across the board can be accommodated. The second stage is then used to remove the intermetallic layer, which is uniform across the entire board surface. This helps to ensure that problems with differential attack on the underlying copper, which may be seen in single-stage processes, are eliminated.

Figure 1 (a)-(d) ‘Pattern Plate’ PCB - tin-stripping process

With tin etch-resists and nitric acid based stripping chemistries the removed tin does not actually form a true solution within the stripper but instead forms a milky white, almost colloidal, dispersion of very fine tin (stannic) oxide particles. The tin is thus very difficult to remove from the acid, since it does not form a filterable precipitate, and it is this fact that has hampered previous studies aimed at developing new methods for recycling spent strippers. These solutions cannot be treated via conventional ion exchange or by using basic metal flocculation methods because of the nature of the tin dispersion. However, recent developments in membrane technology have overcome many of these problems.

After the tin-stripping stage, the final outer-layer circuitry has been defined and the board is ready to move on to the final processing stages. Typically, a solder mask is coated over the board surface to provide subsequent protection of the board surface. The solder mask is coated over almost the whole surface of the board (i.e. over the dielectric surface and the conductors). It is not coated in the holes or any areas, which will be used for subsequent connections (e.g. the solder pads). Finally, a solderable finish will be applied to the metallic areas that are not covered by the solder mask. This has traditionally been a tin-lead finish but in recent years many other solderable finishes have also become widely used. These include nickel-gold and silver-based metallic coatings as well as organic solderability preservatives (OSPs).

In operation, tin-stripping chemistry is mainly used in one of two ways, and this will depend on the company, the volumes being processed and a number of other considerations. A new solution may be made up and simply used until the etching rate drops below a specific figure, (i.e. until it becomes too slow for the equipment within which it is being used). At this point it will be removed from the equipment and drummed for treatment and disposal off-site. A new solution will then be made up. In such batch type operations there may be as much as 200 g dm^{-3} of metal in the final solution since manufacturers will continue to use the chemistry for as long as they can in order to reduce the cost of the process.

Alternatively, the chemistry may be used on a ‘feed-and-bleed’ basis whereby the chemistry is kept at a steady level of activity by bleeding out a fixed quantity of the solution and replacing it with fresh chemistry on a regular basis. When these etching solutions are exhausted they typically contain 150 g dm⁻³ or more of tin and from 2 to 40 g dm⁻³ of copper.

There is currently no viable method for the treatment of these spent solutions other than via the use of precipitative techniques either in situ or via off-site disposal and landfill. Within the UK it was estimated in the mid-1990s that 250,000 litres per month of such spent chemistry was produced for disposal and that 570 tons per annum of metal was ultimately consigned to landfill. At present no schemes exist to recover this metal and, considering that the cost of the original tin anode material is approximately £3.90 kg⁻¹ the industry is effectively disposing of a potentially usable resource each year valued at £1.75 million. An earlier study by the Printed Circuit Interconnect Federation (PCIF) Waste Minimisation Group indicated that the cost of off-site disposal for 1,000 litre quantities of spent nitric acid based stripper solutions containing 150-200 g dm⁻³ of metal varied across the country between £0.20 and £1.11 dm⁻³ and averaged £0.39 dm⁻³. In some areas no facilities existed for off-site disposal. The annual cost to the UK PCB industry of off-site disposal of spent stripper solutions was in the region of £1.2 million and thus, when the replacement cost of new tin anode materials was included, the UK PCB industry was found to be wasting approximately £3 million yr⁻¹. Estimates made by RD Chemical Company in the USA suggested that the value of the tin oxide in each gallon of spent stripping solution was in the region of US\$2.90.

2. ENVIRONMENTAL LEGISLATION

The main driver for the move to more sustainable technology within the UK PCB manufacturing industry is the rising cost associated with ensuring compliance to environmental legislation. Within the PCB industry the cost of environmental compliance is typically in the region of 6% to 8% of total manufacturing costs; a figure which does not compare favourably with the 2% for UK manufacturing as a whole. The main legislative drivers introduced by the European Union (EU) stem from the 5th and 6th Environmental Action Plans, which introduced principles such as the ‘polluter pays’, and ‘producer responsibility’ as well as the need to consider sustainability in all legislation. These policies and measures have given rise to an extensive system of increasingly stringent environmental controls, which have forced industry to address how it operates so as to ensure its business activities have the least negative impact on the environment. The salient points of this legislation can be found at: <http://europa.eu.int/comm/environment/newprg/index.htm> (EU web site). More recently the EU has identified four priority areas where special effort and impetus is required. One of these priority areas is the increasing amount of waste being generated in Europe. To tackle this problem the EU has introduced directives aimed at increasing recycling and recovery rates. Examples include the Landfill and Waste Electrical and Electronic Equipment (WEEE)* Directives and legislation aimed at restricting the use of hazardous materials via the implementation of the Restriction of Hazardous Substances (RoHS)* Directive.

* Further information on these directives can be found at Tin Technology’s www.lead-free.org web site.

Other regulatory frameworks such as Integrated Pollution Prevention and Control (IPPC) will require waste and energy efficiency to be dealt with through a single permitting system, using best available techniques and integrated product policy (IPP) will require products to be designed to be resource-efficient.

In the UK, concern over the ability to continue to consign vast quantities of waste into the ground has forced the government to introduce economic measures with the objective of making it less attractive for waste producers to landfill useful materials and more desirable to recycle and reuse what they are currently discarding as waste.

It is important, therefore, that any programme such as this is cognisant of the emerging policies and economic instruments that will have an influence on the introduction of sustainable technologies within the PCB manufacturing industry. It is also equally important to focus on the opportunities that will be afforded to companies who seize the incentive and take advantage of the well-documented cost savings and improved environmental performance associated with the implementation of these technologies.

2.1 Integrated Pollution Prevention and Control (IPPC)

In 1996 the EU enacted the Integrated Pollution Prevention and Control (IPPC) Directive. The directive was transposed into UK law through the Pollution Prevention and Control (England and Wales) Regulations 2000 and the Pollution Prevention and Control (Scotland) Regulations 2000. The PCB industry is affected by the regulations, as it is specifically cited in section 2.3 of schedule 1 of the regulations on the surface treatment of metals and plastic materials. The overall aim of the Directive is to achieve a high level of protection of the environment as a whole, and it has been designed to prevent, reduce and ultimately eliminate pollution at source via the efficient use of resources and via sustainable waste-management practices. To achieve this objective the Directive sets out an integrated permit system. As the wording suggests, 'integrated' means that the permit conditions must take into account all the environmental impacts of the plant and not just individual processes or activities. Therefore, IPPC covers emissions to air, water and land as well as energy efficiency, the use of raw materials, noise, prevention of accidents and risk management.

At the heart of the Directive lies the concept of 'best available technique' (BAT):

“The most effective and advanced stage in the development of activities and their methods of operation which indicates the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where it is not practicable, generally reduce emissions and the impact on the environment as a whole”.

* For general IPPC information or a direct link to the directive visit the following web sites:

<http://europa.eu.int/comm/environment/ippc/index.htm>

[http://europa.eu.int/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc&lg=EN&numdoc=31999L0061&model=guichett>](http://europa.eu.int/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc&lg=EN&numdoc=31999L0061&model=guichett)

In practical terms this means that affected companies must compare and evaluate techniques that prevent and reduce emissions and identify the best one for offering the lowest impact on the environment. However, the operator of a pollution prevention and control (PPC) site must also consider if the cost of implementing BAT outweighs its environmental advantages. For example, in determining the BAT for the treatment of spent tin-stripping solutions, economic and environmental evaluations would have to be made between the current practice of off-site disposal and the recovery techniques outlined in this report. Moreover, the assessment process must also take into account other factors covered by the IPPC Directive, such as waste minimisation, energy efficiency and the consumption of raw materials, and consideration should be given to techniques that use fewer resources and are less likely to produce hazards or pollution. It is therefore clear that the IPPC Directive is a key driver for the implementation of sustainable technologies, such as those proposed herein, that are able to treat waste in a cost-effective manner and on-site.

2.2 The Landfill Directive

One of the most significant drivers for change in waste-management practices within the UK PCB industry will arise from changes introduced by the EU Landfill Directive*. The Directive came into force in July 1999 and aims to reduce the negative effects of landfilling by setting stringent operational and technical requirements for the disposal of waste to landfill. The Directive is implemented in England and Wales through the Landfill (England and Wales) Regulations 2001 made under the Pollution Prevention Control Act 1999.

A major impact of the Directive will be a reduction in the number of landfill sites operating in the UK. According to estimates, the number of landfill sites licensed to accept hazardous material will drop from 218 to as few as 34. The amount of hazardous waste in the UK is increasing at a rate of 8% per year and currently accounts for some 5.2 million tonnes, most of which is produced by the construction, chemicals and electronics industries. This situation will be further exacerbated by changes in the classification of waste, which will increase the scope of material that will soon be defined as hazardous.

There is also a need to find an additional two million tonnes of treatment capacity to compensate for the loss in hazardous landfill capacity and to meet a further requirement of the Directive, which places an obligation to take measures that ensure that only waste that has been treated is landfilled.

* For general Landfill information or a direct link to the directive visit the following web sites:

http://europa.eu.int/comm/environment/waste/landfill_index.htm

http://europa.eu.int/smartapi/cgi/sga_doc?smartapi!celexapi!CELEXnumdoc&lg=EN&numdoc=31999L0031&model=guichett>

Given the impending situation and the widely held concern that there is insufficient private-sector investment in long-term hazardous waste treatment infrastructure in the UK, there can be little doubt that the costs of sending hazardous waste, such as spent tin stripping solutions, for off-site treatment and disposal will increase dramatically during the next couple of years. It may also become more difficult to identify waste treatment companies that have the ability to handle, or are willing to accept, a waste effluent that is viewed as difficult to treat because of its extremely low pH. This is a dilemma, which has already been experienced by some PCB manufacturers (see details of the site visits for additional information, in **Appendix A and B**).

2.3 Environmental Management Systems

There has been a growing trend in recent years in using the supply chain to impose standards of operations on businesses, and no more so than in the electronics industry. PCB manufacturers have reported an increase in requests from their customers to produce evidence of an accredited environmental management system such as ISO 14001 or the Eco-Management and Audit Scheme (EMAS) before agreeing to enter into contract with them. This may go some way to explaining the high percentage of PCB companies gaining ISO 14001 (certification) in the last few years via a programme of fast-track accreditation organised by members of Intellect's Environmental Working Group.

An environmental management system enables a company to demonstrate environmental compliance and to establish objectives and targets to achieve good environmental performance via resource efficiency and the implementation of sustainable waste-management practices. Since the proper functioning of an environmental management system depends upon a cycle of continuous improvement it acts as a driver to stimulate the development of more sustainable manufacturing and waste-treatment practices.

2.4 The Landfill Tax

One of the most persuasive arguments for implementing sustainable technologies is the associated cost savings through the minimisation of waste, reduced disposal costs and the more efficient use of resources. Historically, the cheapest available option for disposing of waste in terms of the waste hierarchy was to send it to landfill. It is therefore not surprising that final disposal accounts for the greatest proportion of the industrial waste-stream. However, this situation is changing as the incremental increases in landfill tax start to take effect, making landfill economically undesirable and acting as a driver for businesses to minimise the amount of waste produced and to seek more sustainable waste-management options.

The landfill tax was introduced in 1996 and is an economic instrument for diverting significant quantities of waste away from landfill and towards more sustainable waste-management options such as recycling and reuse. The tax is chargeable by weight and there are two rates. A lower rate is charged to inert waste, and a standard rate is chargeable to all other wastes. At the time of writing the landfill tax is £2 per tonne for inactive waste and £14 per tonne for active waste. An escalator of £1 per tonne was introduced in 1999 for active waste, taking the level of the landfill tax to £15 per tonne by 2004. However, this escalator is set to increase to £3 per tonne from 2005 to 2006 and a level of £35 per tonne has been set as a long-term goal. The early

announcement of the planned increases in the landfill tax provides an opportunity for businesses to seek more sustainable alternatives to landfill via the implementation of technologies that can significantly reduce the quantity of waste produced. Therefore, support for companies to undertake more sustainable manufacturing and waste-treatment practices should be encouraged.

3. Literature Survey

3.1 Diffusion Dialysis, Filtration and Electrowinning

From articles cited in the literature and discussions with key personal within the field of PCB manufacture it is clear that industry, through its recycling initiatives, and in response to environmental legislation, have made extensive use of ion membrane technology, especially in areas of solution regeneration and rinse-water reclamation. Early membranes were driven by electrochemical or chemical potential gradients as a means to force water through a semi-permeable material, leaving unwanted contaminants behind. Towards the later part of the 20th century other driving forces were developed (e.g. hydraulic pressure, temperature gradients and proton concentration processes). Each of these new types of process development can be attributed to an improved understanding of ion membrane technology and the subsequent design of new materials. Accompanying this advancement, new types of membranes are now being offered in the marketplace (e.g. tubular and hollow core membranes), which no longer require an applied potential to create the desired gradient. With all the advances made and continuing to be made it is impractical to list all the membrane designs, especially as it is now possible to work with ion membrane manufacturers and get a system tailor-made for your own application. **Table 1** provides a short list of available membranes, which will be briefly discussed in further sections of this report.

Table 1. *Ion Membrane design and Industrial Application*

There is an overwhelming amount of literature cited on the Internet and elsewhere concerning the uses and benefits of processes adopted in the regeneration of acid tin-strip solutions, currently in operation within the PCB industry. It is beyond the scope of this study to review all the processes on offer; therefore this report shall concentrate on the most common and cost-effective systems, which afford the industry the opportunity to comply with current and future environmental demands while remaining competitive. Where applicable, each section will provide brief technical details, highlight the main operations (flow-chart) and offer some alternatives.

As described in section 1, a tin solder coating is applied to protect the underlying copper substrate during the ammoniacal etching process. Once the unwanted copper has been etched away, the protective tin resist needs to be removed. The tin-resist is removed in a one-step tin-stripping process based on nitric acid or methane sulphonic acid (MSA). Like most process solutions they need to be periodically replaced, in the case of tin stripping solutions this occurs once the solution has reach a tin metal content approaching 150 g dm⁻³ (and 40 g dm⁻³ copper) or when the stripping rate falls below an unacceptable level. The discussions below are focused predominantly

on nitric acid tin-strip systems; however, the arguments and descriptions highlighted are not mutually exclusive but are equally relevant to the MSA system.

Once a tin-stripping rate has appreciably slowed it needs to be waste treated prior to being discarded, current practice is either to transport the waste solution away or to neutralising it. Either way, the final waste treatment is to discard the resulting residue to landfill. This is clearly not only environmentally unsound but also a waste of natural resources. There are numerous ways of reclaiming acid tin-stripping solutions and avoiding treatment costs while at the same time make savings on replacing the solutions themselves. The simplest approach in creating a sustainable tin stripping process involves the use of ion membrane technology. To completely regenerate the spent acid tin-stripping solution requires three steps; e.g. firstly an acid reclamation process, followed by a filtration step and, lastly, a metal recovery operation. If economics is a concern or the level of the stripping operation does not warrant the outlay costs of a fully sustainable approach, the technology described readily breaks down into separate simpler modules (e.g. if acid reclamation is the only step you require you can operate a diffusion dialysis only module).

The regeneration of the acid tin-stripping solution (sustainable approach) consists of utilising the following technologies: (1) diffusion dialysis, (2) filtration and (3) electrolytic or electrowinning metal recovery.

3.1.1 Diffusion Dialysis ^[1-19]

A process in which ion exchange membranes are arranged in a stack formation (a similar cell arrangement to an electro-dialysis unit) and the gradient is supplied via a concentration difference between solutions either side of a membrane i.e. there is no applied electrical potential gradient required and such an arrangement is referred to as diffusion dialysis, **Figures 2-3** illustrate the basic principles of diffusion dialysis. Simply, this process requires two compartments: one containing water, and the other the waste or spent tin-stripping solution. These two compartments are separated by an ion exchange membrane, which blocks the transport of metal ions while allowing the passage of hydrogen ions. Diffusion dialysis works on the principle of a concentration gradient between the two compartments, with the overall process efficiency being directly dependent on the surface area available afforded by the ion exchange membrane. For this reason the membranes are stacked upon one another, thereby increasing the surface area. Diffusion dialysis units consist of multiple compartments, each separated by ion membranes where the acid solution is pumped through alternate compartments with water being pumped in the opposite direction through the remaining cells. Hydrogen ions will traverse through the membrane into the water-containing cells. Once concentrated, the acid can be reused; however, additives will also have to be replaced (organic and inorganic additives are also blocked by the membrane, with the metallic contaminants during dialysis) before the process is operational. The treatment process can be performed in batch mode, through complete solution treatment or, alternatively via a bleed-and-feed process. The metal ion removal for a bleed-and-feed system has to be sufficiently fast if the regenerated acid is going to be passed directly into the process solution. Once the nitric acid has been regenerated the solution in the compartment containing the waste metal ions (tin, copper and iron) can either passed into the effluent stream for further treatment or passed on for metal recovery. One great attraction of this process is that the only energy requirement is the energy to drive the circulatory pump.

Figure 2. *Ion Membrane separating a two Compartment Cell*

Figure 3. *Flow Diagram of a Diffusion Dialysis Process*

3.1.2 Filtration ^[20-43]

The metal ions in the spent tin-stripping or residue solution once the acid has been reclaimed have to be separated. The reason for this is that the tin exists in a fine, insoluble suspension (i.e. tin (IV) oxide (SnO_2)) and therefore cannot be electrolytically recovered in this form. One possible method to recover the tin oxide would be to filter the fine suspension; the type of filtration system, and membrane technology required are now reviewed.

Membrane filtration is the separation of the components of a pressurised fluid by a polymer-based or inorganic film (membrane). There are four commonly accepted classes of membrane, defined based on the size of material they remove from the carrier liquid. The smallest pore size and therefore the smallest sized material that can be removed from the flow stream can be found in reverse osmosis (RO) membranes; the pore size increases from nanofiltration (NF) to ultrafiltration (UF) membranes to the largest pores, which are found in microfiltration (MF) membranes. From the description of the four classes of membrane it is clear that the pore sizes in RO (0.5-1.0 nm) and NF (1.0 nm) membranes would be too small and therefore easily blocked while filtering the waste stripping solution.

Before we go any further, it may be useful to define some of the terms used:

- *Ultrafiltration* (UF): 10-50 nm in diameter. UF is a selective separation step used both to concentrate a stream as well as to purify medium to high molecular weight components. Water, salts and low molecular weight compounds pass through the semipermeable membrane, as schematically shown in **Figure 4**.

Figure 4. *Basic Principle of Ultrafiltration (under normal flow conditions)*

- *Micro-filtration* (MF): 1-10 μm in diameter. MF operates under a low pressure and the membrane is ideally suited for separating high molecular weight solids from a process stream. Water, salts and low molecular weight species selectively pass through the semipermeable membrane, while macromolecules and suspended solids are retained and progressively concentrated.

The transfer or transport of waste tin-strip solution removes any possibility of reclaiming raw materials (such as metal contaminants built up in the spent solution) and exploring alternative sources of revenue (e.g. markets for refined tin oxide suspensions).

The tin within the spent tin-stripping solution exists in the form of an insoluble fine suspension and is not readily reduced without further modifications to the solution (i.e. acidifying with hydrochloric or hydrofluoric acid or making the solution alkaline which would require suitable additions of sodium hydroxide). A viable alternative to further chemical treatment would be filtration. Once the tin oxide is removed the remaining metal ions can be reduced electrochemically.

During the past 10 years membrane technology has improved (and continues to improve), which is highlighted by the incorporation of RO, NF, UF and MF membranes into many filtration systems currently being used in treatment of industrial processes. Historically, the membranes used in the filtration of solutions containing fine suspended matter (e.g. tin-stripping solutions; also, see section.3.1.2.2) become blocked as the particles agglomerate as they try to pass through the filter (e.g. because of the fine particulate nature of the tin oxide). However, with improvements and a better understanding of the technology involved in membrane and filter processes, problems associated with blockages resulting from particle agglomeration have now been largely overcome. Coupling cross-flow or improvements to back-flush mechanisms have enabled the SnO₂ particles to pass through the filter pore holes and be reclaimed. The SnO₂ can then be collected and sold, thereby becoming an important marketable commodity rather than a waste product destined for the landfill.

However, it may be possible to use UF and MF membranes as they have been described as the “fine” end of particle filtration possessing pores of higher magnitude compared with membranes from the other classes, RO and NF. Therefore, it would seem highly probable that UF or MF membranes could be used to remove particulate matter, allowing waste process streams containing metal ions to pass. Depending on the nature of the tin oxide, these filters may also be adapted for use in reclamation of acid tin-strip solutions. The solution bearing the filtered tin oxide could then be used to generate slurry or be evaporated leaving the oxide in a dried form.

The correct type of filter system (membrane) adopted for a given operation (e.g. removal of tin oxide from acid) must be carefully considered, and the following information may provide a useful guide when choosing the right type of filter:

Knowledge is required of:

- The chemistry occurring at the membranes surface.
- The steric effects of the colloid or suspension (fouling rate) also known as the ratio of permeate to feed volume.
- The correct pore type (application design).
- Applied pressure requirements.
- The operational temperature of the filter membrane.
- The flux or permeate rate per unit area of the membrane (this parameter is also directly proportional to effective pressure).
- The life expectancy of the filter membrane under normal usage.
- The cost of replacing the filter cartridge or membrane.

When designing a membrane filter system it is important to consider the above and to discuss any designs or applications with an experienced vendor to avoid damage to membranes, (which are costly) that will ultimately give rise to disappointment when membrane operation does not have the desired effect (i.e. when the membranes are ineffective for the chosen application). Some of these considerations are briefly discussed in the following section 3.1.2.1.

3.1.2.1 Design, Construction and Definition of Membrane Filters

Ion exchange membranes used in MF applications are available in tubular, hollow fibre and spiral forms and are designed in such a way as to withstand high-applied operational pressures and to manage the diversity of the many types of industrial process streams.

Spiral membranes; these membranes are produced by winding consecutive layers of feed spacer/membrane / permeate collection channel / membrane around a perforated centre tube for permeate collection. This spiral design affords greater diversity in the number of different membranes that can be incorporated into this design and lowers energy consumption (because of the lower level of pumping needed to maintain the system and to the lower packing density of the material). Other features of this type of construction include elevated operational temperatures and pressures, resulting in a faster throughput.

Tubular membrane; these typically consist of a membrane cast inside a support tube 15-30 mm in diameter. The smaller tubes can be bound together in blocks of several units, and larger tubes can be used as single units. This design provides superior performance at high concentrations of particulates, where blockages are minimised, thereby a high degree of filtration can be achieved with high product recovery. This design also offers a tenfold increase in tube diameter, compared to the hollow fibre, which may be an important factor, because of the large size of the SnO₂ particles. The size of the oxide particles may be variable, depending on the degree of coagulation experienced within the tin-stripping solution. This membrane design confers a large cross-sectional area to the flow stream (if flux determination or rate is a concern, this may be a preferred option). Another advantage of this system is that it operates in environments of extreme pH and temperature.

Hollow fibre designs; the fibre membranes are asymmetric (anisotropic) and self-supported structures. The membrane can be back-flushed, an extremely useful property if the life expectancy of the membrane is a concern. Other properties include membrane reliability and chemical stability. Hollow fibres come with an array of lumen diameters, ranging from the diameter of a human hair to 2 mm.

Special adaptation of ion membrane design; cross-flow filtration operates on the principle of separating the particles in solution under an applied pressure via an inorganic membrane, in which the membrane acts as a surface filter splitting the main feed stream into two. The use of a main stream, which passes through the membrane surface (with small size contaminants such as metal ions), and a second stream, which flows tangentially over the membrane surface, removes larger blocked or unfiltered particles left behind on the membranes surface, giving this particular membrane design its name (cross-flow). The feature of cross-flow filtration (as illustrated in **Figure 5**) can be equally applied to spiral and hollow fibre membrane designs. This

may be particularly important in preventing fine tin oxide particles agglomerating at the pore sites within the membrane filter.

Figure 5. *Illustration of the cross-flow system mechanism used in the separation of particulate matter from process streams: (a) high cross-flow rate (high permeate passage); and (b) no cross-flow rate (low permeate passage)*

3.1.2.2 Difficulties associated with the filtration of tin oxide particles

As the used tin-stripping solutions end up with a ‘milk-like’ very fine suspension of tin oxide which is extremely difficult to filter off or remove from the acidic solution, which also contains some dissolved copper, it seems that the main challenge in any sustainable chemistry approach is the recovery of tin in some form that is use able and that can be obtained economically (i.e. at a cost which at worst is no more than the cost of offsite treatment and disposal via landfill and at best somewhat cheaper). Other possibilities are somewhat limited; however, the tin could be recovered electrolytically or as SnO₂.

Recovery of the tin in the form of tin oxide (i.e. a fine white suspended particulate) is difficult. Filtration using conventional cartridge filters is not very practical as the oxide rapidly blocks the filters thereby quickly rendering them ineffective. There is also the difficulty of recovering the fine oxide from the filters, although they could conceivably be sent away to a metal refiner. This is unlikely to be a viable option, as it would require the use of a large number of filters. Although many of the problems associated with these filters have been overcome with the new membrane/filter design, cost of this process remains high. Modern-day filtration systems have addressed some of these issues; however, improvements to design and to the membranes incorporated into these designs are continually being made. Centrifugal filtration is not much better, and the equipment is also very much more expensive. The possibility of ‘dropping the oxide out’ as a coarser precipitate, using materials such as the Wapur[®] chemistry (see section 3.1.4.2), appears to be more attractive, although the costs of this chemistry would need to be investigated and compared with that of normal offsite disposal. The dissolved copper in the solution can be recovered electrolytically without too much of a problem, although the pH might need adjusting to optimise the efficiency.

If it were possible to decant off the supernatant liquid and to remove any dissolved copper from it by plating, there is the possibility that it could be reused. Ideally, this would enable the acid to be reused in the make up of fresh stripping solution, but it could also be used for other applications. As typical nitric-acid-based tin stripping solutions also contain ferric nitrate and some organic components, it would be necessary to monitor their levels before the acid solution could be recycled. Nevertheless, this should not be too difficult.

3.1.2.3 Uses of tin oxide

In previous studies addressing the issues raised in this report (Shipley, now trading as Rohm & Haas Electronic Materials) in which the recovery of tin-lead stripping solutions were investigated it was discovered that tin oxide was deemed more valuable than the tin metal itself (e.g. it had a market value as a polishing medium for

floor tiles and gems, etc). This is still the case and a means to reclaim the tin in this form would gain considerable support from industry.

Tin oxide is widely used for polishing cabochons (smooth unfaceted gems), but is rarely used for faceting. Some problem stones respond better to tin oxide than to other polishing agents. Tin oxide for this sort of application, which is 99.9% pure, is currently advertised at \$16 a pound!

Tin oxide has a number of diverse uses in the glass industry. It is used, for example, in the manufacture of lead crystal glass. Above 800°C, molten glass becomes electrically conductive, and heating is then achieved by the passage of a high current via suitable electrodes. These are manufactured from tin oxide in the case of furnaces for glass containing over 12% lead oxide, since it does not reduce lead oxide to metallic lead. The electrodes are in the form of cylinders or blocks weighing between 5kg and 50 kg.

Anhydrous tin oxide has been used as an opacifier in ceramic glazes since ancient times. Babylonian and Assyrian wall tiles from the 9th century BC have been found to incorporate this material in a white glaze, and this is probably the earliest known application of a tin compound. Tin oxide is highly insoluble in glazes, giving it a high opacifying power, at levels of 4-8%. It is being challenged at present by cheaper alternatives, but stannic oxide is still used for high-quality art ware and industrial applications, where the highest resistance, purest colours, greatest strength and abrasion resistance are required

Tin oxide is one of the components of a number of binary oxide systems that find extensive use as catalysts in industry, particularly petrochemicals; the other oxides most commonly used in association are those of vanadium, antimony, molybdenum and phosphorus. These catalysts are employed in the manufacture of various chemical intermediates.

3.1.3 Electrolytic Recovery (*Electrowinning*)^[44-65]

Electrowinning is an electrolytic technology process, which can be defined as the removal and recovery of unwanted heavy metal ions from aqueous solutions (electrolyte) by means of electrolysis, although the term “electrowinning” has traditionally been associated only with metal recovery systems involving, for example reclaiming metals from their ores or molten salts. However, its application in a well-designed and controlled spent plating process system can significantly reduce the levels of chemicals used and the cost of waste treatment of these spent solutions. The aim of electrolytic recovery in this instance is to recover the copper from a partially treated waste tin-strip electrolyte. This is achieved by reducing the copper ions in solution at the negative electrode (cathode) of an electrowinning cell; a typical cell arrangement is shown in **Figure 6**.

Figure 6. *A Schematic illustration of the Cross-section of an Electrowinning cell*

The recovered metal can either be sold (if recovered in a sufficiently pure enough form) or discarded as scrap. Other recovery process applications other than acid tin-strip solution recovery (this is an important consideration, which affords the opportunity to maximise the use of this technology) are:

- *Spent electroplating (and/or electroless) baths.*
- *Process rinses.*
- *Spent etch solutions.*
- *Effluent streams.*

Electrowinning works on the principal that electrolytic recovery is essentially an electroplating process, where a potential is applied to the plating cell and the resulting current is utilised in the reduction (deposition) of metal ions at a cathode, as illustrated in **Figure 7**. The current density of the plating cell should be maintained at a level where the maximum rate of deposition occurs without being detrimental to the quality of the deposit. A typical electrolytic recovery process consists of a tank to hold the electrolyte, anode and cathode, a pump to transfer solutions from a feed or storage tank and a power supply. The type of electrode to collect the recovered metal (cathode) is dependent on the concentration of the metal ions that are being recovered, hence the variety of cathodes available: reticulate foam, wire mesh typically stainless steel and expanded stainless steel. All of these examples are used to increase the surface area available for reduction and subsequently low levels of the reduced species can be deposited from the electrolyte, which would not be feasible from a conventional flat designed electrode.

Figure 7. *A Schematic illustration of the electrochemical reduction occurring at the cathode (negative electrode) of a typical electrowinning cell*

The main objective of this process is to remove the unwanted metallic ions remaining in the tin-strip electrolyte after diffusion dialysis (acid recovery) and filtration (tin oxide). Only two types of metal ion remain in the electrolyte: copper ions formed by the overetching off the exposed copper, and ferrous ions from the degradation of the $\text{Fe}(\text{NO}_3)_3$ additive (which is included in the acid stripping formulation to prevent excessive attack of the copper once the tin resist has been removed). Both of these metal ions can be removed electrolytically with the application of a suitable potential, -0.15 V in the case of the electrolytic recovery of copper. The copper metal can be deposited from solution at a sufficiently fast rate with a current efficiency in the range 90-96%; however, these figures are very much dependent on conditions of the electrolyte (e.g. concentration, pH and temperature; section 3.1.3.4). The purity of the electrolytically recovered copper is dependent on the levels of other contaminants within the plating electrolyte that may become co-deposited. From tin-strip electrolytes (once the tin oxide and acid has been recovered) the recovered copper is generally of good quality, and co-deposition of unwanted metallic species will only occur if the deposition potential of the unwanted ions present is sufficiently close to that of copper. In the case of the tin-strip electrolyte, if copper is electrolytically removed after filtration of the tin oxide the only metal ions present in any quantity are those of iron, which has a deposition potential of approximately -0.4 V, and therefore far enough removed from the deposition potential of copper not to be of concern

Electrowinning is applied to a wide variety of chemical solutions found in the PCB industry. Metals most commonly recovered by electrowinning are copper and the precious metals such as gold and silver. This is why this method of recovery is

ideally suited to reclamation of waste tin-stripping solutions. For practical purposes, the degree to which a metal species can be recovered by electrolytic means is very much dependent on its position in the electromotive series. In general, the more positive the standard electrode potential of the metal, the easier it will plate out of solution compared with metals with less positive potentials. For example, in the recovery of precious metals copper and tin, the more noble metals (gold and silver) can be removed from aqueous solution at concentrations less than 1 mg dm^{-3} , whereas with copper and tin solutions the concentration has to be greater than 2 g dm^{-3} . The concentration of electrolytes containing both copper and tin can undergo electrowinning at a much lower concentration (in the mg dm^{-3} range) using a Bute cell/fluidised bed arrangement.

3.1.3.1 Recovery of copper by electrolysis

Recovering metallic copper directly from spent tin-stripping solution is difficult because of the high acidity of the electrolyte. For this reason any diffusion dialysis operations should be carried out prior to the electrolytic recovery process. Once the acid has been reclaimed the operating parameters of the recovery (plating) cell e.g. electrode distance (anode to cathode), pH, temperature and applied current density need to be optimised to maximise the rate of recovery. The current efficiency for depositing copper from acid tin-strip solutions approaches 100%, this figure falling to as low as 20% as the concentration of the metal ions approaches zero).

The time of the electrolytic recovery process can be monitored by analysis of the metal ions remaining in solution. The length of time required for metal ion removal is directly proportional to the operating conditions, hence the reason for optimising the process.

3.1.3.2 Recovery of iron by electrolysis

Deposition of iron is essentially carried out in the same manner as described for copper ion removal, with the exception that the applied potential is -0.4 V . Removing iron from this waste-stream will prevent the $\text{Fe}^{2+}/\text{Fe}^{3+}$ heavy metal ions being discharged to the effluent. Fully treating the tin strip solution allows the resulting solution to be recycled and a fully sustainable approach adopted, which may be an important consideration for closed-loop operations (i.e. where there is no effluent discharge or zero effluent). Again, operational conditions need to be optimised to maximise the recovery rate; an increased current density can be applied as the quality of the metal deposit is not critical and for this reason the cathode can be scrap stainless steel. Although technically feasible, electrowinning or removal of the ferrous/ferric ions by this method is unlikely (in a practical and economical sense) because the levels of iron (ferrous/ferric) in a waste tin-strip solution are very low. Another approach worthy of consideration could be filtration or ion exchange; these methods would certainly remove any remaining metallic contaminants and may afford a cheaper alternative to electrowinning.

3.1.3.3 High-surface-area-electrowinning

A particularly good example of an electrolytic recovery process that could be applied to reclaiming copper from partially treated tin-strip solution is high-surface-area (HSA) electrowinning. This process was developed and commercialised in the late 1980s using a reticulated cathode design; this design enables low levels of contaminants to be removed as well as being applicable to solutions with higher

concentrations. The flexibility of this system enables the end user to adapt this technology to the recovery of metal ions both from rinse waters and from process solutions. Typical recovery concentrations range from the ppm level to g dm^{-3} for a range of metal ions, including copper. Once the metal ion recovery is complete, the cathodes can be recovered and sold on as scrap.

The technology used in HSA electrowinning is more than just a compliance technology (i.e. it is more than a technology enabling legislation constraints to be met); it also benefits the end user by enabling the recovery of valuable metals that otherwise would have to be converted to metal hydroxides by waste-water treatments or some other post-treatment process. Commercial units employ a variety of strategies designed at increasing the recovery or metal reclamation efficiency even at the low levels of metal ion concentration often found in rinses or partially treated or reclaimed process electrolytes. The HSA electrowinning operation can be used to recover metal ions from such dilute electrolytes because of design innovations incorporated within the electrowinning cell. For example, use of agitation that focuses on causing solution movement or flow across the cathode surface. This action helps reduce the effects of concentration polarisation, a condition where the thin film of electrolyte surrounding the cathode is depleted of the reducing metal ions. A HSA cathode also permits an efficient metal ion recovery operation even when the electrolyte in question, contains a low concentration of metal ions.

3.1.3.4 Maximising metal deposition (recovery) rate

Optimising and controlling the electrowinning electrolyte will help improve the overall performance of the electrolytic recovery process. There are three parameters that should be maintained: current density, mixing and cathode surface area.

Current Density: metal deposition occurs at faster rates with higher current densities. However, if the current density is too high the solution surrounding the cathodes can become depleted of the metal ions they are trying to recover; this limits the metal deposition rate. Any excess current will result in alternative redox reactions occurring at the electrodes (e.g. conversion of water into hydrogen and oxygen).

Mixing: solution mixing (an often overlooked parameter); operating a well-aerated system facilitates the reactions occurring at both the cathode and at the anode. Keeping the ions in solution moving (to give a faster arrival at the cathode) and removing those forming at the anode (generating the electrons required in the reduction process) helps maintain the optimum rate of metal recovery. Any resistance in the electrochemical cell, at the surface of either electrode or within the solution itself, will result in reduced process performance and a greater production cost.

Cathode surface area: where the metal recovery rate is proportional to the cathode surface area. Two main types of cathode are commercially available (although with the advent of different materials this number is likely to increase): flat-plate and reticulated cathodes. Flat-plate electrodes are commonly manufactured out of stainless steel; their shape and size can be modified to suit individual requirements. The advantage of this type of electrode is that the stainless steel is reusable and the recovery of the metal can be carried out on-site. Reticulated cathodes are made from metal-coated carbon fibres, and this affords a tenfold area increase in comparison with stainless steel flat electrodes. The advantage of using reticulated carbon fibres is the

increase in surface area and the enhanced recovery rate. However, these electrodes are not reusable, and the fully loaded cathodes have to be sent offsite for recycling.

Anode Effects: in traditional electrowinning operations, metal particles from commercial insoluble anodes flake off the immersed surfaces under high current densities and maybe become occluded on the adjacent cathode surface thereby impairing the purity of the cathode product quality and market grade. This will be a problem if one wishes to sell the recovered metal formed at the cathode, for example copper, for the manufacture of anodes. This also results in an undesirable physical appearance of the metals being reduced at the cathode because of irregular protrusions, which impede subsequent material-handling operations such as packaging, weighing and transportation.

Anodic effects can be offset by consideration of the following: the composition of the anodes, the surface texture of the anode and the configuration of the anodes within the electrowinning cell (e.g., by optimising the geometry and design and the anode-to-cathode distances).

Summary (Key Terms are as follows):

- **Diffusion Dialysis:** Diffusion dialysis acids are separated and recovered by means of the difference in concentration between the solutions either side of a membrane.
- **Class of Filtration membrane:** Ultrafiltration (UF) and microfiltration (MF). Defined by the pore size and therefore the size of species removed.
- **Membrane Elements:** Tubular, hollow fibre and spiral. Membranes are incorporated into the various elements to withstand the rigours of applied pressures.
- **Design adaptation:** Cross-flow describes the type of flow the system (membrane) operates under (i.e. compared with normal flow).
- **Electrolytic Recovery:** Electrowinning is an electrolytic technology used to recover valuable metals from electroplating waste-process solution. An electrowinning unit consists of: an electrolytic cell, a rectifier and a pump.

3.1.4 Alternative Process Steps in Recovering Tin Stripping Solutions

3.1.4.1 Tin oxide recovery from spent stripping solutions:

A **research study** was carried out to evaluate several removal or separating methods to separate the tin oxide from waste tin-stripping solution. The objective of this investigation was to recover as much tin oxide as possible from spent tin-stripping solutions.

Introduction: when tin is stripped in nitric solutions it forms an insoluble salt (stannic oxide). These salts are dispersed in solution and held there by suspension agents, which prevent the tin oxide precipitating out and thus blocking up all the nozzles of the process equipment. As a result, it is current practice for spent tin-stripping solutions to be sent offsite as hazardous waste for treatment and subsequent consignment to special landfill sites.

Experimental evaluation: several methods were evaluated in an attempt to separate the tin oxide from the stripping solution (**Table 2**).

Table 2. *Various methods used to remove tin oxide from tin stripping solutions*

Discussion: the centrifuge system was far superior to any other method tested as a means of concentrating the tin sludge. However, as no analysis of the supernatant solution was carried out it is impossible to establish if this could be reused as a tin-stripping solution. This technique may have removed some of the additives essential to the tin-stripping chemistry. It was decided to look at the centrifuge system more closely. The graph in (**Figure 8**) was generated from various times and spin speeds.

Figure 8. *Tin-strip separations (recovery) as a function of spin rate with time*

Although the centrifuge system works, the efficiency of the separation system is dependent on the dwell time and speed of rotation. The cost of this process may also be a consideration.

ACD Technology, formally known as International Supplies, manufactures hydrocyclone filters for pumice equipment. They can supply the filter casing for €280. The system would still require a pump, relevant plumbing and storage tanks. The inside of the filter is made from Vulkulan[®] (a highly chemical resistant plastic material) and should be compatible with acid tin-strip solutions. There are no metal parts inside the filter, which was approximately 18 inches high.

Keywords: cyclone filtration, hydrocyclone filtration and centrifugal separators

3.1.4.2 Recovery of used tin-stripping solution: Wapur[®] 665

Wapur[®] 665 has been specially formulated to remove tin oxide residues from tin-stripping solutions to prolong the longevity of the stripping solution. Wapur[®] 665 can be used in either batch or bleed and feed mode, and once the tin oxide has been removed (e.g. by a filtration step), the remaining acid solution can be pumped back into the treatment tank. If a continuous system is to be operated, the Wapur[®] 665 should be added on a flow rate basis corresponding to the flow of the solution.

3.1.4.3 Electrolytic recovery of tin from aqueous solutions

An alternative to filtering the fine tin oxide suspension from the acid tin-stripping solution following on from an acid recovery step could be electrodeposition (electrowinning) of the tin metal. However, if the electrolytic option for tin metal

recovery is preferred, two problems must be addressed: formation of foam due to oxygen evolution and the formation of insoluble meta-stannic acid (as a result of Sn^{2+} ion being oxidised to Sn^{4+}). Prior to any successful electrolytic operation these undesirable effects must be addressed. To eliminate foam formation the anolyte and catholyte have to be separated by a membrane to minimise the effects of the reactions occurring at one electro surface interfering with those at the other. An alternative catholyte solution must also be used to prevent the formation of an insoluble tin species. The addition of hydrochloric acid to meta-stannic acid will cause the tin to form the complex H_2SnCl_2 in which Sn (IV) will be reduced at the cathode (stainless steel) at an applied potential of - 0.6 V.

Other adaptations of this method include the ones cited in the literature by Scott *et al* [46] and McKesson [52].

3.1.4.4 Alternative approach to diffusion dialysis (acid regeneration)

Acid sorption (Solvent Extraction): acid sorption is applied in the maintenance of moderately concentrated acid baths (e.g. sulphuric and hydrochloric acid) but is equally suited to plating rack or tin-stripping printed circuit boards with nitric or MSA.

Sorption describes a process in which components move from one phase and are concentrated in another. Simply, this process uses a strongly basic anion exchange resin to absorb the acid from solution and then water to desorb the acid from the resin. The metal-contaminated solution is then pumped upwards through a resin, where the acid is absorbed and the metal ions pass through in a solution that can subsequently be waste-treated (e.g. filtration and electrolytic metal recovery). The acid is then desorbed, as water is then pumped down through the resin bed where the purified acid can be collected and either fed back into the system through a bleed-and-feed regime or collected and analysed or readjusted for further use as a working bath.

Acid sorption recovers from between 80% and 90% of the free acid. A consideration when using acid sorption for the regeneration of nitric acid solutions is that the metallic components from the resin must be treated otherwise a hazardous sludge will build up within the resin bed, rendering it unusable in a short period of time.

The concentration of nitric acid within the tin-stripping solution is approximately 125 g dm^{-3} and uses TBP (Tributylphosphate) as the solvent extractant. From the feed solution containing the nitric acid it is possible to regenerate 95% of the free acid using a 50% TBP solution and deionised water as the stripping agent.

3.1.5 Alternative process to replace tin plated resists

-Using laser organic resists [66]

This process describes an etch-resist method using laser organic materials thereby removing the need of using tin stripping solutions altogether.

In addition to the work done by Rohm and Hass Electronic Materials (formerly known as Shipley Europe Ltd.) to develop an organic etch-resist replacement for

metallic etch-resists which was based on electrophoretic deposition, another possibility for using organic resists has recently emerged. This potential new method is based on the use of a laser to ablate an organic etch-resist and has been made possible by the rapid improvements in lasers and in particular their ablation capabilities over the past two or three years. Historically, the cost of high-speed lasers and their relatively slow speeds when ablating the typically large areas of material required to produce, or define, a circuit pattern have limited their applicability.

However, the use of laser technology in the patterning of PCB inner layers has recently been proposed, and indeed demonstrated, and it would therefore be at least theoretically possible, with some modification, to extend the technology to conventional outer-layer etch-resist patterning and removal.

For example, an inner-layer patterning process was reported by the German laser company (LPKF Laser and Electronic AG, Osteriede 7, D-30827, Garbsen), they have called the process laser direct patterning and have used it for patterning and removing an organic resist deposited on copper inner layers. The laser is used for both the patterning and the stripping of the resists and thus avoids the use of any development chemistry in these two stages (i.e. the conventional development and strip stages become dry processes, thus using no chemicals and generating no waste). LPKF claims to be able to achieve a 2- μm resolution and 20 μm lines and spaces (i.e. the process is more than capable of producing all of the likely boards currently in production and likely to be produced in the immediate future).

Their laser equipment, which uses a moving mask and a translation table, is currently configured to be able to handle up to 18 x 24 inch panels, and average processing times per side are about 90 seconds. The special laser-abatable resist has been developed by Atotech (Berlin) and is currently applied by dip coating, although other means of application are equally feasible. The resist is typically 1- μm thick and thus the resolution capability should be high and the cost low. If the laser could also be used to ablate the underlying copper, which may be possible for thin copper films, they would have the basis of an all-dry etch-resist process.

This new method may, with further development, be capable of providing the basis of an all-dry outer-layer etch-resist process, which is chemistry-free and thus which generates no liquid effluent. However, there would still be a considerable amount of waste generated by the ablation, process and suitable precautions would have to be taken from health and safety and emissions perspectives. Large quantities of organic materials would be volatilised, as would the copper. From a sustainability perspective, no liquid waste would be developed, but the possibilities for recovering and reusing the copper would probably be limited, expensive and difficult. Nevertheless, this route is, at least in theory at the moment, a potentially interesting alternative to conventional solution-based etch-resist technologies based on electrodeposited tin or tin-lead.

4. REPORT FINDINGS: CONCLUSIONS, REFERENCES & USEFUL WEB ADDRESSES

4.1 Conclusion

The PCB industry uses large volumes of tin-plating and acidic stripping chemistries during the process of defining the copper conductor patterns on the surface of its circuit boards. The process generates considerable quantities of waste solutions that are ultimately consigned to landfill without any attempt being made to recover and reuse the valuable materials they contain. This is an expensive waste of raw materials, and the process does not fit within the increasingly desirable sustainable approach that the industry is starting to adopt in the face of increasing legislation and regulation. This scoping study has defined current practices within the UK PCB industry and compared them with what is happening in the rest of Europe and the USA. It is clear that, in all regions, there is a need to develop a more sustainable approach to tin-stripping chemistry waste-treatment. Potentially useable technologies are available, and various techniques have been identified and assessed in possible combinations that could lead to the development of truly sustainable chemistry and recovery technologies for the tin-stripping process.

It is theoretically and technically possible to produce a combination of chemistry and equipment that could lead to the development of a truly sustainable treatment process in which the tin oxide generated during stripping is recovered for secondary uses while the spent acid is concentrated sufficiently for it to be recycled into the make-up of new stripping chemistry. The only new chemistry needed would be in the form of small quantities of additives needed to optimise the performance of the new stripping solution. Thus, it would be possible to operate a process that generates little or no waste whilst significantly reducing the volumes of new chemistry that have to be manufactured, transported and used. Realistically, and for the foreseeable future, it is likely that the adoption of such an approach is unlikely since the technology would need to be developed further for application on an industrial scale. Also, the technology is likely to be relatively expensive compared with traditional techniques until the cost of land filling and the requirements of the increasingly stringent legislation combine to force PCB producers to adopt the technology out of economic and regulatory necessity. In the meantime, there is plenty of scope for the techniques detailed above to be developed and evaluated in tin-stripping applications, and it is recommended that a further more practical programme be initiated as a result of this study to take the technology further towards the ultimate goal of a truly sustainable tin-stripping process.

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Diffusion Dialysis – Useful Web Sites

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<http://www.appliedmembranes.com>
<http://www.osmonics.com>
<http://www.chemindustry.com/popular/N/nanofiltration>
<http://www.watertreatment-ez.com>
<http://www.apv.com/Technologies/filtration/nano.htm>
<http://www.urila.tripod.com>
<http://www.pfonline.com/articles/089907.html>
<http://www.pfonline.com/articles/079704.html>
<http://www.clearh2o.biz/ultra-filters>
<http://es.epa.gov/>
<http://www.lanl.gov/orgs/ibdnew/usrfac/userfac45.html>
http://www.etseq.urv.es/DEQ/Doctorat/index/running/2002_2004/courses_w/memb_sep/Memb07.pdf
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<http://www.epa.gov>
<http://www.turi.org/publications>
<http://www.pcbfab.com>
<http://www.summit-valley.com>
<http://www.finishing.com>
<http://www.apec-vc.or.jp>
<http://www.p2pays.org>
<http://www.deq.state.mi.us/documents>
<http://www.eq.state.ut.us>
<http://cleanerproduction.curtin.edu.au/industry/metals/>

Alternative Process Steps used in Recovering Tin Stripping Solutions (Section 3.1.4)

Tin Oxide Removal from Spent Stripping Solutions – *Web Sites*

<http://www.mtasales.com/CentrifugalFiltration/CentrifugalFiltration.html>
<http://www.powersourcing.com/se/hydrocyclonecoolantfiltrationsystems.html>
<http://www.processregister.com/Centrifugal%20Separators/Suppliers/pid4579>
<http://www.natcogroup.com/>
<http://www.gekkos.com/home.html>
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4.3 Figure & Table Caption(s)

Tables

- Table 1. *Ion Membrane design and Industrial Application*
- Table 2. *Various methods used to remove tin oxide from tin stripping solutions*

Figures

- Figure 1. *Application and removal of tin etch resists.*
- Figure 2. *Schematic Illustration of an Ion membrane separating a two Compartment Diffusion Dialysis Cell*
- Figure 3. *Flow Diagram of a Diffusion Dialysis Process*
- Figure 4. *Basic Principle of Ultrafiltration (under normal flow conditions)*
- Figure 5. *Illustration of the cross flow system mechanism used in separation of particulate matter from process streams*
- Figure 6. *A Schematic illustration of the Cross-section of an Electrowinning cell*
- Figure 7. *A Schematic illustration of the electrochemical reductions occurring at the cathode (negative electrode) and anode (positive electrode) of a typical electrowinning cell*
- Figure 8. *Tin Strip separation (recovery) as a function of drop out with time*
- Figures 9 (a)-(b) *Flow chart(s) illustrating the waste treatment of acidic tin stripping solutions*

5 COMPANY PROFILES

Intellect/PCIF

The PCIF is part of the Components & Manufacturing Services team of Intellect, the Information Technology Telecommunications & Electronics Industries in the UK. Intellect incorporates members of Computer Software and Services Association (CSSA) and Federation of the Electronics Industries (FEI), and represents over 1000 organisations. The PCIF team represents the UK PCB and EMS industries, from designers and suppliers to PCB fabricators and contract assemblers. In addition individual members are welcome through the Institute of Circuit Technology (ICT) and the Electronic Design Realisation Group (EDRG). Its work covers many areas directly relevant and beneficial to the PCB industry and it is committed to improving the environment in which its members do business, promoting their interests and providing them with high-value services. The continued success of the industry relies upon it remaining aware of the challenges ahead and maintaining a sound knowledge of the market. To this end, Intellect's provision of market information is a key service within the industry and one of the most important functions of the association. In order to keep its members informed of events pertinent to the industry, the PCIF team also issues a monthly newsletter *Short Circuit*, the publication *Circuit Review* twice a year and provides daily updates through its powerful websites found at:

www.pcif.org.uk or www.intellectuk.org

The PCIF team also produces an on-line directory in which all corporate members are featured, and this has become the buyers' guide to the industry. It provides full company information, highlighting manufacturing capability and company specific technical information. It is distributed to the electronics industry throughout the world, thereby maximizing members' exposure to potential buyers. The PCIF team and Intellect also hold regular conferences and workshops that address a wide range of pertinent topics, from current technical developments to recent training initiatives. Regular senior executive forums are also popular, as is the annual conference, which continues to be the year's showcase event. For further details of all these services, contact Claire Yarrow on Telephone: 0207 331 2050

Rohm and Haas Electronic Materials Europe Limited

Rohm and Haas (formerly known as Shipley Europe Limited) is committed to the development of products and processes that stress quality and concern for its members, customers and the environment. Rohm and Haas recognises that as a worldwide supplier of chemistry systems, it shares a major responsibility with its customers for the environmental health and welfare of our planet. It demonstrates this responsibility through its commitment to Responsible Care and its environmental management system. Rohm and Haas is proud to announce that it obtained certification to the ISO 14001 standard at its Marlborough facility, Massachusetts, USA, in 1998, at its Sasakami facility, Japan, in 1999, at its Warrington facility, England, in 2000 and at its Coventry facility, England, in 2001. By responsibly managing its environmental aspects, Shipley it able to move toward sustainable development, reduce its operating costs, and increase its competitiveness. All at Rohm and Haas have a personal interest in and responsibility to protect our environment for the enjoyment of our children and our grandchildren. Rohm and Haas looks to its employees, distributors and customers to work in an environmentally responsible manner. This will enable Rohm and Haas to achieve the following goals:

- *Continual, measurable progress in pollution prevention*
- *Efficient resource utilisation*
- *Production of the highest-quality products without adversely impacting the environment*

There are also many things that we, as individuals, can do to be environmentally conscious and enhance our natural surroundings. Reducing our consumption of natural resources, decreasing pollution and using energy wisely are just a few small measures that collectively can make a difference. For further information giving you a better understanding of Rohm and Haas progress in living up to its environmental commitment, please contact us for a copy of our current *Annual Environmental Report*.

Rohm & Haas Electronic Materials Europe Limited:
Herald Way, Coventry, CV3 2RQ. Tel (024) 7665 4557

For further details of Rohm & Haas's environmental activities, please contact:

Dr Martin Goosey: e-mail: mgoosey@rohmmaas.com

Tin Technology Limited

Tin Technology is the world's foremost authority on tin with access to 70 years experience and knowledge through its association with ITRI Ltd (formerly the International Tin Research Institute). Tin Technology comprises four divisions related to current issues on the uses of tin and its applications: Coatings, Technology Information and Forecasting, Materials, and Chemistry.

As part of Tin Technology's commitment to be innovative in serving the tin community two major groups are run at Tin Technology: Firstly, the Tinplate Group is a membership-based organisation that aims to help the tinplate industry maintain and develop its market share through technical support and collaboration. It is a global organisation drawing its membership from Europe, North and South America and Asia-Pacific.

All members of the Tinplate Group are invited to attend three Group meetings, held at Tin Technology, during the year, in which current issues affecting the whole industry are discussed. Results from recent and relevant Tinplate R&D projects carried out at Tin Technology are also reviewed at these meetings. In order to focus on topical issues facing the industry, collaborative Working Groups (membership to these Groups are open to the Tinplate Group) have also been formed.

The Coatings Technology Division has been responsible for the commercial development of several electroplating systems for producing environmentally acceptable corrosion resistant and decorative finishes. The automotive and aerospace industries have benefited from the electrolytic deposition of tin and its alloys to modify the surface properties of components to improve corrosion resistance, hardness or lustre. Other recent projects include the commercial development of new, improved tin-nickel and tin-zinc electrolytes.

Secondly, the Soldertec Global Group, which has gained "world-wide" acclaim for its work on issues relating to the development of lead-free solders. Soldertec has helped numerous industrial sectors change from operations containing lead processes to lead free alternatives.

Tin Technology has well equipped modern laboratories that are capable of short-term investigative work, or long term project work. With a wealth of experience in project management and troubleshooting investigations, the Coating technology Division

offers leading laboratory facilities and services to support technical programmes and specific training for all general metal finishing requirements, as well as those involving Tin and its alloys.

Tin Technology Limited: Unit 3 Curo Park, Frogmore, St. Albans AL2 2DD.
For further details of Tin Technology's environmental & coating activities, contact:
Dr Charles Kerr: Tel (0870) 458 4604 or e-mail: charles.kerr@tintechnology.com

APPENDIX A-D

- A Tin Stripping Case Studies on a Selection of UK Printed Circuit Board Manufactures**

- B Questionnaire - Regeneration of Spent Etch Stripping Solutions**

- C Details of the EIPC Winter Conference Feb 12-13th 2004**

- D A copy of the Article Titled: "Sustainable Technologies for the Regeneration of Acidic Tin Stripping Solutions used in PCB Fabrication", submitted to Circuit World for publication early in 2004 and to be presented at the EIPC Winter Conference - see also (iii)**

6. APPENDIX A

Tin-Stripping Case Studies of a selection of UK PCB manufacturers

In order to obtain additional information on current tin-etch resist stripping practices, issues and requirements, visits were made to several UK PCB manufacturers. Altogether five companies were visited and these were selected to give a representative cross section of UK PCB manufacturing capability ranging from the very small to the largest in the country. From these visits it was possible to gain a better understanding of the key factors that were important to these companies and in particular to determine what would be the key drivers and limitations for moving towards the implementation of a more sustainable approach to the tin etch-resist stripping process.

A.1 Case Study 1

This company is based in the north of the UK and is one of the largest producers of PCBs. The company is a major supplier of circuit boards to the automotive industry and produces both double-sided and multilayer boards. The etch-resist metal used was pure tin, the company having moved away from the use of a tin-lead alloy some years ago. The horizontal stripping line accommodated a two-stage tin stripping process based on a nitric acid containing formulation. The process was operated continuously using a feed-and-bleed arrangement with the component and metal levels being monitored and maintained on an automatic basis. Waste from the process was pumped outside the factory into 1,000 litre intermediate bulk containers (IBCs), which were used to store the highly acidic liquid prior to removal. The company was typically filling between one and two IBCs per week.

The tin-stripping process was designed to operate at approximately room temperature (i.e. 25°C) but, because of the volume of work processed and the exothermic nature of the tin dissolution reaction, the etchant temperature was reported as often reaching 35°C. Whilst this did not cause major problems with the etching process, it was leading to an increased attack on the subsequently exposed underlying copper. This in turn was causing an undesirable increase in the levels of copper in the effluent produced by the process. Consideration was being given to the introduction of a chiller unit to enable better temperature control and lower temperatures to be maintained.

Being a large producer of PCBs this company was producing approximately 75, 000 litres of spent stripping solution per annum and the cost of disposal was given as 9 pence per litre with an additional shipping cost of 2.5 pence per litre. Thus the annual disposal costs for spent stripper were approximately £8, 625. Disposal took place via the services of a local agent but the final destination of the spent strippers was to a company called Park, in South Wales. It is worth noting that, although this PCB maker was spending £8, 625 per annum on disposal, it was spending much more on etch-resist plating and stripping solutions. The figures given were ~£15, 000 for plating solutions and ~£100, 000 on stripping solutions.

There would thus be a good level of interest in the implementation of a more sustainable tin-stripping process that could lower overall costs through a reduction in effluent generated, the ability to recover tin and copper and the ability to reuse the stripping solution's nitric acid and other components. As with many UK-based PCB companies, the company is exposed to an intense competitive pressure that is forcing the reduction of costs in all aspects of the business. Consequently, investment in capital equipment that has a long payback period, however environmentally beneficial, would be highly unlikely in the current difficult climate. This company stated that it would be unwilling to implement such a recycling technology unless the overall process costs savings would cover the initial equipment outlay in less than a year.

From the figures above, it is clear that the overall costs of the tin etch-resist plating and stripping process (and subsequent disposal), are in the region of £123, 625. Assuming that the plating costs of the etch-resist would remain the same, the annual cost for the stripping and disposal would be just under £110, 000. Consequently, there is a significant amount of money that could be used to fund a piece of equipment if concomitant annual savings could be made through reduced waste-treatment costs and reduced chemistry costs via recycling. Basically, although the cost of a suitable piece of equipment for recycling the acid is not yet accurately known, it does seem reasonable to suggest that for a larger company such as this one the switch to a more sustainable approach may not be out of the question.

A.2 Case Study 2

The second site visit was undertaken at a medium-sized PCB manufacturing plant based in the West Midlands. The company specialises in fine-line and small-hole drilling, supplying technically advanced, time-critical PCBs in pro-type and production quantities to a wide range of industry sectors including the automotive, consumer electronics and telecommunications sectors. The company does not have an externally audited environmental management system (EMS) but indicated a willingness to implement an EMS in the near future largely as a result of pressure from customers based in Europe.

The company currently uses a nitric-acid-based tin stripping solution, spending approximately £1, 500 per year on stripping chemicals and spending a further £1, 000 year on etch-resist plating solutions. This type of nitric-acid-based chemistry was preferred to methane-sulphonic-acid (MSA) containing solutions because of speed, reliability and consistency in stripping properties. Several years ago the company made the switch from the use of tin-lead-based etch-resists to purely tin-based chemistry. The decision to use a more environmentally benign resist was prompted by concerns over the widely publicised health implications of using lead-containing products and not as result of pressure from customers.

At the time of the visit the company was not treating its tin-strip wastes on-site. Waste effluent from the tin-strip process was being sent off-site for treatment and disposal through a registered, local, waste-treatment company, although the interviewee did not know the exact destination or the methods used to treat the waste. The volume of waste tin stripper produced by the company was quite low, approximately 1, 000 litres per annum. The precise cost for treating and disposing of the spent stripper solution in this manner was not known because the different types of effluent waste-streams

produced by the various chemical processes had not been calculated on an individual basis. However, the cost of off-site treatment for the waste tin-strip solutions was estimated to be in the region of £500 to £1, 000 per year. The company had adopted a proactive approach to reducing and treating other waste effluents generated during the PCB manufacturing process. A Chemlec cell was being used to recover metals from micro-etches, and an effluent treatment plant had been installed some years ago. Metal-bearing filter cake produced by the waste-treatment plant was being landfilled at a cost of approximately £2, 000 per year.

The company expressed an interest in implementing a regenerative technology for treating spent tin-stripping solutions if funding was available to help offset capital expenditure and training costs. It was believed that implementing an EMS would also act as a driver for introducing sustainable technologies and for further reducing waste because of the commitment to minimise waste and to reduce environmental impacts. The company also expressed a strong interest in any available technologies for recovering precious metals and reducing water consumption, although any “kit” would have to achieve a payback period of between 2-3 years.

A.3 Case Study 3

The third PCB manufacturing facility visited during the course of the tin-strip project was a small company based in the West Midlands. The company expressed a mild interest in introducing technology to regenerate spent tin-stripping solution. This interest was driven largely by a desire to reduce disposal costs and to meet legal compliance. In common with other the other sites visited, the payback period for introducing equipment capable of regenerating spent tin-stripping solution would have to be very quick, within a one-year to two-year period. The company also believed that any initiative to implement sustainable technologies would require some form of financial support either from government agencies or from the chemical suppliers.

The company did not have an effluent treatment plant; therefore all the waste effluent generated on-site was disposed of by using a registered, waste treatment firm. The chemical supplier to the PCB manufacturer acted as a third-party waste broker, arranging the collection, transport and treatment of the spent chemistries. The cost of this collection and disposal service was added as a surcharge to the purchase price and was typically charged at 30 pence per litre for the spent stripping effluent. The tin-stripper effluent was stored on-site in 200-litre drums until a sufficient quantity was available for collection. The interviewee had not calculated the cost of storage, however the company generates about 800 litres of tin-stripper effluent per annum. The interviewee did not know where the waste was being treated before being landfilled.

The company used a nitric-acid-based stripping solution. The decision to use this type of chemistry was not based on preferred performance characteristics but was founded on cost benefits and the disposal service arranged by the chemical supplier. The company had changed to a tin-based etch-resist after pressure from customers and was not aware of any alternatives to metal-based etch-resists.

A.4 Case Study 4

This company is classed as a small to medium-sized enterprise (SME) employing around 60 people and is situated in the southern region of the UK, just north of London. The company produces a range of circuit boards, including single-sided (rarely) and double-sided boards for, in the main part, the military sector both in the UK and in the USA. The etch-resist used is pure tin, which is removed using a nitric-acid-based proprietary solution via a horizontal tin-stripping line. The process was not operated on a continuous basis but only when required during two 8-hour shifts. Replenishment was carried out adopting a bleed-and-feed regime, with additions being added based on specific gravity determinations. Currently, this facility consumes approximately 800 litres (per six-week cycle) of tin-stripping solution, which is collected once used and then returned to the supplier for waste-treatment.

The stripping operation is designed to work at room temperature, however during operation the working temperature increases due to exothermic reactions occurring within the stripping solution. To control the working temperature and to prevent the stripping action over etching the copper substrate a water-cooling system is in operation.

Owing to the level of consumption of tin stripping solution it was expected that interest in using technology that would enable the process to become fully sustainable would be slight. However, as this company is currently undergoing ISO 14001 assessment any EMS are actively encouraged. Benefits the company would be looking for include the following: reduced water costs, ability to comply with current and future EU directives, reduced waste-transportation costs, reduced waste-treatment costs and a reduction in waste storage around the factory. The only concern or reservation would be the cost of implementing sustainable technology, therefore any new technology; would have to be adaptable (i.e. used in other areas of environmental control, such as for rejuvenating rinse-water or reclamation of other spent process solutions).

The company has not completely replaced all of its tin-lead operations; it is currently using tin-lead etch-resists for solder levelling operations, which are a customer requirement. However, the company was expecting to replace these operations with lead-free alternatives within the following 18 months, just prior to the 2006 deadline.

A.5 Case Study 5

The company cited in case study 6 is also a SME, employing only 24 people, with only two people understanding anything about the chemistry involved in double-sided and multi-layer PCB manufacturing. Therefore, the problems experienced and the needs and requirements at this facility are different from those already expressed in the previous four case studies. This company is also situated in the southern region of the UK and, again, lies just north of London. Its main customer base comes from the avionics and military sectors.

The etch-resist used at this facility is pure tin and is stripped off using a nitric-acid-based proprietary solution via a horizontal stripping line. The line has no cooling facility as only small batches of boards are stripped at any one time. A bleed-and-feed regime is in operation and is controlled by the specific gravity of the working solution.

The total amount of tin-stripping solution consumed within the year is less than 500 litres. The spent solution is again sent to the supplier twice a year at a cost of 25 pence per litre. Space at this facility is at a premium and therefore storage even of small amounts of waste can be problematic.

The amount of tin-stripping solution consumed in a year would not warrant the implementation of sustainable technology; however, the company is already involved in an environmentally funded project looking at ways to minimise waste production as it is considering applying for ISO 14000 registration some time in the future. ISO 14000 registration is also viewed as a marketing strategy; the company envisages substantial growth within the avionics and automotive sectors, especially in Scandinavia, where its customers are insisting on this type of management control. The company's location within an industrial estate also warrants the need to investigate closed-loop or zero-effluent options, as at present it has to have all waste transported off-site. So although the technology described in this report is for application with tin-stripping solutions it is clear that the sustainable approach can be adapted elsewhere for the benefit of the environment and profit margins alike.

Another problem facing this particular facility is the ability to implement such technology even if it were made available. Only two employees have the basic understanding of the processes involved and therefore would be extremely stretched in their day-to-day duties to implement any new technology.

Owing to customer requirements the company still manufacture's hot-air-levelled boards which use tin/lead etch resists. Unlike the companies cited in some of the previous case studies, they have a deadline in mind to replace this process; their actual comments were "we are waiting to see what methods the industry adopts". This is not an unusual remark, as many UK (and probably European) companies have not become totally lead-free, although electroless nickel/immersion gold alternatives are being investigated. Apart from custom pressure to keep on using tin-lead finishes, there are serious issues with converting to pure tin (e.g. relating to the operating temperatures of alternatives, whiskers and the use of certain additives).

7. APPENDIX B

B.1 QUESTIONNAIRE - On the Regeneration of Spent Etch-Stripping Solutions

Tin Technology Ltd, together with the Information Technology Telecommunications & Electronics Association (INTELLECT) and Shipley Europe Ltd have been awarded a contract by the Department of Trade and Industry under their Sustainable Technologies Initiative (STI) to assess current practice in waste recovery technology applicable to the PCB industry.

In particular, there is a move away from tin-lead etch-resists to lead-free tin-based alternatives. Large volumes of acidic waste containing useful quantities of both tin and copper generated through stripping processes are recyclable.

This confidential survey aims to assess current practice in metal and solution recovery in the PCB processing sector with the aim of identifying best practice but also with the aim of identifying and potentially developing new and more cost-effective recycling technologies.

Regeneration of Waste Tin-Stripping Solution

1. What benefits, if any, would be of interest to your company in using this type of technology to regenerate waste tin-stripping solutions and, thereby, reducing waste?
2. Would you consider implementing a regenerative technology if grant funding was available to offset training and setting-up costs?
3. Are you aware of the STI initiative or any other development programmes (schemes) for minimising waste from tin-stripping solutions and reducing the social/environmental impact of this?

Environmental Policy

4. Does your company operate an environmental management system such as ISO 14001?
5. Is your company taking action on other environmental issues e.g. reducing the level of toxic metals being consigned to landfill sites?

Current Waste Tin Stripping Solution Practices

6. Approximately how many litres of waste tin-stripping solution does your company dispose of every year?
7. Do you currently have waste tin-stripping solutions taken off-site for treatment?
8. If the answer to question 7 was yes, approximately how much do you spend each year on this disposal?
9. If the answer to question 7 was yes, approximately how much do you spend per litre on the disposal of spent stripping solutions?

10. How much does your company spend on etch-resist plating solutions and tin-stripping solutions, including related consumables each year?
11. What type of tin-stripping chemistry do you use?
12. Is there an advantage in using this type of chemistry?

Lead-Free Etch Resist Solutions

13. Does your company use tin-based or tin-lead-based etch-resists as part of the PCB manufacturing process?
14. If you use tin-lead-based resists do you plan to convert to tin-based resist?
15. Is there, or has there been, pressure from your customers to move away from the use of lead in etch-resists?
16. Are you aware of any alternatives to metal-based etch-resists?

The USA Questionnaire

The questionnaire put to the American PCB manufactures was slightly different from the one given in the UK and Europe (similar questions were asked but in a different order).

- (1) Does your company operate an environmental management system such as ISO 14001?
Yes/No
- (2) Approximately how many gallons of waste tin stripping solution does your company dispose of per year? **US Gallons**
- (3) Is waste stripping solution treated **on-site** or **off-site**?
- (4) If off-site, approximately how much does it cost per gallon or per year?
- (5) Approximately how much does your company spend buying tin strip solutions per year?
- (6) Approximately how much does your company spend on etch- resist plating solutions per year?
- (7) What type of tin-stripping chemistry is being used? **Nitric, MSA or Other**
- (8) What is the main advantage in using this type of chemistry?
- (9) Does your company use **tin** or **tin-lead** etch-resist?
- (10) If tin-lead is being used is there a plan to convert to tin? **Yes/No**
- (11) If the answer was Yes, to question 10, how soon?
- (12) Have your customers ever asked your company to switch away (or use specific alternatives) from the use of tin-lead etch-resists? **Yes/No**
- (13) Are you aware of any alternatives to metal-based etch-resists? **Yes/No**
- (14) If YES, do you think the alternatives will be widely adopted over the next few years? **Yes/No**

- (15) Are you aware of any development programmes for reducing the waste from tin-strip solutions and reducing the environmental impact? **Yes/No**
- (16) If there was regenerative technology developed to reuse tin-stripping solutions on-site, is this something your company would have interest in? **Yes/No**

B.2 Survey Response to the above Questionnaire:

(The company responses from the UK, Europe and the US are given in Tables B.2 to B.4)

B.3 Summary

B.3.1 United Kingdom

On initial inspection of the completed forms, the response to the questions of the *regeneration of waste tin-stripping solution* were similar for all UK-based companies, whether they were small, medium or large PCB facilities. This definition is based on the levels of tin or etch-resist stripping solution consumed annually, as illustrated in **Table B.1**. All the PCB manufacturers taking part in this questionnaire are required to comply with environmental legislation and reduce waste management costs while still remaining competitive. Without exception, all the companies approached would implement some form of process solution regeneration technology if funding was available or there was some way of reducing the costs of this technology. The first question to produce a mixed response (60:40) was the awareness of the sustainable technology initiative (STI) or other available grants dealing with sustaining production processes or waste minimisation.

The next section in the questionnaire addressed the issue of *Environmental Policy*. The majority of companies in the PCB sector are aiming for ISO 14001-validation over the next few years, and this is reflected in the response to **question 4**, where 5 out of the 7 companies replied that this was directly in response to customer pressure.

Question 5 deals with taking action arising from environmental pressures companies failing to take any action regarding the reduction of their tin-stripping waste have agreements with their chemical supplier to remove this waste off-site. Treatment of waste on site was carried out predominantly by large consumers (with only one notable exception) of tin-stripping chemicals and, in the main, was done so through existing regimes (e.g. presumably neutralisation and ultimately landfill).

The consumption of tin-stripping solution and subsequent waste-treatment (current waste tin-stripping solution practices) obviously varies according to the level of usage and to the size of the facility, as described in **Table B.1**.

Predominantly the small producers of PCBs have their tin-stripping waste taken off-site; the only small UK-company that did not, treated its own waste via its internal treatment plant, used only 1,000 litres per annum. The total amount of money spent on off site waste treatment varied from £500-1,000 for SMEs; however, this figure can rise to as much as several thousand for the large consumer of tin-stripping solution. These prices were also reflected in the disposal costs per litre.

SIZE OF PCB FACILITY	DEFINITION (<i>Tin-strip consumption in litres per annum</i>)
SMALL	< 10, 000
MEDIUM	10, 000 to 39, 000
LARGE	> 40, 000

Table B.1. Definition of PCB facilities used in this report

Questions 10-12, were aimed at attaining information on the type of chemistry used in the plating and removal of etch-resists. Obviously, the size of operation dictated the levels of chemistry used; however, the most interesting information arising from these questions was that all companies, without exception, favoured nitric-acid-based tin-stripping solutions for their ease of use and the fact they did not over-etch the board substrate after the removal of the etch-resist.

The last part of the questionnaire covers the issues of lead free etch resist solutions, which is a very topical subject facing the PCB industry at present. Specifically, this section addresses the following issues: what solutions are going to be employed as replacements to tin-lead etch-resists and how are they going to be removed once lead-free legislation is enforced in 2006?

Some of the smaller companies questioned still use tin-lead resists, having not converted to tin-only as the lead-free option. The main reasons for not converting to a lead-free replacement, sooner rather than later, are that customers (e.g. the military) still require a tin-lead finish, and the uncertainty and costs associated with change, (i.e. costs of choosing the incorrect alternative). Therefore, the smaller facilitates are waiting to see if an industrial acceptable standard comes to the fore prior to any etch-resist solution changes. However, from the replies to **question 14**, the overall consensus indicates that this choice has been made and tin-only etch-resists will be the alternative choice, with conversion being complete within the next 18 months. **Question 15** asked whether there was any pressure from customers to convert to a lead-free etch-resist; again 5 out of the 7 UK companies stated YES, with those replying NO suggesting they would expect consumer pressure in the future in the guise of dealing with companies who possess accreditation, to the ISO 1400 series.

Finally, companies were asked if they would adopt or employ new technology to regenerate their tin-stripping solutions; overwhelmingly, their response was NO. However, when prompted, some companies yielded that this may become highly probable in the future as ISO 14000 series requirements widen and new environmental legislation comes into force (e.g. closed-loop (zero-effluent) operation. Others said they would review this technology if funding were available, either in the form of grants or incentive packages offered by their chemical supplier. The bottom line in implementation of technology of this kind is to keep the company competitive and not reduce profit margins even further.

Overall, there seemed to be no obvious differences in the needs and demands of a small enterprise compared with those of a larger consumer of etch-resist chemicals,

with the exception of throughput and the ability to offset the costs of regenerating process solutions, in other words, implementation of expensive new technology (i.e. the acceptable payback period, which is considered to be 1-2 years after installation). With large usage comes the opportunity to make large savings, which could be expected by regenerating tin-stripping solutions (e.g. chemical savings and waste-treatment savings). This is not the case for smaller consumers, who may need to take a partial regeneration approach so as not to ignore the advantages of this technology because of it being prohibitively expensive.

The questionnaire as previously described was also sent out to European and USA PCB manufacturing companies, as the problems with respect to etch-resist plating and stripping in the UK are not unique, but apply equally to PCB facilities world-wide. The situation in Europe is discussed in the next section.

B.3.2 Europe

The European response to the questions on the regeneration of waste in tin stripping solutions mirrored those of their British counterparts - with compliance to environmental legislation, reduction in process costs and ISO 14000 series (ratification being the main driving force for adopting this type of technology).

The European companies responding to the questionnaire were either large consumers of tin-stripping solutions or small facilities; this factor was reflected in the total amount spent on etch-resist chemistry and the level of waste treatment required (as seen in responses to questions on current waste tin stripping solution practices).

Some 2 out of the 3 largest consumers of tin-stripping solution (responding to this survey) had their waste transported and/or treated by their chemical supplier as part of an overall package that included supply of the tin-stripping chemicals. Only the small users and one of the larger consumers dealt with stripping chemistry waste in-house (presumably via a neutralisation step) and on-site. Insufficient data were received to confirm whether consumption was in any way related to off-site treatment.

As with PCB manufactures in the UK, nitric-acid-based formulations were the tin-stripping chemistry of choice, and for the same reasons (i.e. ease of use, fast etch rates and minimal over-etch).

Cost of plating and stripping etch-resists in Europe was difficult to gauge, as this question was not answered as most companies dealt with chemical supply houses and did not want to disclose what their individual agreements were. However, from the one response from a large consumer the costs it disclosed were comparable to charges facing British companies for the same plating chemicals.

From the responses to the question on lead-free etch solutions, European PCB companies seemed already to have complied with the forthcoming lead-free legislation. None of the companies taking part in this questionnaire used tin-lead-based etch-resists as they had already converted to tin-only chemistry; this conversion was not directly customer driven (**question 15**), but was more to do with ISO 14000 series validation. The response to **question 16** once again showed that no new alternatives to, or possible replacements of electrodeposited etch-resists were known and certainly none that were comparable in price.

B.3.3 USA

The questionnaire sent to USA companies differed slightly from the one sent to the European and British facilities: not in the questions asked but in the order they were shown.

The majority of the companies questioned had no immediate plans to apply for ISO 14000 series registration (**question 1**), which clearly differed from the European response when addressing this issue. Of the four companies returning a completed questionnaire only 1 was not a large consumer of tin-stripping solution (i.e. > 40 000 litres per annum). This again was reflected in whether the waste was removed off-site for treatment or not; only the small (< 14 000 litres per annum) consumer thought it was cost-effective to treat waste in this manner. The remaining companies treated their waste tin-stripping solutions on-site; this clearly differed from the response from European PCB manufactures, as most large consumers of tin-stripping solutions had agreements with their chemical supplier to remove the waste off-site as an overall package, including the purchase of the chemicals used in etch-resist chemistry.

Question 4, was answered only by the small consumer of tin-stripping solutions, which spent approximately \$0.64 a litre to treat its waste (including any off-site transportation costs).

The large companies, however, were a little more forthcoming when disclosing their total costs per year for tin-stripping chemistry (**question 5**), which was in the order of \$60 000-\$80 000. This amount was between \$15 000-\$20 000 for the smaller facility. The amounts the PCB manufactures spent in total on their etch-resist chemistry (i.e. tin or tin-lead etch-resist + acid tin-stripping solution), was not disclosed. **Question 9** raised the issue of what type of etch-resist was applied; surprisingly only one company had converted to a lead-free bath, the other facilities operating either tin-lead or a mixture of tin-lead and tin-only baths. This factor may be attributed that lead-free legislation is not pressurising PCB companies to use lead alternatives in markets within the USA; however, this may not be the case in the future, especially if companies are thinking about exporting their goods to Europe or Japan. If and when this comes into being, tin-only baths would be the alternative choice for the companies returning this questionnaire.

The tin-stripping solutions are without exception nitric-acid-based (**question 7**) with the reasons for this choice mirroring those responses given by the European PCB manufactures. The reasons cited in response to this questionnaire were as follows: the ease of use, the cheaper cost compared with MSA-based chemistry, reduced over-etching and that they had never used anything else. Like the European and British responses to (question 15), their awareness of an alternative to metal etch-resists was unanimous i.e. none (they were aware of, or they did not know of any commercially available options that would be on the market anytime in the foreseeable future).

From discussions with personnel working in the PCB sector within the USA any findings borne out of this report would be interesting; however, from a practical standpoint, the report would be relevant only if substantial process savings (**question 16**) could be made implementing sustainable technology; with the levels of cost associated with etch-resist removal, this could be a distinct possibility.

Question	COMPANY						
	1	2	3	4	5	6	7
Q 1	Environmental Compliance	Environmental Compliance, Costs	Environmental Compliance, Costs	Environmental Compliance, Costs	Environmental Compliance, Costs	Environmental Compliance, Costs	Environmental Compliance, Costs
Q 2	YES	YES	YES	YES	YES	YES	YES
Q 3	YES	NO	NO	YES	YES	YES/NO	YES
Q 4	YES	YES	YES	NO <i>In the Future</i>	NO	YES, ISO 14000	YES
Q 5	NO	YES, PPT & Smelted	NO	YES, <i>Involved in Environ Project</i>	YES, Waste taken away for incineration only	YES, If part of ISO 14000	YES
Q 6	>2000 I	>2000 I	>2000 I	<500 I	1000-1500 I	>7000 I	>50 000 I
Q 7	YES	NO	YES	YES	YES	Return to Supplier	YES
Q 8	£500-£1000	-	>£750	£500	£500	£1000-£2000	£9000
Q 9	£0.36	-	-	£0.25	£0.20	£0.13	£0.10
Q 10	£2.3K & -	£5K & £3.5K	~£3K & ~£2.5K	~£1K & ~£1K	£3K & £1.75K	£10K & £15K	£80 000
Q 11	NITRIC	NITRIC	NITRIC	NITRIC	NITRIC	NITRIC	NITRIC
Q 12	YES, Ease	YES, Lower cost than MSA	YES, Ease & cost	YES, Only one ever used	NO	YES, Only one ever used	YES, Ease & cost
Q 13	TIN	TIN	TIN & Tin/Lead (Sn/Pb MOD work)	TIN	TIN/LEAD	TIN & Tin/Lead (Sn/Pb MOD work)	TIN
Q 14	-	-	YES	-	<1 yr	1 yr – 18 months	-
Q 15	NO	YES	YES	YES, Scandinavia	YES, Customers	NO	NO
Q 16	NO	YES	NO	NO	NO	NO	NO

TABLE B.2. Responses from UK companies

NB Partially returned forms were not included in this survey

Question	COMPANY				
	1	2	3	4	5
Q 1	Environmental Compliance, Costs	Reduction in Costs	Regeneration done by ENTHONE	Environmental Compliance, Costs	Environmental Compliance, Costs
Q 2	YES	YES	YES	YES	-
Q 3	YES	NO	NO	NO	NO
Q 4	NO	YES	YES	YES, ISO14000 reg.	-
Q 5	YES, <i>Lead Free</i>	YES	YES, <i>Lead Free</i>	YES	NO
Q 6	>6000 l	>2000 l	>50,000 l	>55,000 l Tin-strip >33,000 l Jig-strip	>10,000 l Tin-strip
Q 7	NO	NO	YES	YES	YES, after treatment
Q 8	-	-	£ zero - Taken away	>£8K & >£9K	£ zero - Taken away
Q 9	-	-	Inc. in Price	Tin Strip £0.15 Jig Strip £0.28	-
Q 10	6K EU & 5K EU	-	No comment!	65K EU & 40K EU	-
Q 11	NITRIC	NITRIC	NITRIC	NITRIC	NITRIC
Q 12	YES, <i>Cheap</i>	YES, <i>It works</i>	<i>Removal of intermetallic</i>	<i>Etch rate, no copper attack, ease to rinse, metal content</i>	<i>Etch rate, & ease to rinse</i>
Q 13	TIN	TIN	TIN	TIN	TIN
Q 14	-	-	-	-	-
Q 15	NO	YES	NO	NO	NO
Q 16	YES, <i>in 5-10 yrs</i>	NO	NO	NO	NO

TABLE B.3. Responses from European companies

NB Partially returned forms were not included in this survey

QUESTION	COMPANY					
	1	2	3	4	5	6
-						
1	None	In less than 1 yr	None	None	None	None
2	>50,000 l	>50,000 l	40,000 l	45,000 l	>50,000 l	14,000 l
3	On-site	On-site	On-site	On-site	On-site	Off-site
4	No response	No response	No response	No response	No response	\$9,000
5	\$60,000	\$60,000	\$50,000	\$55,000	\$60,000	\$20,000
6	-	Panel plate	-	-	-	-
7	Nitric	Nitric	Nitric	Nitric	Nitric	Nitric
8	Safer & easier	Treatable	Treatable, * ENIG	Treatable	Treatable	Treatable
9	Both	Tin-Lead	Both	Tin	Tin	Tin-Lead
10	No- IR Reflow	Yes	No-Reflow	No response	No response	No-Reflow
11	No response	1 year	No response	No response	No response	No response
12	No	No	No	Yes	No	No
13	No	Yes, panel plate	No	No	No	No
14	No response	No response	No response	No response	No response	No response
15	No	No	No	No	No	No
16	Yes, if costs were reduced	Yes, if costs were reduced	Yes, if costs were reduced	Yes, if costs were reduced	Yes, if costs were reduced	Maybe

TABLE B.4. Responses from USA companies

NB * ENIG = Electroless Nickel Immersion Gold

NB Partially returned forms were not included in this survey

8. Appendix C

Programme for the EIPC Winter Conference

- Adapting to the changing PCB World-
Simultaneous translation in French language will be provided!

Location: Radisson SAS Montfleury

Place: Cannes, France

FEBRUARY 12 & 13th 2004

C. 1.0 Programme

The European Institute of Printed Circuits (EIPC) extends an invitation to all those companies and individuals who are active in the packaging and interconnection industry to participate in the EIPC Winter Conference in Cannes, France.

The purpose of the EIPC Winter Conference is to provide a platform for speakers and delegates to exchange information on the current market conditions, future innovation on interconnection and packaging as well as assembly of electronic and opto-electronic circuits. Delegates from throughout Europe will attend this event, offering presenters the opportunity to reach a targeted audience of decision makers and leaders of the international packaging and interconnection industry.

This conference is an absolute 'must' for companies associated with PCB fabrication who wish to stay up to date with the latest market requirements, materials, fabrication equipment and manufacturing processes who also need to improve the efficiency of their processes and the reliability of their products. For more details contact the EIPC:

Ms. Sonja Derhaag (Event Manager)
Hertogsingel 49b, 6211 ND Maastricht
The Netherlands
Tel: 0031-43-3440872
Fax: 0031-43-3440873

E-mail: sderhaag@eipc.org

C.1.1 Calendar of Events and Sessions – Day 1

Session 1: Management overview

13:15 “Key Note speech: PWB Market trends”
Walter Custer President, Custer Consulting

13:45 “Changing the business model to compete with Asian suppliers...a necessity for survival in the Western world”
Eric McLean, Dupont International S.A.

14:15 “Trends in Build-Up Board Technology”
Tarja Rapala, Development Director, Aspocomp OY

14:45 “Innovation of products and processes with science and technology”
Gunther Leising, Senior Vice president Technology, AT&S

Session 2: Adv. HDI PWBs Design, Insp. & Plugging

15:30 “Advanced Microvia PCB design”
Flemming Boisen, Senior PCB Designer, Texas Instruments Denmark A/S

16:00 “Optical inspection of microvia holes”
Richard Frisk, President, Lloyd Doyle

16:30 “Periodic Pulse Reverse Acid Copper Plating Technology.”
Mark Lefebvre, Research Manager, Shipley Company LLC

17:00 “Production processes in horizontal and vertical technology for blind micro via filling.”
Steven Kenny, Atotech Germany GmbH

Session 3: Progress in PWB Imaging Technology

08:30 “Which imaging technology for which product?”
Frédéric Baradel, Sales and Marketing Director, Automa-tech

09:00 “Inc Jet Technologies in the PCB Industry”
Hans Fritz, SAT Electronics GmbH

09:30 “High resolution inkjet printing for HDI PCB manufacture.”
Stephen Jones, Invotec/ Fujifilm

10:00 “In the face of the greatest slump the pwb industry has ever experienced, LDI imaging continues to expand....Why?”
Russ Crockett, Sales Manager, Dupont International S.A.

C. 1.2 Calendar of Events and Sessions - Day 2

Session 4: Developments in PWB laminates

10:45 *"High frequency pcb base materials-A comparison of thermomechanical properties"*

Sylvia Ehrler, Project Office, Multek

11:15 *"New base material for high frequency application"*

Manfred Cygon, Isola AG

11:45 *"Performance of polymeric ultra thin substrates for use as embedded capacitors: comparison of unfilled and filled systems with ferroelectric particles"*

John Andresakis, VP of Strategic Technology, OAK Mitsui Technologies LLC

12:15 *"A novel Method for sequentially-building Multilayer Circuits using LCP laminates, cap layers and bond plys."*

Steven Heytens, Marketing Manager& Cliff Roseen, Technical Service Engineer, Rogers Corporation

Session 5: Pb free challenges and PWB surface finish

14:00 *"Getting the lead out"*

Ed Greenwood President, Alchemetal Corporation

14:30 *"Sustainable technologies for the regeneration/recovery of spent acid tin stripping solution."*

Charles Kerr, Manager Coatings Technology Division, Tin Technology

15:00 *"Effect of electroless Nickel deposit composition on electroless nickel gold (ENIG) process performance"*

Martin Bayes, Research Fellow, Shipley

16:00 *"Immersion Tin a proven final finish for printed circuit boards"*

Peter Meeh, MacDermid GmbH

16:30 *"How does lead free soldering influence the recommended immersion Tin thickness?"*

Sven Lamprecht, Global Product manager, Atotech Deutschland

17:00 *"Electroless Nickel Gold substitution by Sn finish for military applications: a good solution?"*

Bernadette Guillaume, Thales group

C.1.3 Presentation Summary

The paper was generally well received, by an attentive audience, as the subject matter has far-reaching and wide-ranging effects on the PCB industry as a whole. Below are quotes kindly given by delegates who were in the audience. Finally an extract from the Conference summary (to be published in *Circuit World*) is provided, highlighting the importance of this topic to PCB manufactures worldwide. **Presented 13th Feb 2004.**

“The paper fitted very well in the trend towards lead-free. It was an excellent presentation that showed the PCB industry the direction and option how to treat acidic tin-stripping solutions in PCB fabrication. The information presented in this paper is a MUST KNOW for engineers responsible for the environmental issues in a PCB factory”.

Michael Weinhold *EIPC*

“Charlie Kerr from Tin Technology in the UK gave the delegates at the EIPC winter conference in Cannes (13th Feb '04) clear evidence that a good number of dedicated people are currently working towards a truly sustainable tin-stripping process”.

John Ling *Circuit World*

“The EIPC winter conference is one of the Europe’s best meetings for the exchange of technical information within the PCB community. DR Kerr’s paper was presented to an audience of over 100 industry experts and it was extremely well received. The need to adopt a more sustainable approach to the use of tin based etch-resists and the potential re-use of the materials that are currently consigned to landfill is a very difficult. Dr Kerr’s presentation illustrated some very interesting routes to achieving this aim and was thus of great interest to the conference attendees”.

Martin Goosey *Circuit World*

“Charlie Kerr hails from Tin Technology in the UK and told us about a project carried out as part of the Sustainable Technology Initiative funded by the DTI. The TINSTRIP project, as it known, showed that the UK PCB industry produces significant volumes of waste tin in stripping solutions. This waste tin is consigned to landfill, however, landfill is not desirable and there is a need for sustainable chemistry and recovery technologies. The landfill directive in the UK (originating from Brussels) means that the number of landfill sites in the UK will reduce from 218 to 34, and at present there is insufficient waste treatment capacity and a dearth of wastetreatment companies in the UK. Moreover, the landfill tax, currently £15 per tonne, will rise to £35 per tonne from next year. Against that cheerful background Charlie Kerr went into a look at all potential recycling technologies that are available, including acid reclamation, tin oxide removal, and membrane filtration. Much work is needed before any system becomes commercially available, and when it does it is likely to be expensive. Happily a good number of dedicated people are currently working towards a truly sustainable tin-stripping process.”

Summary *EIPC winter conference Circuit World*

9. APPENDIX D

Sustainable Technologies for the Regeneration of Acidic Tin-Stripping Solutions used in PCB Fabrication

A project carried out as part of the Sustainable Technology Initiative funded by the UK DTI

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ABSTRACT

Electroplated tin deposits are used as etch resists during the processing of printed circuit boards (PCB). The tin coating protects the copper tracks during etching but is subsequently removed (stripped) to expose the defined copper circuitry. The commonly used stripping solutions are based on nitric acid and after use they represent a very acidic waste product with a high metal content. The disposal of these spent strippers is typically via off site neutralisation and precipitation followed by subsequent landfill. This is clearly a non-sustainable waste of valuable resources and a practice that is increasingly undesirable as environmental legislation becomes more stringent.

This paper outlines the results of a scoping study carried out into current industry practices for tin stripping and details components of a potential integrated treatment system for these stripping solutions. Individual technologies for such an integrated system incorporate the recovery of the tin oxide by filtration, the concentration and re-use of nitric acid solutions by diffusion dialysis and the reclamation of other metals (i.e. copper by electrowinning).

Key words: Etch Resists, Tin, Ion Exchange Membranes, Diffusion Dialysis, ultrafiltration (UF), microfiltration (MF), Filtration, Cross-flow, HSA Electrowinning

INTRODUCTION

The need to adopt more environmentally responsible manufacturing processes in response to both public opinion and existing and forthcoming legislation is forcing industry to make many changes in the way it makes products and offers services. This is evident throughout the electronics industry and especially, for example, in the PCB manufacturing sector.

This change in thinking is highlighted by the need to adopt a more sustainable approach to the tin-stripping process. Making this process fully sustainable would help to alleviate the ever-increasing burden on landfill sites as ultimately the waste-treated stripping solutions are transferred to these facilities. The levels of toxic materials legally transferred in this manner will become substantially lower (and eventually zero), as more stringent environmental legislation comes into force.

The cost of waste treatment, transport of waste or treated waste and replacement of valuable chemistry and so on, is also a major concern. New technologies are required that will address these concerns and issues yet that also do not compromise the competitiveness of the PCB manufacturing industry. Consequently, any proposed new technology must be carefully considered in terms of overall costs. For example, the cost of implementing and running the new technology must not put an excessive burden on a company. For the PCB industry to install and operate any regeneration system of this type, whatever the driving force, it must be cost effective, (i.e. pay its own way) within 1-2 years (i.e. capital and running costs must be repaid in terms of savings).

Although there are many types of tin etch-resist stripping solutions available, the two most common processes are based on nitric acid and methane sulphonic acid (MSA) formulations. The choice of which is used is typically determined by a combination of economic and technical factors. A typical acid stripping formulation also includes a component to promote dissolution of the tin-copper intermetallic layer and an inhibitor species to reduce any acid attack on the underlying copper substrate once the tin resist has been removed. When the level of tin has reached approximately 150 g dm^{-3} and the copper concentration is in the region of 40 g dm^{-3} (i.e. total metal content is ~ 180 to 200 g dm^{-3}) the dissolution or stripping rate falls and the bath has become exhausted. At this point the highly acidic waste needs to be treated and the bath is either neutralised on-site prior to transportation or removed for off-site waste treatment. Either way, the resulting waste is ultimately destined for landfill. This not only wastes natural resources (e.g., tin oxide and copper metal), which could otherwise be recycled, but also means it is necessary to replace the stripping chemistry. Thus, it can be seen that the tin etch-resist plating and stripping process is both inefficient from a materials utilisation perspective and a waste of valuable resources. There is clearly considerable scope for the development of a sustainable technology to address this wasteful part of the PCB manufacturing process. This paper reviews some of the techniques that could be used either individually or in combination to take the process towards a truly sustainable approach whereby the waste materials generated are recovered and re-used. The paper also reviews some of the legislation that is likely to be a key factor in forcing the adoption of more sustainable approaches and reviews the responses from a survey carried out to assess the PCB industry's opinions about tin-stripping practices.

ENVIRONMENTAL LEGISLATION

The main driver for the move to more sustainable technology within the UK PCB manufacturing industry is the rising cost associated with ensuring compliance with environmental legislation. Within the PCB industry this cost is typically $\sim 6\%$ to 8% of

total manufacturing costs, a figure which compares unfavourably with the 2% figure for UK manufacturing as a whole. The main European legislative drivers stem from the fifth and sixth environmental action Plans, which introduced principles such as ‘polluter pays’, and ‘producer responsibility’ as well as the need to consider sustainability in all legislation. These policies and measures have given rise to an extensive system of increasingly stringent environmental controls, which has forced industry to address how it operates so as to ensure its business activities have the least negative impact on the environment.

More recently the EU has identified four priority areas where special effort and impetus is required, one of these priority areas is the increasing amount of waste being generated in Europe. In order to tackle this problem the EU has introduced a number of directives aimed at increasing recycling and recovery rates, for example, the Landfill and Waste Electrical and Electronic Equipment (WEEE) Directives and legislation aimed at restricting the use of hazardous materials via the implementation of the Restriction of Hazardous Substances (RoHS) Directive. Other regulatory frameworks such as the integrated pollution prevention and control (IPPC) Directive will require waste and energy efficiency to be dealt with through a single permitting system, and use of best available techniques (BAT) and integrated product policy (IPP) will require products to be designed to be resource efficient.

In the UK, concern over the ability to continue to put vast quantities of waste into the ground has forced the government to introduce economic measures with the objective of making it less attractive for waste producers to landfill useful materials and more desirable to recycle and re-use what they are currently discarding as waste.

It is important, therefore, that any programme to assist the PCB industry is representative of the emerging policies and economic instruments that will have an influence on the introduction of sustainable technologies. It is also equally important to focus on the opportunities that will be afforded to companies who seize the incentive and take advantage of the cost savings and improved environmental performance associated with these technologies.

Integrated pollution prevention and control (IPPC)

In 1996 the EU enacted the Integrated Pollution Prevention and Control (IPPC) Directive. The directive was transposed into UK law through the Pollution Prevention and Control (England and Wales) Regulations 2000 and the Pollution Prevention and Control (Scotland) Regulations 2000. The PCB industry is affected by the regulations, as it is specifically cited in section 2.3 of schedule 1 of the regulations – the surface treatment of metals and plastic materials. The overall aim of the Directive is to achieve a high level of protection of the environment as a whole, and it has been designed to prevent, reduce and ultimately eliminate pollution at source via the efficient use of resources and sustainable waste-management practices. In practical terms this means that affected companies must compare and evaluate techniques that prevent and reduce emissions and identify the best ones for offering the lowest impact on the environment. It is therefore clear that the IPPC

directive is a key driver for the implementation of sustainable technologies, such as those proposed herein, that could be used cost-effectively to treat wastes in situ ^[1].

The Landfill Directive

One of the most significant drivers for change in waste-management practices within the UK PCB industry will arise from changes introduced by the EU landfill directive. The directive came into force in July 1999 and aims to reduce the negative effects of land-filling by setting stringent operational and technical requirements for the disposal of waste to landfill. The Directive is implemented in England and Wales through the Landfill (England and Wales) Regulations 2001 made under the Pollution Prevention Control Act 1999.

A major impact of the directive will be a significant reduction in the number of landfill sites in the UK. By July 2004, when the co-disposal of hazardous and non-hazardous waste is proscribed, the number of landfill sites licensed to accept hazardous material will drop from 218 to as few as 34 ^[2]. The amount of hazardous waste in the UK is increasing at a rate of 8% per year and currently accounts for some 5.2 million tonnes, most of which is produced by the construction, chemicals and electronics industries. This situation will be further exacerbated by changes in the classification of waste, which will increase the scope of material that will soon be defined as hazardous.

The costs of sending hazardous waste, such as spent tin-stripping solutions, for off-site treatment and disposal will increase dramatically over the next couple of years. It may also become more difficult to identify waste-treatment companies that have the ability to handle, or are willing to accept, a waste effluent that is viewed as difficult to treat because of its extremely low pH value. This is a dilemma, which has already been experienced by some PCB manufacturers. Evidently, it will make increasing economic sense for companies to implement sustainable technologies to minimise the amount of hazardous waste they generate.

Environmental management systems

PCB manufacturers have reported an increase in requests from their customers to produce evidence of an accredited environmental management system (EMS) such as ISO 14001 or the Eco-Management and Audit Scheme (EMAS). An environmental management system enables a company to demonstrate environmental compliance and to establish objectives and targets to achieve good environmental performance via resource efficiency and the implementation of sustainable waste-management practices. Since the proper functioning of an environmental management system depends upon a cycle of continuous improvement, it acts as a driver to stimulate the development of more sustainable manufacturing and waste-treatment practices.

The landfill tax

A key argument for implementing sustainable technology is the associated cost savings through the minimisation of waste, reduced disposal costs and the more efficient use of resources. Historically, the cheapest available option for disposing of waste in terms of the waste hierarchy was to send it to landfill. It is therefore not surprising to learn that

final disposal accounts for the greatest proportion of the industrial waste stream. However, this situation is beginning to change as the incremental increases in the landfill tax start to take effect, making landfill economically undesirable and acting as a driver for businesses to minimise the amount of waste produced and to seek more sustainable waste-management options.

The landfill tax was introduced in 1996 and is an economic instrument for diverting significant quantities of waste away from landfill and towards more sustainable waste management options such as recycling and re-use^[3]. The tax is chargeable by weight, and there are two rates. A lower rate is charged to inert waste, and a standard rate is chargeable to all other wastes. At the time of writing the landfill tax is £2 per tonne for inactive waste and £14 per tonne for active waste. An escalator of £1 per tonne was introduced in 1999 for active waste, taking the level of the landfill tax to £15 per tonne by 2004. However, this escalator is set to increase to £3 per tonne from 2005 to 2006, and a level of £35 per tonne has been set as a long-term goal. The announcement of planned increases in the landfill tax provides an opportunity for businesses to seek more sustainable alternatives to landfill via the implementation of technologies that can significantly reduce the quantity of waste produced.

INDUSTRY SURVEY: *The PCB Industry's use of tin-based etch resists and the potential for regeneration of spent stripping solutions*

As part of a project carried out by Tin Technology Ltd. (formerly ITRI International Tin Research Institute) and INTELLECT (the Information Technology Telecommunications & Electronics Association), a confidential survey was made to assess current practices in the use and disposal of tin-based etch-resists by PCB fabricators. The objective was to identify best practice and to determine the potential for developing new and more cost effective recycling technologies.

The responses received were similar for all UK-based respondents, whether they were small, medium or large facilities. All the PCB manufacturers that took part in this survey have the need to comply with environmental legislation and to reduce waste-management costs while remaining competitive. The companies approached would like to implement process solution regeneration technology, but only if funding were available or if there were some way of reducing the costs of this technology. It was also found that the majority of companies in the UK PCB sector were aiming for ISO 14001 validation over the next few years, and the majority of companies replied that this was directly in response to customer pressure.

Treatment of waste on-site was carried out predominantly by large consumers of tin-stripping chemicals and, in the main, was done so through existing regimes (e.g. neutralisation and ultimately landfill). The consumption of tin-stripping solution and the subsequent wastetreatment methodology varied with the level of usage and the size of the facility.

Predominantly, the small producers of PCBs had their tin-stripping waste taken off-site for treatment. The amount of money spent on off-site waste treatment varied from £500 to £1000 per annum for small and medium-sized enterprises (SME's), with the figure rising to as much as several thousand for the larger consumers of tin-stripping solutions. These costs were also influenced by variations in the disposal costs per litre of solution. All companies questioned favoured nitric-acid-based tin stripping solutions for their ease of use and the fact they did not overetch the underlying copper after the removal of the etch-resist.

Some smaller companies still used tin-lead-based resists, having not yet converted to tin-only resists. The main reason for not converting to a lead-free replacement was that certain customers (e.g. the military) still require a tin-lead finish and the uncertainty and costs associated with change. However, the overall consensus was that this choice has already been made' and tin-only etch-resists will be the alternative choice, with conversion being complete within the next 18 months. There was also pressure from customers to convert to lead-free etch-resists and the suggestion that there would be more consumer pressure in the future.

Finally, companies were asked if they would adopt or employ new technology to regenerate their tin-stripping solutions and overwhelmingly their response was negative. However, when prompted, some companies yielded that this may become highly probable in the future as ISO 14001 requirements widen and the new environmental legislation as detailed above comes into force. Others said they would review this technology if funding were available, either in the form of grants or incentive packages offered by their chemical suppliers. The bottom-line requirement for implementation of this type of technology is to keep the company competitive and not reduce profit margins any further.

Overall, there were no obvious differences in the needs and demands of the smaller enterprises and the larger consumers of etch-resist chemicals, with the exception of through-put and the ability to absorb the costs of regeneration technology (i.e., the acceptable payback period, which is considered to be 1-2 years after installation). With large usage comes the opportunity to make significant savings, which could be expected from regeneration of tin-stripping solutions (e.g. chemical savings and waste-treatment savings). This is not the case for smaller consumers, who may need to take a partial regeneration approach so as not to ignore the advantages of this technology because of it being prohibitively expensive.

Although mainly UK-focused, the survey was also extended to selected European and USA PCB manufacturing companies, as the problems with respect to etch resist plating and stripping in the UK are not unique but apply equally to PCB facilities worldwide.

The European responses to the survey mirrored those from the UK - with compliance to environmental legislation, reduction in process costs and ISO 14001 being the reasons given for why they would adopt this type of sustainable technology. The main driving

force for adopting an environmental policy was once again found to be the requirements for ISO 14001 registration and the lead-free legislation coming into being in 2006.

As with PCB manufacturers in the UK, nitric-acid-based formulations were the tin-stripping chemistry of choice and, for the same reasons (i.e. ease of use, fast etch rates and minimal overetch). The disposal costs were comparable to charges facing British companies for the same plating chemicals. None of the companies surveyed used tin-lead-based etch resists as they had already converted to tin-only chemistry. This conversion was not directly customer-driven but more to do with ISO 14001 validation. No new alternatives to, or possible replacements for, electrodeposited etch-resists were identified.

The same survey was also carried out with a small number of PCB manufacturers in the USA as it was felt that the problems facing British and European board fabricators were similar to those facing their USA counterparts. The majority of the USA based companies questioned had no immediate plans to apply for ISO 14001, certification, which clearly differed from those in Europe. Of the companies questioned, only one was not a large consumer of tin-stripping solution (i.e. > 40 000 litres per annum). Company size again influenced whether or not the waste was removed off-site for treatment, only a small consumer (< 14 000 litres per annum) stated that it was cost-effective to treat waste in this manner. The remaining companies treated their waste tin-stripping solutions on-site and this clearly differed from European PCB manufacturers, as most of these large consumers of tin stripping solutions had agreements with their chemical suppliers to remove the waste off-site as part of an overall package including the purchase of the chemicals used in etch-resist chemistry.

The small US company, questioned paid \$0.64 a litre to treat its waste (including any off-site transportation costs). The large companies were spending in the order of \$60 000-\$80 000 per year for tin stripping chemistry. The amount was between one third and one quarter of this figure for the smaller facility. The amounts the PCB manufacturers spent in total on their etch resist chemistry (i.e. tin or tin-lead etch-resist plus acid tin stripping solution) was not disclosed. Surprisingly, only one company had converted to a lead-free bath; the other facilities operated either tin-lead or a mixture of tin-lead and tin-only baths. This may be attributed to the fact that lead-free legislation is not yet pressurising PCB companies to use lead-free alternatives in markets within the US. However, this may not be the case in the future, especially if companies are exporting their goods to Europe or Japan.

The tin-stripping solutions used in the USA were, without exception, nitric-acid-based with the reasons for this choice mirroring the responses given by the European PCB manufacturers i.e. ease of use, cost compared with MSA-based chemistry, reduced overetching and established history of use.

POTENTIAL RECYCLING TECHNOLOGIES

From articles cited in the literature, those posted on various internet websites and discussions with key personnel working in the field of PCB manufacture it is clear that the industry, through its own recycling initiatives and in response to environmental legislation, sees regeneration as a key element of its approach to complying with legislation and indeed remaining competitive. In this section potential recovery and recycling methodologies are introduced and the possibility of producing a fully sustainable (regeneration) process utilising a combination of new equipment and chemistry is discussed. The potential process elements presented reflect the results obtained during various discussions with key personnel within the PCB industry.

The principle aim of this paper is to outline a variety of alternatives to the conventional waste-management methods for the treatment of tin-stripping solutions and to provide a brief overview of the most common practices that could provide a practical approach to a sustainable waste treatment process. Information on current practices and opinions was obtained from a range of PCB manufacturers, not only in the UK but also from North America and mainland Europe, and this was complimented by an extensive survey of the published literature.

Once a tin-stripping solution needs to be discarded, there are a number of alternative technologies that could enable it to be regenerated, thereby addressing environmental concerns, avoiding the costs associated with waste treatment and saving money on replacement of expensive stripping chemistry. The simplest approach to achieving a fully sustainable tin-stripping process involves using ion exchange membrane technology, which in combination with other techniques could enable the chemistry to be completely regenerated. This type of process can be envisaged as comprising three separate and distinct operations:

1. Acid reclamation.
2. Metal recovery (electrowinning).
3. Filtration.

However, the cost of implementing this type of technology could be prohibitive and, if economics are an overriding factor (e.g. if there is insufficient tin-stripping chemistry to enable capital costs to be recovered in a reasonable time frame, say, 1 to 2 years), a fully sustainable operation may be not practical. The three-step process outlined above has the advantage, however, of being able to be split-up into three distinct operations and therefore offers a partially sustainable option. For example, to reduce the levels of waste and, therefore, the cost of the stripping process, a diffusion dialysis unit may be used, allowing the acid component to be reclaimed, with the remaining waste having to be treated or transported off-site.

(1) **Acid Recovery** – *Diffusion Dialysis* ^[4-5]

This is a process that requires a divided cell with only two compartments: one containing water, and another containing the waste acid tin-stripping solution, the compartments are separated by an ion exchange membrane (see **Figure 2 in the main part of this report**). The essential difference between this process and electro dialysis units is that no potential is applied during the diffusion process. The basic principle of diffusion operates via a concentration gradient between the two compartments, with the overall efficiency of the process being directly dependent on the surface area of the ion exchange membrane. The membrane allows transport of the acid and water molecules but prevents the larger metal ions crossing. In industrial units the two cell compartments are stacked to enable large quantities of solution to be treated. The treatment of the spent acid solution can be performed in either batch mode or via a bleed-and-feed operation. One of the major attractions of this type of process is that the only energy requirement is that required to drive the circulatory pump.

(2) **Tin Oxide Removal** – *Filtration* ^[6-7]

Once the tin has been stripped from the circuit boards it enters the stripping solution in the form of an insoluble fine suspension that is not readily reduced to its metallic form without major solution modification (e.g. acidification with hydrofluoric or hydrochloric acid or neutralisation of the acid with sodium hydroxide to form a precipitate). Therefore, a more viable and practical alternative for removing the suspended tin oxide is required, and one possible solution could be filtration.

Briefly, membrane filtration (see **Figure 4, of the main part in this report**) is the separation of components of a pressurised fluid by a polymer or inorganic film (membrane). There are four commonly accepted classes of membrane filter currently being used for the waste treatment of industrial processes (e.g. rinse water, effluent and process reclamation). The class of filter is further defined by its pore size (i.e. the size of particles or material that is removed from the carrier liquid):

- (1) Reverse osmosis (RO) 0.5-1.0 nm.
- (2) Nanofiltration (NF) 1.0-10 nm.
- (3) Ultrafiltration (UF) 20-50 nm.
- (4) Microfiltration (MF) 1.0 μm .

The tin suspended within the waste tin-stripping solution exists in the form of a very fine oxide; the size of these particles range between 20 nm to 1 μm (these values have not been verified experimentally but are cited from industrial sources). It is clear from the range of pore sizes listed above that only UF and, possibly, MF would be suitable for the removal of the tin oxide.

Historically, the membranes used to construct the filters become easily blocked while filtering solutions containing the tin oxide particulates - the particles agglomerate at the pore sites as they attempt to pass through. To make use of this technique, modifications

to the filtering process would be required and this can be achieved by using an adaptation called *cross-flow filtration*. This technology prevents the build-up of particles at the pore site (see **Figure 5 in the main part of this report**). Other recent improvements to these filtering processes include back-flushing techniques that enable all of the filtered particulates to be removed by washing, thereby enabling the filter cartridges to be re-used and the filtrate to be recovered. In this case the tin oxide, which is currently being transported to wastetreatment or off-site disposal sites, once back flushed and reclaimed, becomes a valuable raw material for which there are many applications.

For the process to be fully sustainable, a third step is required to remove any copper dissolved in the stripper (a consequence of the acid tin stripper etching some of the underlying copper substrate. For this step the technology required is well established and is called electrolytic metal recovery or copper electrowinning. This is essentially metal deposition from a weak electrolyte.

(3) **Copper metal deposition:** *Electrolytic metal recovery (electrowinning)* ¹⁸⁻⁹¹

Electrowinning is an electrolytic technology process, which can be defined as the removal and recovery of unwanted metal ions, in this instance copper. Recovery is achieved by the electrochemical reduction of the copper in solution at a negative electrode (cathode). **This is schematically shown in Figure 6 in the main part of this report.** Electrowinning can be applied to a wide range of electrolytes used in the manufacture of PCBs (e.g. spent process solutions, rinse waters and effluent). It is therefore ideal for use in the reclamation of copper from spent tin-stripping solutions. The flexibility of this technique may well make it an attractive tool for complying with environmental legislation as the capital cost of this equipment can be spread over several different processes.

A particularly good example of an electrolytic recovery process that is versatile and can be used for various electrolytes is the high surface area (HSA) electrowinning process. HSA electrowinning was developed in the 1980s using a reticulated electrode design. This design enabled the cathode area to be dramatically increased so that low levels of contaminants (mg dm^{-3}) could be removed from dilute solutions as well as those with higher concentrations (g dm^{-3}). Maximising the metal deposition rate is an important feature in any plating process and electrowinning of waste solutions is no different. To maximise efficiency, even with very dilute electrolytes the operating parameters have to be monitored (such as the operational current densities and voltages, electrolyte mixing, cathode surface area and anode effects).

CONCLUSION

The PCB industry uses large volumes of tin-plating and acidic stripping chemistries in the process for defining copper conductor patterns on the surface of its circuit boards. The process generates considerable quantities of waste solutions, which are ultimately consigned to landfill without any attempt being made to recover and re-use the valuable materials they contain. This is an expensive waste of raw materials, and the process does not fit within the increasingly desirable sustainable approach that the industry is starting

to adopt in the face of increasing legislation and regulation. A scoping study has been used to define current practices within the UK PCB industry, and these have been compared with what is happening in the rest of Europe and the USA. It is clear that, in all regions, there is a need to develop a more sustainable approach to tin-stripping chemistry waste treatment. Potentially useable technologies are available, and various techniques have been identified and assessed for use in possible combinations that could lead to the development of truly sustainable chemistry and recovery technologies for the tin-stripping process.

It is theoretically and technically possible to produce a combination of chemistry and equipment that could lead to the development of a sustainable treatment process in which the tin oxide generated during stripping is recovered for secondary uses while the spent acid is concentrated sufficiently for it to be recycled into the make-up of new stripping chemistry (**See Figure 3 in the main part of this report; see also Figure 9**). The only new chemistry needed would be in the form of small quantities of additives to optimise the performance of the new stripping solution. Thus, it could be possible to operate a process that generated little or no waste whilst significantly reducing the volumes of new chemistry that had to be manufactured, transported and used. Realistically, and for the foreseeable future, it is likely that adoption of such an approach is unlikely since the technology would need to be developed further for application on an industrial scale. Also, the technology is likely to be relatively expensive compared with traditional techniques until the cost of landfill and the requirements of the increasingly stringent legislation combine to force PCB producers to adopt the technology out of economic and regulatory necessity. In the meantime there is plenty of scope for the techniques outlined above to be developed and evaluated in tin-stripping applications and it is recommended that a further more practical programme be initiated as a result of this study to take the technology further towards the ultimate goal of a truly sustainable tin-stripping process.

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Copies of the Scoping Study detailed in this paper are available on the ITRI and Intellect websites at <http://www.tintechnology.com> and <http://www.intellectuk.org>.

Methods ^(a)	Ion exchange membrane used ^(b)	Purposes ^(b)
Diffusion Dialysis	Cation, and anion ion exchange membranes	Recovery of various acids such as Nitric acid (HNO ₃) Meta Sulphonic acid (MSA)
Electrolytic Recovery (Electrowinning)	Cation and anion ion exchange membranes	Deposition and recovery of valuable metals onto electrodes
Filtration	Polymeric, cationic and anionic exchange membranes	Low pressure for separating suspended solids and high molecular weight species from waste streams

Table 1. Ion membrane design and industrial applications

(a) Methods: membrane technology has progressed remarkably and its applications have diversified in recent years. Membranes are used mainly for separation processes, which can be classified into three categories: electro-dialysis and electrolysis (applied current), ultrafiltration, and diffusion dialysis (through use of a difference in concentration).

(b) Ion exchange membranes and their uses: styrene-divinyl benzene has been commonly used for ion exchange membranes, but perfluorocarbon membranes have recently been developed. Membranes generally used for separation are hydrophilic films with a three-dimensional mesh structure. The films are impregnated with strong dissociative radicals such as sulphonic acid or a quaternary amino group as a fixed ion and in many cases they are reinforced with synthetic fibre such as poly vinyl (PVC) and poly propylene (PP) to confer mechanical strength and dimensional stability. Ion exchange membranes for general purpose are required to have the following attributes: Excellent permselectivity for ions, high mechanical strength, dimensional and chemical stability, small electric resistance, diffusion of salts and permeability of water and durability to both pressure and heat.

	Test	Result	% Separation	
			17 h	65 h
1	NaOH. 2.5 mls of 47% NaOH was added to 20 ml of Tin-strip (T.S.) solution.	A lot of heat was generated. The interface between the NaOH and Tin-strip solution turned brown. The solution was shaken vigorously in a test tube. No separation was noted. (Far greater volumes of NaOH would be required to use this technique.)	0	0
2	Ammonia. 2.5 mls of ammonia to 20 ml of T.S.	Similar results were seen as with NaOH.	0	0
3	Penguin. 2.5 ml of Penguin to 20 ml of T.S.	The solution became more viscous after around 20 minutes.	5	45
4	Bunny. 2.5 ml of bunny to 20 mls of T.S.	Bunny was not soluble in the tin strip solution and separated after 17 hours to float on top.	10	30
5	Nako. 2.5 ml of Nako to 20 ml of T.S.	The solution became a little more viscous.	3	45
6	Catboat. 2.5 ml of catboat to 20 ml of T.S.	Solution became very thick and viscous after 15-20 minutes.	10	15
7	3 marble chips added to 10 ml of T.S	The marble chips gave off CO ₂ and eventually (when the reaction died down) turned blue. (Cu out of the tin-strip solution?)	0	0
8	0.5 g of aluminium to 10 ml of T.S.	Nothing happened until the solution was heated up. The aluminium started dissolving giving off brown (NO ₂ ?) gas. The solution did not dissolve all the Al.	0	0
9	Centrifuge	10 mls of solution were run on a centrifuge machine for 15 minutes at 4500 rpm.	60	60
10	Air was bubbled through the soln. (17 hours).	This was left on overnight. The solution was quite viscous in the morning. (17 Hours)	0	0
11	Ultrasonic bath	No effect after 20 minutes treatment.	0	0

Table 2. Various methods used to remove tin oxide from tin stripping solutions

Figure 1 (a) 'Pattern Plated' PCB showing the plated Sn etch-resist

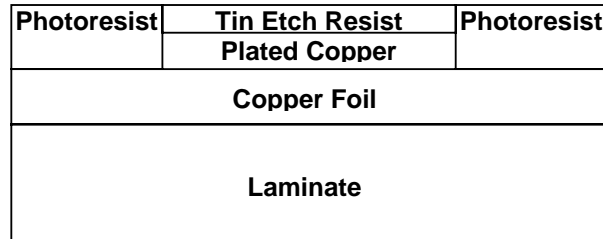


Figure 1(b) 'Pattern Plated' PCB - the Sn etch resist (photoresist removed) ready for Cu etching

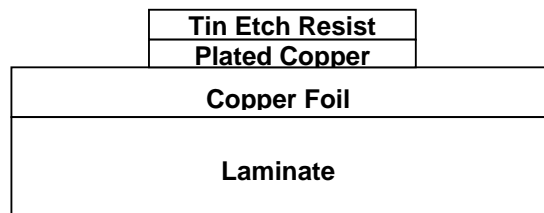


Figure 1 (c) 'Pattern Plated' PCB after Cu etching - the Sn etch resist & defined copper patterns

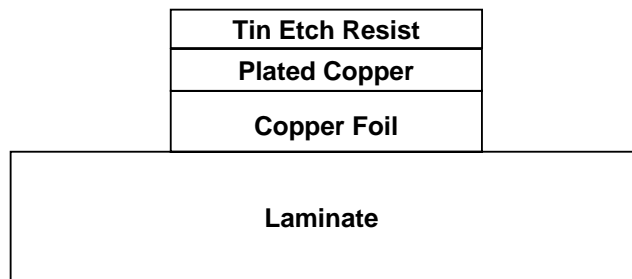
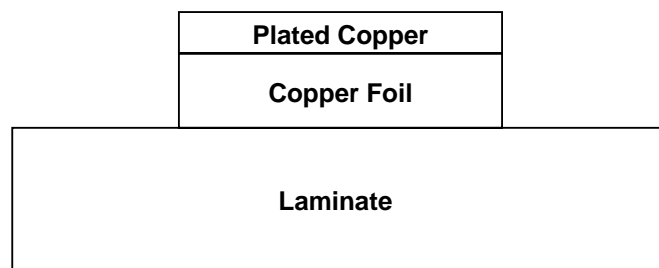


Figure 1 (d) The final 'Pattern Plated' PCB - after Sn etch resist stripped to leaving Cu tracks



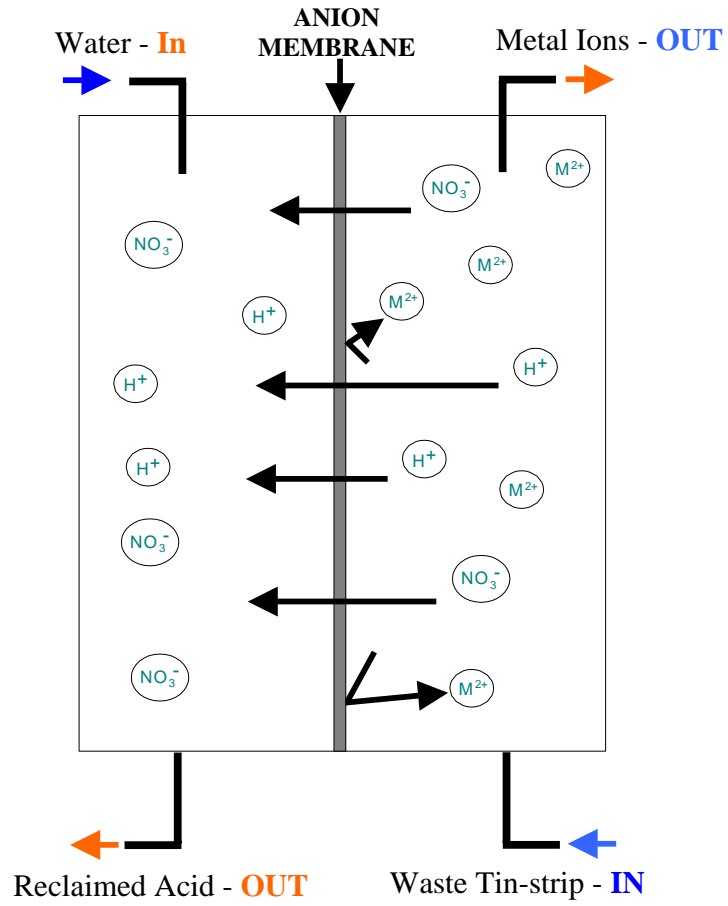


Figure 2. Schematic Illustration of an Ion membrane separating a two Compartment Diffusion Dialysis Cell

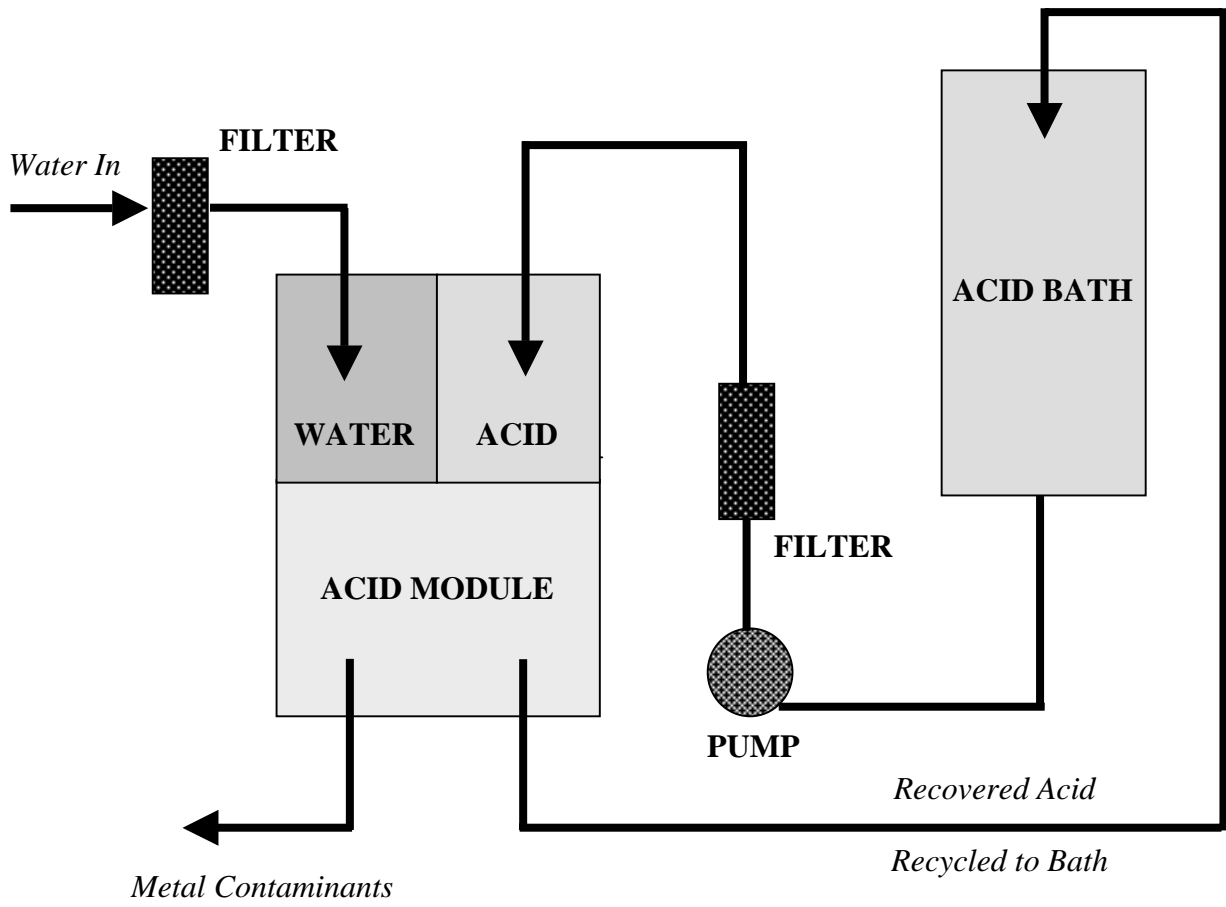


Figure 3. A Schematic Illustration of the Diffusion Dialysis Set-up

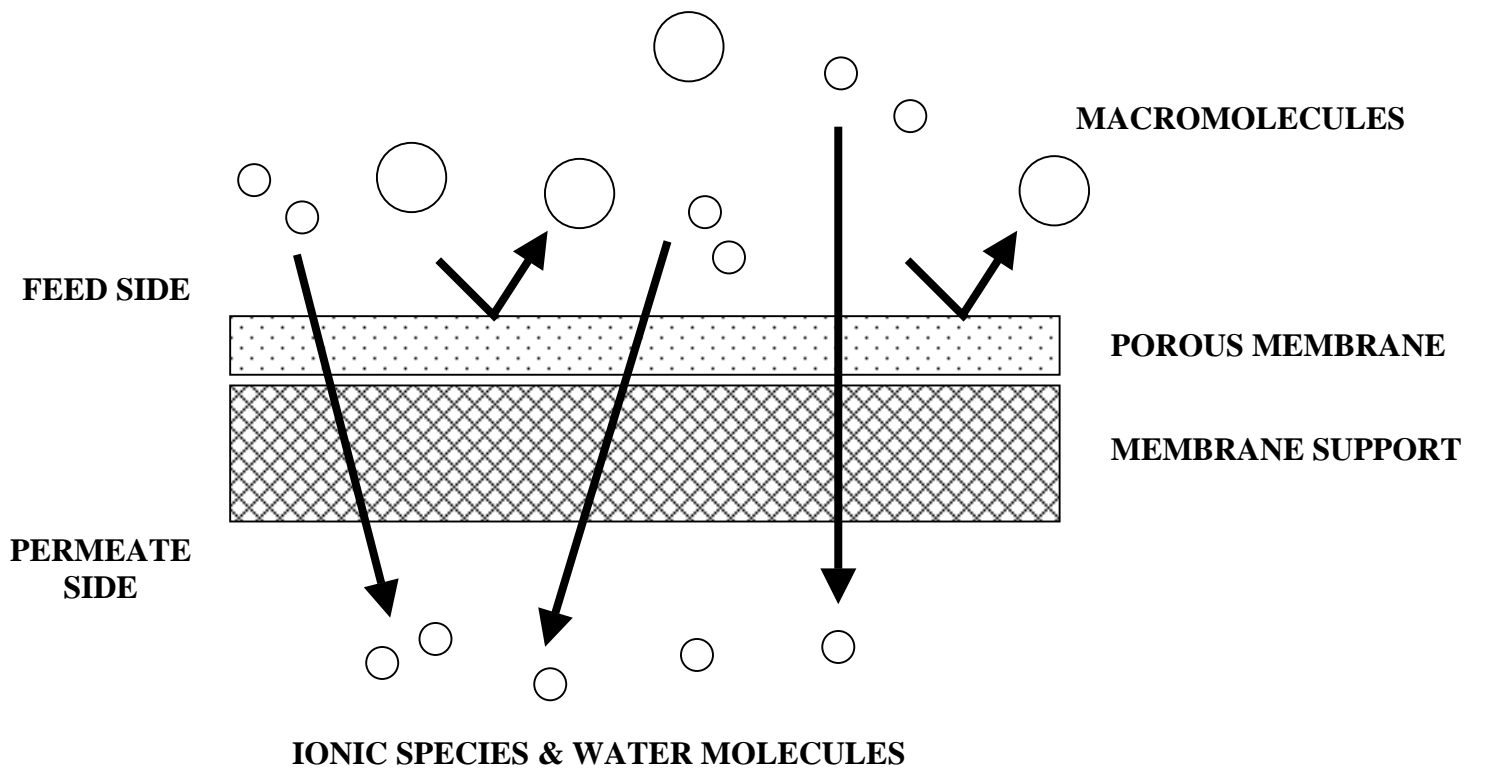


Figure 4. Basic Principle of Ultrafiltration (*under normal flow conditions*)

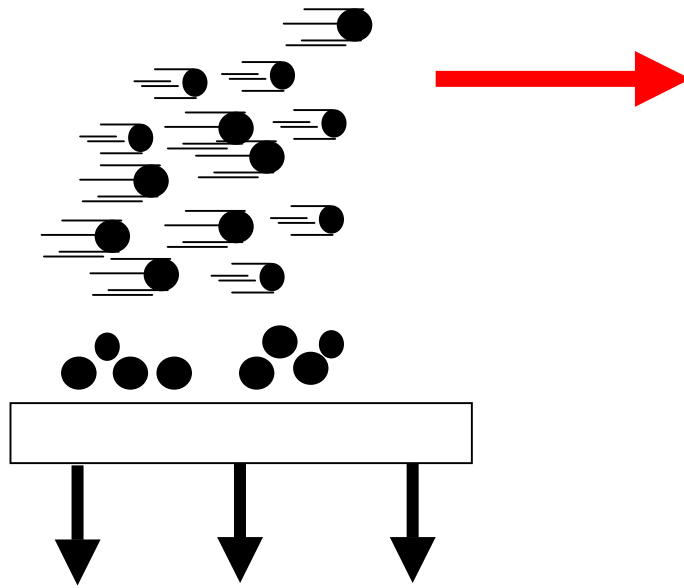


Figure 5 (a) High Cross Flow Rate (*high permeate passage*)

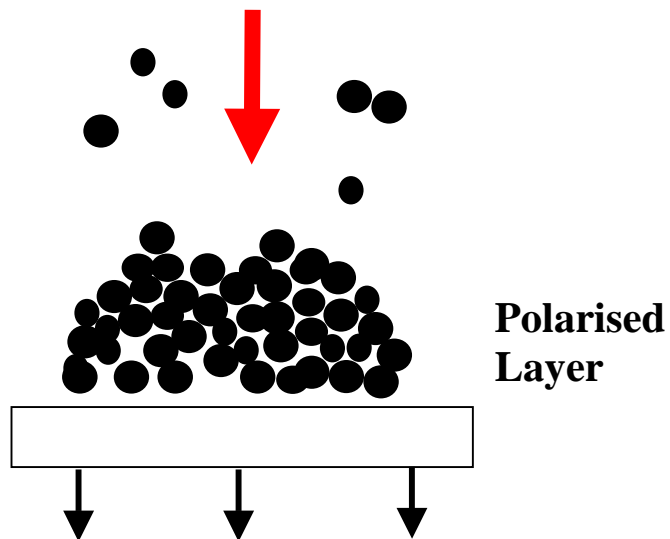


Figure 5 (b) No Cross Flow Rate (*low permeate passage*)

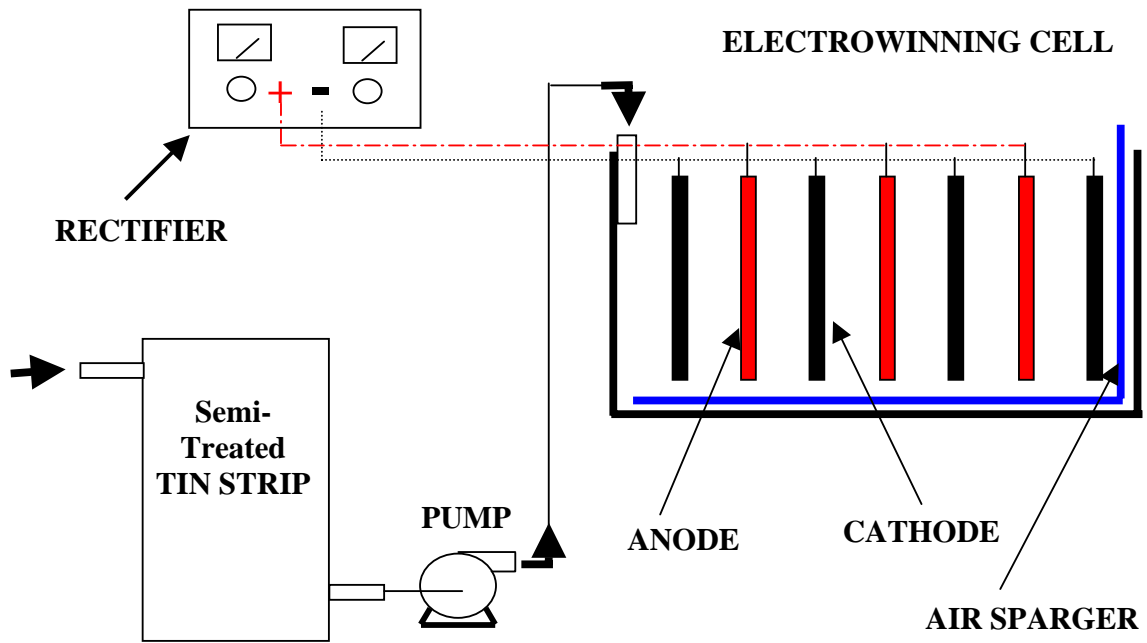


Figure 6. Schematic Illustration: Typical arrangement of an Electrowinning Cell

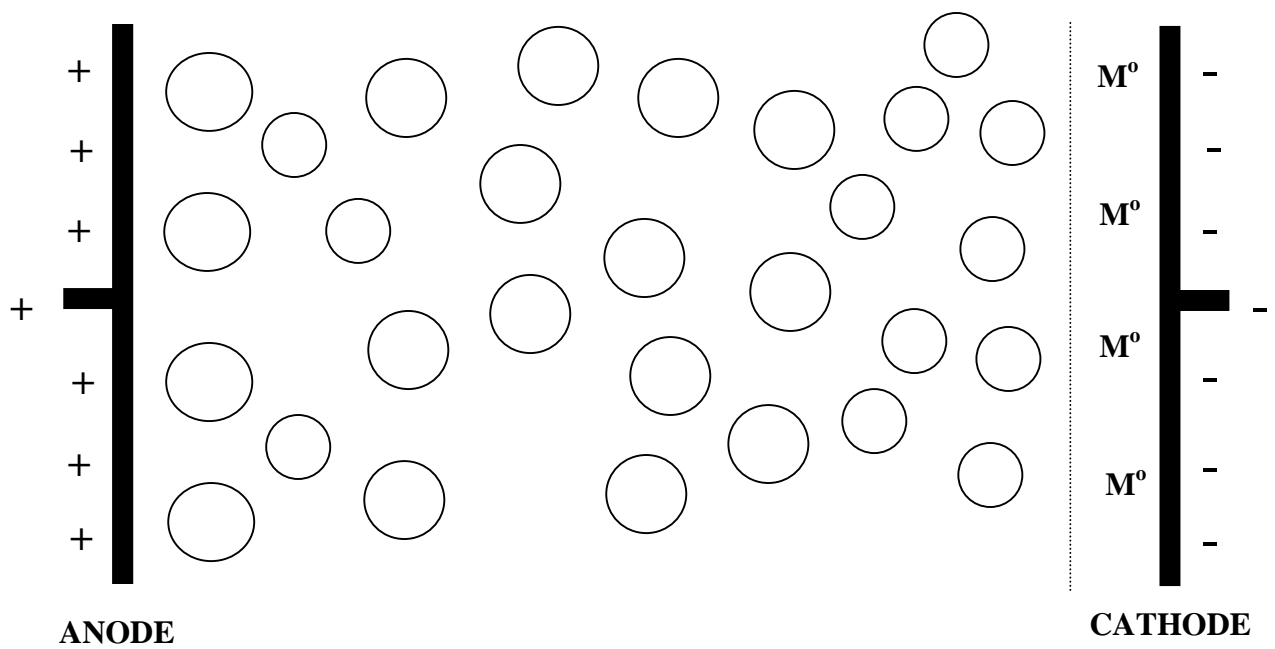


Figure 7. Electrowinning of Metals - Anodic *Oxidation* and Cathodic *Reduction* reactions occurring within an electro-winning cell

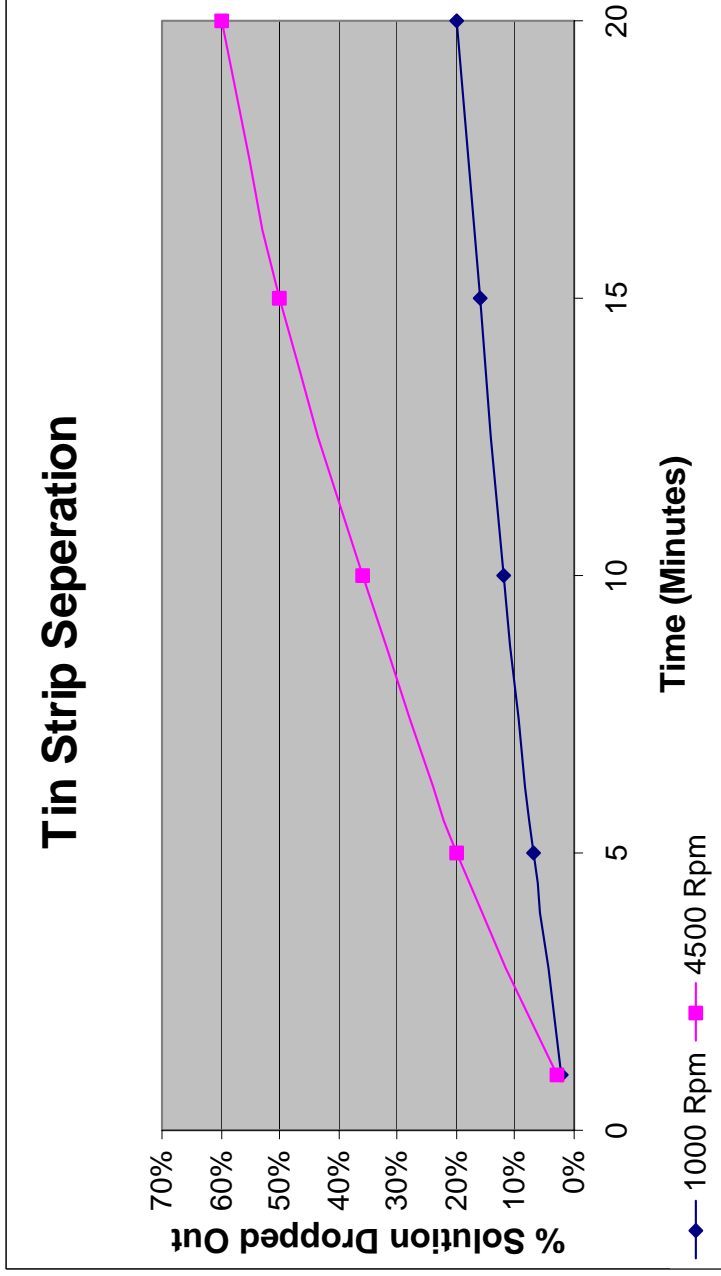


Figure 8. Tin-strip separations (recovery) as a function of spin rate with time

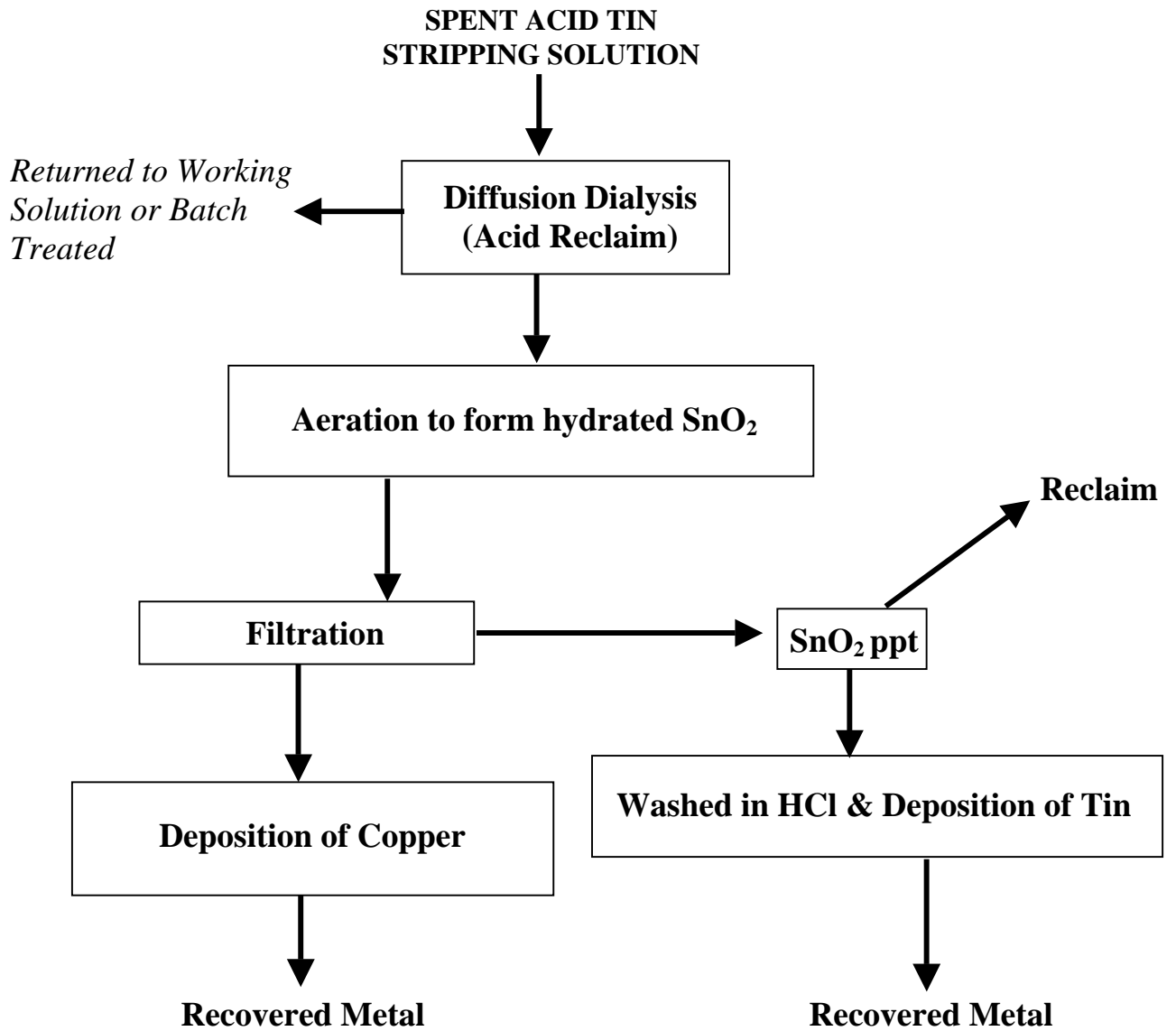


Figure 9 (a) Schematic Representation of a Possible Acid Tin Stripping Solution Reclamation Process

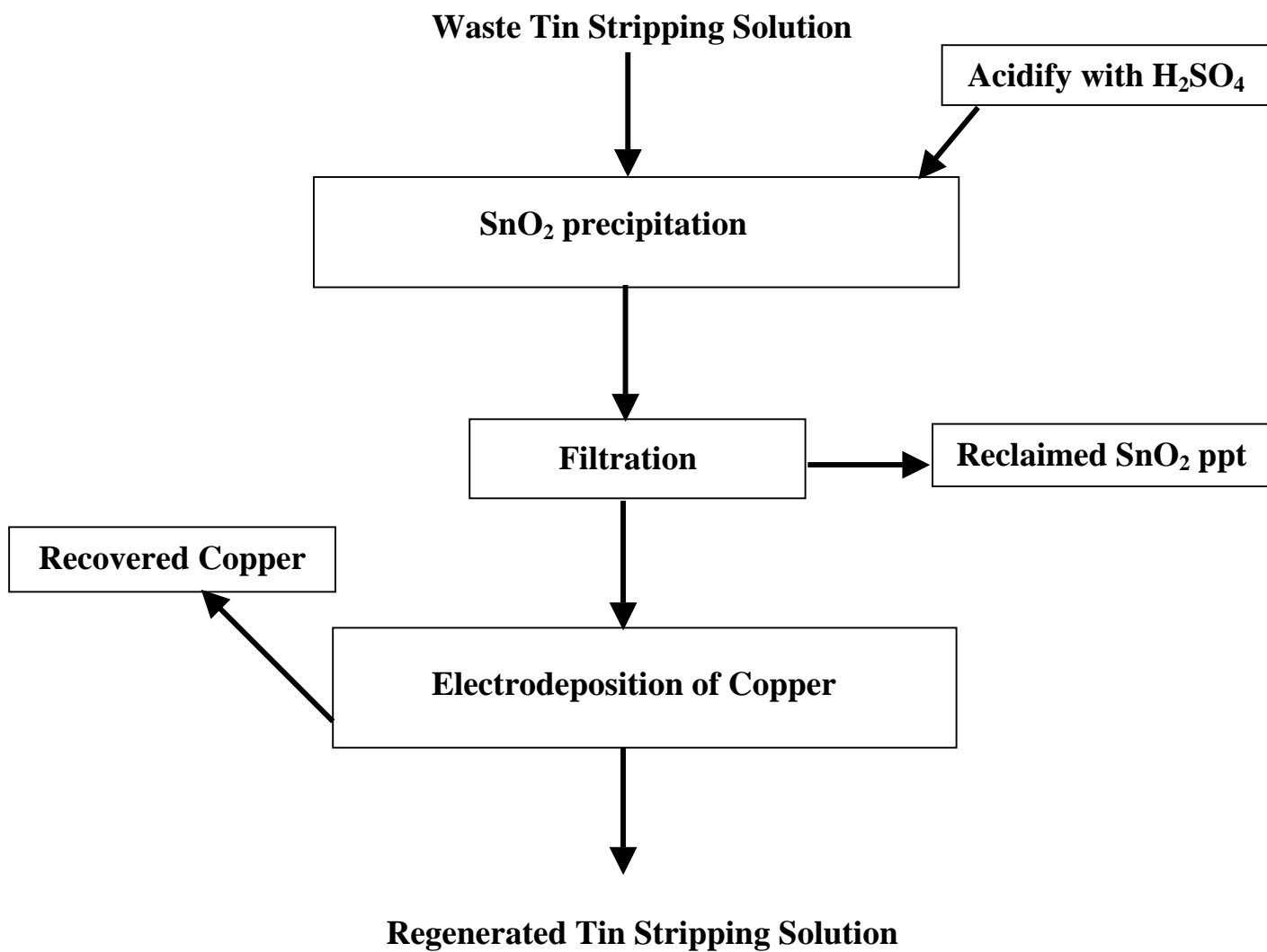


Figure 9 (b) An Alternative Schematic Representation for the Regeneration of Acid Tin Stripping Solution