# POLLUTION PREVENTION AND RESOURCE CONSERVATION FOR ELECTRONICS INDUSTRY; A CASE STUDY IN ISTANBUL

by
BAŞAK BÜYÜKBAY
BS. in Environmental Engineering, Yıldız Technical University, 1998

Submitted to Institute of Environmental Science in partial fulfillment of
the requirements for the degree of
Master of Science
in
Environmental Science

Boğaziçi University
2007

# POLLUTION PREVENTION AND RESOURCE CONSERVATION FOR ELECTRONICS INDUSTRY; A CASE STUDY IN ISTANBUL

APPROVED BY:

Assoc. Prof. Dr. Nilgün CILIZ…………………………
(Thesis Supervisor)

Assoc. Prof. Dr. Ali Kerem SAYSEL………………….

Prof. Dr. Ayşegül TANIK………………………......

DATE OF APPROVAL (05/April/2007)

# ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude to my thesis supervisor Associate Professor Dr. Nilgun KIRAN CILIZ for her guidance, encouragement, support, shared knowledge and endless patience throughout this study.

I would like to thank my jury members; Prof. Dr. Ayşegül TANIK and Associate Professor Dr. Ali Kerem SAYSEL for their kindness and valuable suggestions.

I also would like to express may special thanks to the PCB production manager of Canovate Inc. Co.; Mr. Erol YENICI, Production and Planning Manger; Mr. Gün Evren GÖREN for their support, tolerance, sharing valuable technical information and for their time, effort and kindness and also to all the Company employees who have supported the work for its successful implementation and for their continued cooperation.

I would like to thank Ms. Çiğdem CENGIZ from Atotech İstanbul, for her shared experience and technical information.

I would like to thank my dear friends Özlem, Gonca, Suna, Yasin, Cenk and Mete for their support and help.

Finally, I would like to express my thanks especially to my dear parents Fevziye and İsmet BUYUKBAY and to my sisters and brothers for their continuous and endless support and love. Also, I would like to dedicate this thesis to my father İsmet BUYUKBAY.

# ABSTRACT

Electronics industry consumes large amounts of hazardous chemical and process rinsing water which creates severe pollution load in process wastewater. Within this framework, the Cleaner Production (CP) application through resource conservation and waste reduction at source has been applied for the selected enterprise.

The existing barriers that cover lack of recorded data and data collection systems were overcome during Organization and Planning Phase of the study. Also commitment of enterprise which was achieved as a result of a series of meetings and a seminar was continuously supplied throughout the study. During the assessment phase, process flow diagrams with material balances for selected production lines were conducted in order to identify the sources of the waste and emissions as well as the factors that influence volume and the composition of waste and emissions generated. Environmental performance indicators were calculated to determine the production lines with the highest annual production that in the meanwhile lead to excess amount of wastewater and chemical consumption. The generated list of audit focus points recommended to the manager who has selected and prioritized the CP options for further steps of study.

Feasibility study covering technical, environmental and economic issues has been succeeded for the options on technology modification and reuse/recycling/recovery applications for chemical and water. These studies can be grouped as; substitution of “plasma desmear” and “closed loop cleaning system” in order to minimize both water consumption and hazardous waste production and “alkaline/micro etchant reuse/ recovery” systems to reduce hazardous etchant production. Another water saving issue covers application of counter current rinsing in metal plating department. Also, metal losts thourgh drag-out can be prevented by drag-out minimization methods.

The feasibility results of the investigated CP options varied with payback periods of 1 month to 7.2 years. As a result of this, for the implantation phase, the CP options were categorized depending on their payback period and the ones with less than 2.5 years were considered for application.

# ÖZET

Elektronik sektörü, fazla miktarda tehlikeli kimyasal ve proses suyu tüketiminden dolayı yüksek kirlilik yüküne sahip atıksu oluşmasına neden olur. Bu kapsamda, seçilen elektronik sektörüne, kaynakların korunması ve atık minimizasyonunu hedefleyen Temiz Üretim (TÜ) çalışması uygulanmıştır.

Kayıtlı veri ve veri toplama sistemlerinin eksik olmasını kapsayan mevcut bariyerler, çalışmanın planlama ve organizasyon aşamasında değerlendirilmiştir. Ayrıca, yatırımcının Temiz Üretim uygulamasına katılımı, tüm çalışma boyunca yapılan bir dizi toplantı ve seminerler ile sağlanmıştır. Değerlendirme aşaması boyunca, seçilen üretim hatları için atık ve emisyonların kaynaklarının ve miktar/kompozisyonlarına etki eden faktörlerin tespit edilmesi amacıyla kütle dengelerini içeren proses akım şemaları oluşturulmuştur. Aşırı miktarda atık su oluşumuna ve kimyasal madde tüketimine neden olan, yıllık en yüksek üretim seviyesine sahip üretim hatlarının belirlenmesi için çevresel performans indikatörleri hesaplanmıştır. Üretilen TÜ seçenekleri listesi, fabrika müdürüne sunulmuş ve öncelikli TÜ seçenekleri, çalışmanın ileri aşamaları için fabrika müdürü tarafından seçilmiştir.

Teknik, çevresel ve ekonomik konuları kapsayan fizibilite çalışması, teknoloji modifikasyonu ve geri kazanım/yeniden kullanım uygulamalarını kapsayan TÜ seçenekleri için gerçekleştirilmiştir. Bu çalışmalar su kullanımı ve tehlikeli atık oluşumunu azaltan “plazma desmear” ve “kapalı devre temizlik sistemi” uygulamaları ile tehlikeli atık aşındırıcı miktarını azaltan “alkali/mikro aşındırıcı geri kazanım/yeniden kullanım” sistemleri şeklinde gruplandırılabilir. Metal kaplama ünitesinde ters yönlü durulama uygulaması, diğer bir su tasarrufu yöntemini oluşturmaktadır. Ayrıca, süzüntü suyu minimizasyon yöntemleri ile metallerin süzüntü suyu ile taşınması engellenebilir.

İncelenen TÜ seçeneklerinin fizibilite sonuçları 1 ay ile 7.2 yıllık geri ödeme süreleri arasında değişmektedir. Bunun sonucunda; uygulama aşaması için, TÜ seçenekleri geri ödeme sürelerine göre sınıflandırılmış ve 2.5 yıldan daha az süreye sahip olanlar uygulanacak seçenekler olarak değerlendirilmiştir.

# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# LIST OF SYMBOLS/ABBREVIATIONS

| **Symbol** | **Explanation** | **Units Used** |
|---|---|---|
| CP | Cleaner Production | - |
| DI | Deionized | - |
| DS-PCB | Double Sided Printed Circuit Boards | - |
| EDTA | Ethylenediaminetetraacetic acid | - |
| EEC | European Waste Code | - |
| EMS | Environmental Management Systems | - |
| eop | End-of-pipe | - |
| EPA | Environmental Protection Agency | - |
| EU | European Union | - |
| HASL | The hot air solder leveling | - |
| ISO | International Standardization Organization | - |
| MSDS | Material Safety Data Sheet | - |
| MΩ-cm | Megaohm-centimeter | - |
| NF | Nonofiltration | - |
| OR | Overflow rinsing | - |
| OSP | Organic Solder Preservative | - |
| PCB | Printed circuit board | - |
| P2 | Pollution Prevention | - |
| ppm | Parts per million | - |
| RCRA | Resource Conservation and Recovery Act | - |
| RF | Radio frequency | MHz |
| RO | Reverse osmosis | - |
| RoHS | The Restriction of the Use of Certain Hazardous Substances in Electrical and | - |
| SIC | Standard Industrial Classification | - |
| SME | Small and medium-size plant | - |
| SS | Sheet Steel | - |
| TOC | Total Organic Carbon | ppm |
| UF | Ultrafiltration | - |

| | | |
|---|---|---|
| UN | United Nations | - |
| UNEP | United Nations Environmental Programme | - |
| US | United States | - |
| UV | Ultra violet | - |
| WEEE | Waste Electrical and Electronic Equipment Directive | - |
| WWTS | Wastewater Treatment Service | - |
| VOC | Volatile organic compounds | - |
| µm | Micrometer | - |
| µS/cm | Microsiemens per centimeter | - |
| ηm | Nanometer | - |
| $^{o}$C | Centigrade | - |
| % | Percent | - |

# 1. INTRODUCTION

PCBs are electronic circuits created by electronic components on a nonconductive board and creating conductive connections between these components with copper coating. They are employed in the manufacturing of business machines and computers, as well as communication, control and home entertainment equipment. Zinc, a bluish-white metal, is one of the mostly used metals in the electroplating industry. Zinc electroplating involves immersion of the items to be coated in a solution containing zinc ions and applying an electric current to coat the surface uniformly (UNEP–UNIDO, 1991).

The scope of this study is to conduct an operational procedure to identify optimal process modification with respect to reduction in wastewater generation and cost which in the meanwhile leads to reuse and recovery networks for electronics industry. The electronics sector has been selected for this study since it has gained importance in terms of pollution prevention actions and sustainable production measures through certain European Union (EU) Directives such as Waste Electrical and Electronic Equipment (WEEE-2002/96/EC) and the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS-2002/95/EC). These Directives have brought obligatory reductions in hazardous metal or toxic material content of wastewater.

This study aims the reduction of wastes generated, treated, stored or disposed in the selected electroplating plant. This includes both source reduction and material reuse/recovery that will result in “the reduction in total amount of waste and emissions” and “the reduction in the toxicity of waste”. Source reduction operations include (a) chemical substitution, (b) technology modification and (c) on site-reuse/recovery/recycling opportunities (Şişman, 2002). It is important to note that cleaner production technologies are not only desirable from the environmental point of view as a pre-emptive strategy, but also make good economic sense (Unnikrishnan and Hegde, 2006).

The most common conventional technologies for many industries dealing with water pollution are controlled by using end-of-pipe treatment. These treatments have proven to be costly and unsustainable. An alternative approach to this is to eliminate the problem at source using cleaner production and waste minimization approaches that generate significant financial savings, improvements in product quality and working conditions (Abou-Elela et al., 2006; Şişman, 2002). In this study, the successful implementation of CP methodology with waste reduction at source rather than the end-of-pipe treatment was achieved.

In general, CP assessment covers mainly the following steps such as; (a) evaluation of barriers and solutions and commitment of enterprise, (b) industrial audit for the existing situation in the company, (c) checking on resource utilization (raw material/water/chemical) and determination of major sources of waste and emission, (d) description of existing environmental situation in the company, (e) qualitative determination of raw material/water/chemical/wastewater, (f) studying the different approaches for pollution prevention and waste minimization in the company and suggesting possible alternative remedial integrated schemes, (g) constitution of list of CP options by literature survey and recommendation to the company manager (h) selection and prioritization of CP options by the manager, (i) technical and economical cost benefit analysis and (j) preparation of the tender documents of the proposed solutions (Abou-Elela et al., 2006 ; DPPEA, 2002).

During the application of CP methodology developed by United Nations (UN), material and energy balances at each stage of electronics plant is derived and evaluated. For each electronics unit operation, annual water and chemical costs are determined. A detailed understanding of the sources and causes of waste and emissions is gained in order to generate cleaner production options (UNEP, 1995).

The UNEP-CP methodology includes (a) Planning and Organization, (b) Pre-assessment, (c) Assessment and (d) Feasibility phases. The objective of the Planning and Organization Phase is to define the goal of the study for its successful implementation in the selected sector; electroplating plant. Also, evaluation of barriers and solutions and commitment of enterprise is achieved in this phase. Lack of recorded data was one the barriers which was overcome by measurement and collection of water and chemical consumptions for the selected production lines. In the pre-assessment phase, determination of quantities of raw material, auxiliaries and process water consumption, waste and emission generation, product and by-product given to the market on annual base is made.

The detailed material balance of each unit operation is carried out during the Assessment Phase. The material balance is not only used to identify the in and outputs, but also the costs of associated with these in and outputs (UNEP, 1995). Environmental performance indicators, which identify overconsumed resources or excessive waste generation for the selected processes, are developed from the material balance data (Fresner, 1998). Moreover, a list of CP options, which are identified according to the literature survey made, is recommended to the enterprise and CP options are selected by the manager depending on the needs and priorities of the product types of the plant.

For the selected enterprise, raw material/chemical/water consumption and waste production amounts for each unit operation were determined since there isn't any recorded data in the company at the Assessment Phase. In order to overcome this barrier, a project team which consists of product managers of the selected production processes was constituted for data collection. A continuous program for a duration of two months was carried out to identify the quantity of raw material/water/chemical consumptions and wastewater production. Once the review was completed, a detailed feasibility was performed on systems and equipment required to reduce chemical and water consumption and environmental impact.

On the other hand, during the Feasibility Phase economical, environmental and technical evaluation of the prioritized CP options are considered. As there exists variety of process in selected plant, special emphasis was given to the double sided PCB production and zinc plating, which have the highest annual production rates causing excess amount of wastewater production and chemical consumption, from the point of minimization of rinsing water consumption and recovery of waste etchant and metals such as copper/tin/zinc. Adoption of European Directive (RoHS- 2002/95/EC) to the products was carried out for lead free coatings of printed circuit boards which provide market opportunities with greener products.

Besides the environmental benefits, the economic advantages of prioritized options are considered for successful application of CP methodology (UNEP, 1995).Within this frame;

managers have started to develop an organizational procedure for implementation of CP options with a payback period less then 2.5 years. On the top of this, as the product market is of utmost importance for the manufacturers, the priority is given to the product quality during the Cleaner Production Assessment.

# 2. LITERATURE REVIEW

## 2.1. Cleaner Production (CP) Methodology

United Nations Environmental Programme (UNEP) defines Cleaner Production (CP) as the continuous application of an integrated preventive environmental strategy applied to processes, products and services to increase overall efficiency and reduce risks to humans and the environment (Berkel, 1999). CP is an option for environmental management that is available to commercial activities. It includes pollution prevention at source and the minimization of waste flows which are alternatives that seek to avoid pollution generation as a preferable strategy to end-of-pipe treatment (Chmielewski et al., 1997).

The aim of CP Methodology is obtaining more efficient use of natural resources (raw materials, energy and water), reducing generation of hazardous wastes and reduction of risks at the source and reduction or elimination of toxic products (Berkel, 1997; UNEP, 1998a). This can be achieved in various ways. The most common prevention practices are product modification, technology modification, input substitution and on-site recycling.

- Product modifications change the product characteristics, such as shape and material composition. The lifetime of the new product has been expanded or the manufacturing of the product is less polluting. Changes in product packaging are also viewed as product modifications.
- Input substitution refers to the use of less polluting raw materials and the use of process auxiliaries with a longer service lifetime.
- Technology modifications include improved process automation, process optimization, equipment redesign and process substitution.
- On-site recycling refers to the useful application of waste materials or pollutants at the company where these have been generated. This could take place through re-use of wastes as raw material or recovery of materials (Zufía et al., 2004).

CP insists on the need of a sustainable growth and increase in productivity and financial benefits. In CP methodology, wastes are considered as products with the actions to reduce consumption of raw materials and to prevent generation of waste at all life cycle stages (Arnaiz et al., 2004). This results in improved efficiency, better environmental performance and increased competitive advantage. Benefits of CP are reduction in production costs through greater efficiency, decrease in waste material inputs, increase in productivity, improvement in products, reduction in energy consumption, recovery of valuable by-products and minimization in waste disposal, including charges for waste treatment (CCPIC, 1996). Also, the greater environmental benefits can be gained by market opportunities with greener products (Morina, 2000).

The main focus of CP is always to create awareness for the prevention of pollution, to find the source of wastes and emissions, to define a program to reduce emissions and increase resource efficiency by implementing and documenting Cleaner Production options. By introducing material and energy flow management into the companies instead of end-of-pipe measures, CP aims to avoid wastes and emissions and use materials and energy as efficiently as possible (Fresner, 1998).

One of the pollution control methods is worker and public education which is the least costly but most effective method. It is very important to make the workers in industrial plants, management, building maintenance personnel, and others fully understand the sources and effects of pollutants on health. Their cooperation can markedly reduce pollutant exposure (Unnikrishnan and Hegde, 2006).

CP including Pollution Prevention (P2) focus on a strategy of continuously reducing pollution and environmental impact through source reduction which eliminates waste within the process rather than at the end-of-pipe (Berkel, 1999). End of pipe treatment (eop) is a costly method and it is not in compliance with sustainable development vision. On the contrary, pollution prevention is a broader term and includes the issues of source reduction (Glavič and Lukman, 2005). Optimizing production processes not only reduces waste loads and therefore disposal costs, it may lead to better yield, better product quality and finally to increased profit and sustainable production processes.

Table 2.1. Comparison of eop treatment and CP (UNEP, 1995)

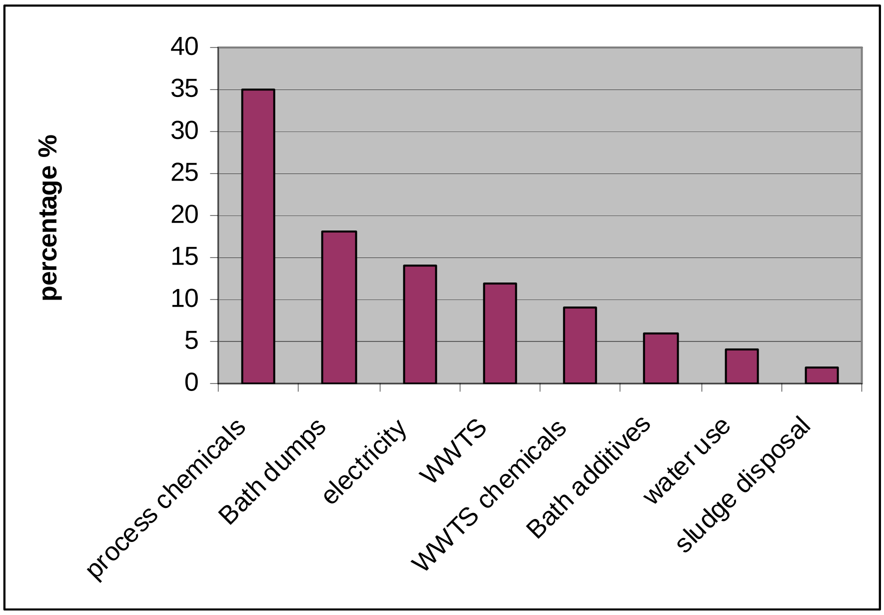
| “eop” technology | CP technology |
|---|---|
| Environmental problems are transferred from a medium to another | Savings in energy and raw materials associated to less pollution generation |
| It is a specific technology for each medium | CP is valid for all medium |
| It causes additional cost which grows as business production increases with time with no pay back period and as a result of any new regulation | Do not generate added cost with the approach of pollution prevention at source |
| Higher energy and materials consumption to operate additional “eop” facilities | Reduction of emissions |
| Non or low potential to diminish some urgent environmental problems (greenhouse effect, ozone layer depletion, etc.) | Potential to diminish environmental problems that can not be deal with “eop” technologies |
| Additional investment and operative costs without increasing production | Reduction in energy and material costs due to greater efficiency |
| Reduction of total productivity | Increase of total productivity |

Economic and environmental comparison of eop treatment and CP is given in Table 2.1. P2 is beneficial to both the public and workers. Benefits include reduced risks to both human health and safety and reduced worker exposure to toxic chemicals. It also helps to organize work structure and increase technical level and training status of the enterprise. Companies are implementing and publicizing pollution prevention activities to enhance their public image**.** P2 has the potential to increase the efficiency and competitiveness of industry. It provides easiness to obtain external financing for the company. Cost savings of pollution prevention can include reduction in waste treatment and disposal costs, reduction in raw material costs, reduction in transportation costs, reduction in compliance costs for permits, monitoring and enforcement, reduction in production costs through better management, reduction in energy costs and income derived through sale or reuse of waste (CCPIC, 1996).

P2 measures reduce regulatory exposure and could eliminate the need for frequent monitoring, saving time and money, and it can be an integral part of a company's Total Quality Management. Reduction in toxic chemical consumption improves the work environment and could reduce or eliminate the need for protective equipment. Long-term savings can be achieved on the basis of reclamation of inputs and reduced disposal costs. Many P2 strategies, such as general housekeeping and process improvements can be implemented at low cost and can have immediate benefits, up to 30% in some cases. Substantial process modifications will require capital investment; however numerous case studies demonstrate that pay-back periods can be range form months to 2 years (UNEP, 1998a).

During the last decades, the amount of waste from electronic and electrical equipment manufacturing has been growing; as a result, the environmental concerns about this industry have been increasing. The content of hazardous substances, which are mainly used in electronics sector, is not being treated properly but mainly incinerated or deposited in landfills. The EU therefore decided to address the electrical equipment manufacturing sector (Kjær et al., 2005). The European Union Directives Waste Electrical and Electronic Equipment (WEEE-2002/96/EC) and the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS-2002/95/EC) promote recycling and re-use of materials which is the one of main issues of CP methodology (Kjær et al., 2005; Milad, 2002).

Studies on the cost of environmental management indicate that these costs are typically 10–25% of total production costs. Figure 2.1 illustrates some environmental management costs for metal finishing industry. For metal finishers, these costs are usually on the high end of this range due to the number of toxic compounds used in metal finishing processes (EPA, 1998a). All of these reasons forced the metal finishers to apply pollution prevention assistance to their production facilitates.



WWTS: wastewater treatment services

Figure 2.1. Typical environmental cost assessment (EPA, 1998a).

The implementation phases of the CP methodology that have been evaluated for the selected industry in this study are as follows:

Planning and organization: The important elements for the successful application of a CP program are management commitment through meetings and seminars, employee involvement, organizing a project team, identifying barriers and solutions and setting goals. An effective CP planning process ensures the selection & implementation of the most cost effective CP options, broader business planning investment and decision-making analysis and the CP objectives and activities which are consistent with those identified in the organization's planning process.

Pre-assessment phase: The prime objective of the pre-assessment phase is the selection of assessment focuses. In the next phases, these assessments focus are evaluated in detail in order to identify and implement the CP options. The selection of these assessment focuses requires a preliminary identification of process flow charts, evaluating inputs and outputs for the selected electroplating processes. An audit of environment aspects of the company such as raw material/chemical/water consumption and wastewater production are conducted and compared with best available practices. From this environmental audit, environmental indicators are determined in order to identify prioritized CP options.

Assessment phase: This phase consists of the evaluation of the selected assessment focuses, which result in waste minimization, resource conservation and recycling at their source, in order to develop a comprehensive set of CP options. This requires the "source identification" (material flow diagram to identify sources of waste and waste generation), "cause diagnosis" (investigation of factors that influence the volume and composition of waste and emissions generated) and "option generation" (create a vision on how to eliminate or control each of the causes of waste and emission generation and CP option generation). The generated list of CP options, identified according to the literature survey, recommended to the company manager for prioritization of the options. Cost estimation and economic assessment of the proposed CP options are evaluated in order to estimate the feasibility of the option in the following Feasibility Phase.

Feasibility phase: This phase evaluates technical and economic feasibility of options. In terms of technical evaluation, availability and reliability of equipment, effects of the options on product quality and productivity and expected maintenance and utility requirements will be evaluated. Also, investments and operational costs and benefits, pay back period of the CP options are the other considerations of the feasibility phase. The cost estimate and assessment for all equipment needed for the proposed CP options are based on tentative market survey. The economic assessment is based on the expected capital cost for each recommended solution in addition to the operation costs for the different components (Abou-Elela et al., 2006).

Implementation phase: This phase covers the evaluation of the feasible prevention measures which are implemented. The development of such an ongoing program requires monitoring and evaluation of the results achieved by the implementation of the first batches of prevention measures. The expected results of this phase include implementation of feasible CP measures, monitoring and evaluation of the progress achieved by the implementation of the feasible options and initiation of the ongoing CP activities (ESCWA, 2001).

The implementation phase of CP methodology was not evaluated at this work since there was not sufficient time and position neither to implement the recommended CP options to enterprise, nor to the monitor and evaluate the results of CP options (Morina, 2000).

## 2.2. Overview of the Electroplating Processes

The fabricated metal products industry comprises facilities that generally perform two functions: forming metal shapes and performing metal finishing operations, including surface preparation. The Standard Industrial Classification (SIC) code 34 which consist of electroplating/metal finishing (SIC 3471) is composed of establishments that fabricate ferrous and nonferrous metal products. Also, the electronics manufacturing industry (SIC 36) includes the manufacture of passive components (resistors, capacitors, inductors), semiconductor components (discretes, integrated circuits) and printed circuit boards (SIC 3672) (single, double and multilayer boards) ( EPA, 1995; ESCWA, 2001).

### 2.2.1. Description of Metal Finishing Process

Electroplating is an electrochemical process used to deposit a metallic coating on the base material of an object by immersing it in an electrically charged solution so that a suitable low voltage electric current flows through it, causing the metallic coating to be attracted to the object being plated. Some of the more common electroplated coatings include brass, cadmium, chromium, copper, gold, nickel, silver, tin and zinc plating (EPA, 1998b). The aim of metal finishing is to enhance the properties of metal products such as appearance, resistance (corrosion, wear, electrical and chemical), electrical conductivity and solderability. Metal finishing, therefore, plays a key role in many sectors of economic activity including construction, automotives and electronics industries (Randal, 1998).

Also electroplating is a chemical reduction process which provides a uniform plating thickness on all surface area of the plating part regardless of the configuration or geometry of that part. However, it requires high purity rinsing water with 0.06-0.1 µS/cm conductivity (10–15 Megaohm-cm (MΩ-cm) resistivity) value after solvent, alkaline or acid cleaning to avoid spotting or deterioration of the plated part. This value is almost near to ultra-pure deionized (DI) water which can have 0.05 μS/cm conductivity (18 MΩ-cm resistivity) (Wong et al., 2002).

In metal plating industry, both raw water and deionized water are used for rinsing of solvent, alkaline and acid solution baths and plating and final rinsing, respectively. Deionized water has been purified from all other cations such as sodium, calcium, iron, copper and anions ions such as chloride and bromide and it has 0.1-10 μS/cm conductivity (10-0.1 MΩ-cm resistivity) value. The process wastewater generated is highly contaminated due to the drag-out which can be defined as the plating solution that clings to parts as they are removed from different process baths (Bingham and Hand, 2005; Qin et al., 2002). It has been reported that approximately 8 L/day can be lost in drag-out from each tank in rack plating but this value varies depending on the size and shape of the part and temperature and viscosity of the chemical bath (UNEP, 1998a).

Typically, metal finishing facilities involve several operations for the modification of surface properties of metallic products, based on three main stages: (a) pre-treatment (cleaning and degreasing), (b) plating (electroplating, coatings, electroless plating, etc.) and (c) post-treatment processes (EPA, 1998b; Randal, 1998; Viguri et al., 2002).

Pre-treatment can be grouped broadly as being chemical, electrochemical or mechanical. In chemical methods, a cleaner or solvent act as displacing, dissolving or in some way chemically altering to contaminant and hence causing its removal. Electrochemical methods often are employed prior to electroplating and consist of applying a current (direct, reverse or periodic) through a workpeace. Water decomposition causes small bubbles of hydrogen or oxygen to form at the metal surface and helps to lift away contaminant particles. Mechanical methods control fluid impingement on a surface and vary considerably with the type of process equipment being used. Simple agitation, turbulent flow, spraying and ultrasonic action are typical methods used to enhance cleaner performance (Randal, 1998).

Table 2.2. Typical pre-treatment bath composition (ESCWA, 2001)

| Cleaning Bath Type | Chemical components | Bath make up concentration at 21 $^{o}$C |
|---|---|---|
| Alkaline for copper or steel | Sodium hydroxide<br>Sodium carbonate<br>Trisodium phosphate<br>Wetting agent | 38-50 g/L<br>75-115 g/L<br>60-115 g/L<br>4 g/L |
| Acid | Emulsifying agent, wetting agents, water-miscible solvents | 75-115 g/L |
| | Inorganic acids (sulfuric, phosphoric) and organic acids (gluconic) | 10-15 % by volume |
| Detergents | Buffering salts, dispersants, inhibitors, surfactants or wetting agents | 45-90 g/L |
| Electro-cleaner for steel | Sodium hydroxide<br>Trisodium phosphate<br>Glutamic acid<br>Surfactant | 75-150 g/L<br>38-75 g/L<br>60-120 g/L<br>As required to limit foaming |
| Steel or copper pickling | Hydrochloric acid | 55 % by volume |

Various solvents, such as soak cleaners, electro-cleaners and acid cleaners are widely used to remove oil, grease, soil and other substances from metal surfaces. Thus, large quantities of spent solvents are generated. While aluminum surfaces are cleaned with acidic strippers since caustic is very corrosive to aluminum, steel and brass are dipped in caustic cleaning solutions containing emulsifiers and surfactants to remove and dissolve the oils and solids present. The cleaning baths can also incorporate an electrical current or heat as part of the cleaning process (Erol and Thming, 2006; UNEP, 1998a; Bingham and Hand, 2005). Typical pre-treatment bath compositions are given in Table 2.2.

After cleaning and degreasing, the objects to be plated are suspended in an electrolytic solution; these objects become the cathode in the electrolytic deposition process. The anode is introduced and it is typically a plate of the metal to be deposited. A low-voltage direct current applied to the system induces metallic ions to migrate to the cathode where they are deposited (Sullivan et al., 2000). The process is regulated by controlling a variety of parameters including voltage, temperature, residence times and purity of bath solutions. It has been estimated that in a non cyanide alkaline zinc electrolyte bath which contains 10 g/L Zinc (Zn) and 120 g/L Sodium Hydroxide (NaOH), 3.21 cell voltage is used with steel anodes at 25 ºC (Luoa and Huang, 1997).

The two most common types of plating are barrel and rack plating. Objects are placed in barrels or on racks and lowered in and out of plating. Each stage is followed by rinsing stages with water, leading to a high volume of liquid waste effluents (Viguri et al., 2002; Luoa and Huang, 1997).In barrel plating, the parts are loaded into a perforated container that is rotated in the chemical bath. Barrel plating is typically used for small production parts. In rack plating, parts are clamped onto racks that are then dipped into the chemical baths. Rack plating is used for parts that are larger, fragile or more complex in geometry. It has been reported that 37.4% of plating shops used barrel plating, 30.9% were rack only, and 31.7% had both types of operations in US metal plating industry in 2004 (UNEP, 1998b).

The discharge of process bath solutions is required after they exceed their useful life time, due to contaminants which are mainly metallic compounds. The life time of process bath solution can be extended by filtering the cleaning solutions to remove the sludge build up, rejuvenating the solution by topping up with fresh solution and the continuous improvement of rinsing efficiency (Allen and Rosselot, 1996). Deionized water usage and mechanical agitation applications are considered among case studies. If properly maintained, a plating bath can be used for as long as 15 years without discharging, thereby greatly reducing the chemical cost and sludge volume (Luo and Huang, 1997). It has been reported by some of the American companies that filtering systems of cleaner tanks can extend the life of cleaning solutions up to 5 years before they need to be dumped (UNEP, 1998b).

The waste solutions can be bled into on-site-treatment facilities for pretreatment; otherwise, they can be encapsulated for off-site treatment and disposal. Treatment residues always occur in the form of sludge, such as degreaser sludge, filter sludge and wastewater treatment sludge (Luo and Huang, 1997; Allen and Rosselot, 1996). Metal finishing sludge which is classified as metal hydroxide hazardous wastes primarily contain heavy metal hydroxides such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Ferrous (Fe), Nickel (Ni), Lead (Pb) and Zinc (Zn), depending on the metal finishing operation. Chemical characterization of the sludge from different metal finishing companies shows that cadmium, chromium, copper and nickel is the main pollutant responsible for the classification of the hazardous waste (Bingham and Hand, 2005; Viguri et al., 2000).

### 2.2.2. Description of Printed Circuit Board Production

The printed circuit board (PCB) is the platform upon which microelectronic components such as semiconductor chips and capacitors are mounted (La-Dou, 2006). These boards provide both the physical structure for mounting and holding electronics components as well as the electrical inter connection between components. PCB consists of a non-conductive substrate (typically fiberglass with epoxy resin) upon which a conductive pattern or circuitry is formed. Copper is the most prevalent conductor, although nickel, silver, tin and tin-lead may also be used. PCBs are used in several sectors such as automotive, communication equipment, consumer electronics, computer-business equipment and industrial electronics machine (DPPEA, 2002).

The PCB material is composed of an epoxy (glass-fiber) sheet with copper laminated on both sides. The uncut boards are received from the suppliers in large sheets with the size of approximately 1m x 1m which depends on the supplier's production standard and pass through a shearing stage to cut them to the desired size which ranges according to the PCB's application area. This value changes in deferent ranges such as 250mmx360mm, 100mmx166mm, 270mmx485mm, etc and the main objective of this unit is to achieve the minimum wastage of the sheets (UNEP-UNIDO, 1991).

PCB manufacturing is highly complicated, requiring large equipment investments and over 50 process steps. The main processes, common to all PCBs, are drilling, image transfer, and electroplating. Holes are drilled into PCBs to provide layer-to-layer interconnections on circuits. After drilling, boards are passed through a surface conditioning stage (deburring, desmear-clean holes) before undergoing a series of processes such as direct metallization. This treatment essentially coats copper into the holes which prepares the holes for electroplating. These holes are subsequently made conductive by plating copper onto the hole barrels by pattern plating unit (La-Dou, 2006).

Image transfer is the process by which an image of a circuit layer is transferred from film or directly from image data files to the copper foil of the PCB material. For inner layers, this includes the application of a photoresist (a photosensitive film which also serves as the etch resist), imaging, developing and etching. For outer layers, image transfer may include the electroplating of copper, tin, tin–lead, or nickel-gold coatings. The printed circuit areas are subsequently developed (to remove unexposed resist areas which are to be plated) and pass through microetching, copper electroplating, solder electroplating, resist stripping, copper etching and a number of other selected finishing treatments as specified by the costumer. The last stages of manufacture involve final fabrication and electrical testing (UNEP-UNIDO, 1991).

Layer count is a common method of categorization of level PCBs because it relates to overall technology.  PCB can be produced as single sided, double sided and multi layer printed circuit boards. While single sided boards have a conductive pattern on one side only, double sided PCBs have conductive patterns on both sides and multilayer PCBs consist of alternating layers of conductor and insulating material bonded together (DPPEA, 2002).

## 2.3. Rinsing Operations of Electroplating Industry

The rinsing process is the primary source of wastewater in metal finishing industry. Surveys of 29 different South African metal finishing companies, which plates nickel, zinc and chrome finishes, indicate that water consumption is as high as 4 L/dm$^2$ of metal surface treated, whilst best available practice can achieve less than 0.1 L/dm$^2$ (Telukdarie et al., 2006a). In some countries in the Mediterranean Basin, a maximum water consumption of around 0.8 L/dm$^2$ is considered acceptable for each rinsing position depending on the surface being treated (Mediterranean Action Plan, 2000). Large amounts of water also are used in printed circuit board (PCB) manufacturing, mostly to rinsing the boards between process stages. Water consumption can be more than 1.5 $m^3$ /$m^2$ of board processed (ENVIROWISE, 2001).

Rinsing operations are fundamental in electroplating processes. The volume depends on many factors such as electroplating plant design, production capacity and rinsing type. It is reported that one of the electroplating industry which has 200 $m^2$/day metal part production in America produced 15,600 $m^3$/year wastewater with the associated material cost of $ 9,360 and treatment cost of $ 23,400 on annual base (UNEP, 1998a).

The rinsing systems include the rinsing tanks, water inlet points, water flow rate, dripping time and tank agitation. Dripping time can be described as the length of time during which the items are placed above the process bath for different range-mostly 4 to 30 seconds before being moved to the next bath. By agitation it is understood to be the physical motion of the liquid. If the liquid is not agitate, the replacement of the liquid film on the item surface will be very slow and as a result, chemicals can be dragged out with the items before they have been exchanged from the surface layer (Telukdarie et al., 2006b).

Controlling the inlet flow of water to a rinsing tank is probably the most important factor influencing the water consumption. An automated flow meter should be used to control and monitor water flow rate. It has been estimated that, a metal finishing company in United States reduced the amount of water usage in the processes by around 40% by installing water meters and through teaching staff about the value of water (UNEP, 1998a).

Multiple, counter-current rinsing also significantly reduces water consumption. In a counter-current rinsing system, fresh water is fed into the final rinsing tank and overflows backwards through the flowing rinsing tanks until it reaches the rinsing tank immediately after the plating tank. Counter-current rinsing can further reduce the demand for fresh water by returning drag-out to the process tank (Reeve, 2006). It was reported that one of the metal finishing industry in South Africa was made revealed savings of water (80%) and chemicals (45%) after a cleaner production project, which comprise chemical and water reuse/recycle/recovery, process optimization, optimum use of recourses and improved product quality (Telukdarie et al., 2006b). The conductivity sensors are another method for the improvement of rinsing operations. They measure the concentration of contaminants in the rinsing water and adjust the flow accordingly; the higher the conductivity, the higher the flow. The conductivity sensors can reduce water consumption by 40% and have an economic payback of about one year (ESCWA, 2001). Final waste rinsing water contains a much lower level of heavy metals (measured conductivity generally less than 30 μS/cm) (Wong et al., 2002).

A metal finishing industry in the United States demonstrates the potential benefits of installing conductivity control systems to control the inflow of water to rinsing tanks. The company installed control devices at nine sites and water consumption at these sites reduced dramatically by around 42%, from 1,960 $m^3$/month to 1,125 $m^3$/month. The total savings were around $14,300/year, resulting in a pay-back period of just over 12 months (reduction in water, wastewater discharge and the demand for wastewater treatment plant chemicals) (UNEP, 1998a).

It has been estimated that a metal finishing company in Spain specializing in surface coating (Zn, Cr and Ni) and structural elements for the automobile, telephone and computer industries installed a new technology based on a vacuum evaporator which replaces with the traditional physical-chemical treatment plant for wastewater effluent and spent chemical baths. Savings can be seen as 100 % reduction in water consumption with zero discharge, 97 % savings in chemical consumption used for conventional water treatment and control, 80 % savings in labor costs due to the reduction of water treatment and sludge disposal operations and 90 % in reduction of sludge produced by conventional wastewater treatment (DPPEA, 2000).

DI water should be used to replace tap water for process bath makeup and in rinsing operations. The natural contaminants such as carbonates and phosphates found in tap water can reduce rinsing water efficiency, minimize the potential for drag-out recovery, and increase the frequency of process bath dumping. These contaminants also contribute to sludge volume when removed from wastewater during treatment (Luo and Huang, 1997).

Segregation of waste streams from the different plating lines also will greatly improve the rinsing water consumption and the ultimate treatment efficiency. If all the waste streams are treated together, the different contaminants can interfere with each other (UNEP, 1998a).Collection of strong wastes and isolating them from heavily diluted effluent would substantially reduce the quantity and, accordingly, the strength of the wastewater for easy and economical treatment (Randal, 1998; Visvanathan et al., 1998; Baban et al., 2004).

In metal finishing wastewater stream segregation systems, final waste rinsing water is segregated from other more heavily contaminated rinsing for treatment. This will allow the consumption of a lower energy system for heavy metal removal to produce a high purity product water (Wong et al., 2002; Baban et al., 2004, Visvanathan, 1996). Segregation of wastes can offer enhanced opportunities for recycling and reuse with resultant savings in raw material cost. If a highly concentrated waste is mixed with a large quantity of weak, relatively uncontaminated effluent, the result is a larger volume of waste requiring the treatment (UNEP-UNIDO, 1991; Uner et al., 2000).

Most companies are aware of the potential cost savings through efficient and minimum water consumption, since metal finishing systems generally use a lot of water. For a more sustainable metal finishing process, the common rinsing system could be substituted with zero-water discharge reuse and recovery network (Erol and Thming, 2006; Yang et al., 2000). It is based on the theory that water and metals contained in the liquid waste streams can be recovered and reused again in the process.

As the costs for treating and disposing of wastewaters to sewer become more expensive, it is more cost effective to treat and reuse the water than to treat and dispose (UNEP, 1998a). Solvent extraction, reverse osmosis (RO) and ion exchange are the established techniques for recovery of metals and recovery and reuse of wastewater.

Solvent extraction is principally used for high contaminants concentrations where these values are between 0.6-600 g/L, on the other hand, 0.01- 10 g/L and $10^{-6}$-1.0 g/L are the suitable contaminant concentrations for reverse osmosis and ion exchange systems, respectively (Kentish and Stevens, 2001).

It is estimated that a wastewater recycle/reuse system, which comprise (a) segregation of final waste rinsing water from more pollutant rinsing water, (b) a pretreatment system through a series of filters which suspended solids ( 5 to 75 microns) were removed, (c) a nanofiltration (NF) system (suitable for 0.0001 μm to 0.001 μm pore size) which removes the heavy metals and (d) a polishing steps which provides a super DI grade water with an ion exchange resin, can be used to produce a recycle water stream which have a high purity with a conductivity of less than 0.06 μS/cm for an electroless plating operation (Wong et al., 2002). An other closed loop RO system was applied one of the metal finishing industry in Australia and the contaminant concentrations of wastewater has been dramatically reduced to 0.022, 0.05, 0.05 and 46 mg/L from 105, 79, 38 and 9958 mg/L for Chromium, Copper, Nickel and Oil/Grease (Berkel, 1999).

### 2.3.1. Conservation of Rinsing Water in Electroplating Industry

Wastewater streams have traditionally been treated by a combination of physico-chemical processes such as flocculation, precipitation-filtration and biological processes such as activated sludge. These methods are based on metal hydroxide precipitation by pH adjustment with an alkaline reagent and subsequent removal of the precipitate by sedimentation or filtration (Adhoum et al., 2004; Alvarez-Ayusoa et al., 2003; Qin et al., 2003). Such treatments are usually effective in reducing organic pollutants to a level and suitable for disposal of effluent into public sewer or natural water sources, however, they often fail to reduce the concentration of heavy metals below permissible limits (Adhoum et al., 2004).

These conventional technologies require high concentration of chemical addition, and require disposal of sludge containing large amount of chemicals and heavy metals. Most of these processes are effective for removing specific metals from solution, but they do not produce the recovery of water produced by the electroplating industry (Telukdarie et al., 2006a; Kentish and Stevens, 2001; Adhoum et al., 2004; Benito and Ruiz, 2002; Solisio et al., 1999). On the other hand, the development of effluent-free, closed loop cycles of water reuse/recycle systems for electroplating has been considered as an ultimate aim when developing new water purification methods (Zhao et al., 1999).

Table 2.3. Recovery technologies in use in United States (US) (UNEP, 1998a)

| **Recovery Technology** | **% of businesses where it is in use** |
|---|---|
| Ion exchange | 25.0 |
| Atmospheric evaporators | 22.3 |
| Electrowinning | 19.0 |
| Vacuum evaporators | 7.2 |
| Reverse osmosis | 1.8 |
| Electrodialysis | <1.0 |
| Waste Reduction Institute for Training and Applications Research (WRITAR), “Profile of the Metal Finishing Industry” | |

Recovery technologies which are used in the United States with % of businesses are given in Table 2.3. Among these recovery systems, electrolytic recovery and reverse osmosis that are used for recovery/reuse option for electroplating operations were evaluated in this study. These methods can reduce total metal output to less than 0.1 ppm. When not used correctly, operational costs accelerate rapidly and metal levels in the effluent rise to higher level (Zhao et al., 1999).

Electrolytic recovery (Electrowinning): The removal of heavy metals from wastewater, especially those from electroplating and surface finishing industry is possible with electrochemical recovery technology (Janssen and Koene, 2002; EPA, 1993). Electrolytic recovery involves implementation of electrochemical methods to recover metals from rinsing or process baths. Briefly, electrolytic recovery involves electroplating of the metal from waste process solutions onto the cathode of an electrolytic cell (Scott et al., 1997; Juang and Wang, 2000). Electrolytic recovery is different from other recovery technologies (e.g., evaporation, ion exchange) in that an elemental metal is recovered rather than a metal bearing solution.

Electrolytic processes have been used for electroplating waste effluents to come up as an alternative to treat leaching solutions in order to recover metals or even recycle the metals for reuse. It has been estimated that a membrane cell with graphite can achieve copper recovery and recycle/reuse of the cyanide solution from an electroplating plant. At this system, copper recovery up to 60% was achieved with an energy consumption of 1–2 kWh/kg (Lemos et al., 2006).

The major application of electrolytic recovery is the recovery and reuse of waste ammoniacal etchant in PCB manufacturing. In order to recover valuable metals and regenerate the etching solution from the waste etching solution of PCB, a closed loop system which consists solvent extraction, stripping, electrowinning and precipitation methods have been performed (Scott et al., 1997; EPA, 1999; Sage and Schnitzer, 1994; Lee et al., 2003). The results of experiments were shown that 99 % copper can be removed from 7.84 mol Cu/m$^3$ copper containing etch solution by electrowinning system (Lee et al., 2003; Hunsom et al., 2005) .

Before electrolytic recovery, metals are separated from the solution. The most commonly used separation system for wastewater recycling is solvent extraction. This process is principally used for large-scale operations where the concentrations of contaminants are high (0.6-600 g/L) (Bingham and Hand, 2005). A water insoluble metal-complexing agent in a non-polar organic solvent is contacted with the waste stream and the metal ions are transferred into the organic phase. This loaded organic phase is then further contacted with a second aqueous strip phase. The metal ions which are transferred back into this aqueous stripping solution can be recycled. The final step is the recovery of metals which is accomplished by electrowinning (Juang and Wang, 2000). However when contaminant concentrations are below 0.5 g/L, this process becomes uneconomic (Kentish and Stevens, 2001).

Since the copper concentration is relatively high in spent etching solutions, electrolytic regeneration seems an appealing alternative for PCB, electronic and metal finishing industries. In these systems, copper recovery is performed in acidic condition and the recovery efficiency is almost 99.9%. Electrolytic treatment is environmentally friendly and can save the cost of disposal and reduce the cost of purchase of new acid and alkali etchant chemicals (Juang and Wang, 2000; EPA, 1999; Lee et al., 2003; Fornari and Abbruzzese, 1999; Melling, 1986; DEP, 1997).

An electrowinning unit consists of a reaction chamber with anodes and cathodes. In the simplest design, a set of cathodes and anodes are set in the reaction chamber containing the electrolyte. When the process is energized, metal ions are reduced onto the cathode. The rate at which metal can be recovered from solutions depends on several factors, such as the concentration of metal in the electrolyte, the species of metal being recovered and cathode area. Electrolytic recovery works well for process solutions containing cadmium, copper, nickel and precious metals. However, it is not practical for process solutions containing chromium or aluminum. Electrowinning is particularly applicable for removing metal from solutions containing a moderate to high concentration of metal ions (>3,000 mg/L). Below 1,000 to 2,000 mg/L of metal, the electrowinning process becomes very inefficient. It is a beneficial method in terms of recovering valuable metals which would otherwise be converted to metal hydroxide sludge by the wastewater treatment system (Keskitalo et al., 2006).

Reverse osmosis: RO involves separating water from a solution of dissolved solids by forcing water through a semi permeable membrane. As pressure is applied to the solution, water and other molecules with low molecular weights (less than about 200 g/mole) pass through micro-pores in the membrane. Larger molecules, such as organic dyes and metal complexes, are retained by the membrane. The purified stream that passes through the membrane is called permeate and the concentrated stream containing a high concentration of dissolved solids is called concentrate (ESCWA, 2001; Benito and Ruiz, 2002). A schematic diagram of RO membrane system is given in Figure 2.2.

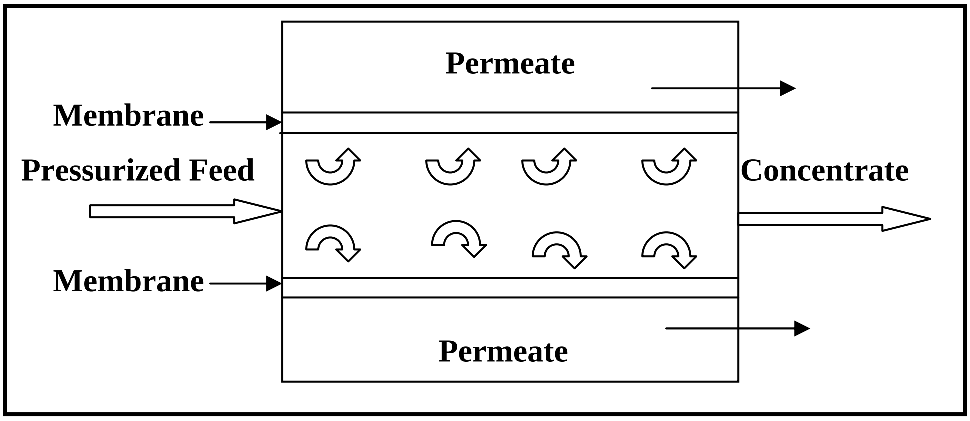


Figure 2.2. Reverse osmosis cross-flow filtration (NMFRC, 1995)

Membrane technology can be used to treat the global effluent from the electroplating industry. Previously it is necessary to make some pre-treatments which comprise eliminating solid by using a 5 nanometer (ηm) filter and adjusting the pH in the inlet of effluents that feeds the membrane system (Benito and Ruiz, 2002).

RO unit operation involves adjusting valve and pump settings to control the pressure and flow rates of the feed and concentrate streams. Diluted or concentrated rinsing waters are circulated through the membrane at pressures greater than aqueous osmotic pressure. The membrane allows water molecules to pass through, blocks metallic salts and additives. This action results in the separation of water from the plating chemicals (EPA, 1993).

The essential components of a RO unit include a strainer, a pressure booster pump, cartridge filters and the RO membrane modules. The strainer removes large, suspended solids from the feed solution to protect the pump. The booster pump increases the pressure of the feed solution. Commercially available cartridge filters are used to remove particulates from the feed solution that would otherwise foul the RO units. Filter pore sizes are typically between 1 and 5 microns (NMFRC, 1995).

The design and capacity of an RO unit is dependent upon the type of chemicals in the plating solution and the drag-out solution rate. Certain chemicals require specific membranes. For instance, polyamide membranes work best on zinc chloride and nickel baths, while polyether/amide membranes are suggested for chromic acid and acid copper solutions. The flow rate across the membrane is very important. RO systems have a 95% recovery rate with optimum membrane selection (Chmielewski et al., 1997). The membrane is susceptible to fouling, which is often caused by the precipitation of suspended and dissolved solids that plug the pores of membrane. The combinations of sand filters which have finalizing filters of a pore size of 5 microns should be used in order to overcome this saturation problem. This filtration is also necessary to eliminate organic materials that could damage the membrane (ESCWA, 2001).

Metal solubility varies with the pH of the solution**.** Solubility of Zn, and Cu increased with a decrease in pH. Zinc has low solubility at high pH, but forms a suitably concentrated solution at pH 7.0 (solubility of 100 mg/L). Solubility further drops to 8 mg/L at pH 8.0 and 0.5 mg/L at pH 9.0. At a pH of 10, for example, most heavy metals have concentrations of 1.0 mg/L or less. In the insoluble or precipitated state, the metal particle size is 0.1 micron or larger. An ultrafiltration (UF) membrane has submicroscopic pore size of < 0.01 micron and thus will retain the metal precipitate. Membrane life expectancy (normally 3 to 5 years) is dependent on the process conditions and the cleaning frequency (Hunsom et al., 2005).

An appropriate UF pretreatment step using a well-selected membrane could be beneficial for reducing the fouling of RO membrane (Qin et al., 2002). It has been estimated that a polyacrylonitrile hollow fiber UF membrane is a suitable pretreatment before RO unit for a combined nickel plating rinsing water which has 9, 4.5 and 4.5 $m^3/h$ alkaline rinsing, acid rinsing and nickel plating rinsing waste stream, respectively. The product water with conductivity below 95 μS/cm can be produced from the pilot plant which wastewater stream enter the system with 650, 2480 and 685 μS/cm conductivity for alkaline rinsing, acid rinsing and nickel plating rinsing, respectively (Qin et al., 2003).

A RO system, which was used for a combination of alkaline, acid and nickel-plating rinsing operations containing 1590 μS/cm of conductivity, 3.36 ppm of nickel, 26.5 ppm of nitrate and 11.8 ppm of total organic carbon (TOC) concentrations, can reduce the permeate concentrations with 27.3 μS/cm, 0.003, 0.31 and 1.5 ppm, respectively. These values met the requirements for reuse of the effluent as alkaline rinsing water. It has been showed that an appropriate ultrafiltration (has a pore size of < 0.01 micron) pretreatment could reduce fouling of RO membrane and increase the flux of RO membrane by 30–50% (Qin et al., 2002).

A metal finishing facility in Ontario, California, which facilitates cleaning, etching, anodizing, chromate conversion and several types of dying with 30 personnel installed a RO unit into the black dye operation. A seen in Figure 2.3, the system consists of a closed-loop unit which returns reclaimed rinsing water (permeate) to the rinsing baths and return concentrated process chemicals (concentrate) to the process baths. When the RO units were installed, the industry replaced its single stage rinsing system with two-stage, counter flow rinsing to reduce the rinsing water flow rates needed for effective rinsing. Particulates are removed from the feed solution by 1-micron cartridge filters. The feed solution then flows in RO membranes. Permeate is conveyed to the second rinsing tank and is reused as clean rinsing water and concentrate is sent to the plating bath. A small amount of fresh deionized water from an outside source is added to the process baths in order to make up for evaporative water losses. The results show that the black dye use rate decreased to 4.2 kg /month from 9.3 kg/month after installation of the RO unit. Also the consumption of water was decreased to zero water discharge from 110 m$^3$/month (NMFRC, 1995).

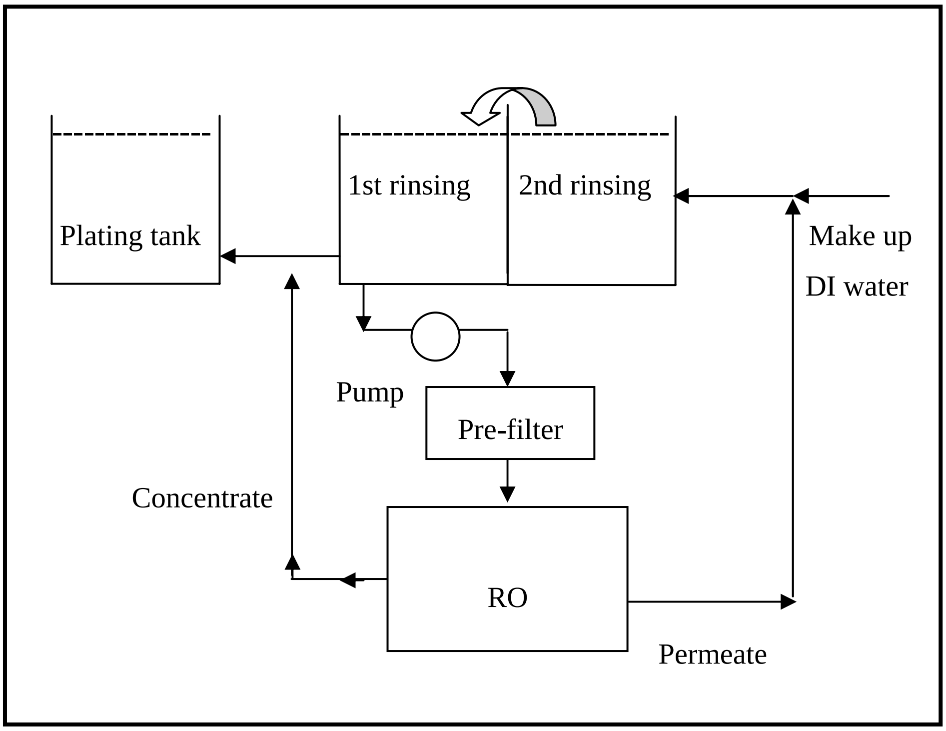


Figure 2.3. The recycle/reuse of rinsing water by reverse osmosis (NMFRC, 1995)

In RO units, the separation is produced by mechanical effect by applying pressure, so there is no need for addition of chemicals to separate the pollutants. Another advantage of reverse osmosis is plating chemicals can be recovered from temperature sensitive solutions. However, the performance of the membranes used up to now has improved but they still show problems of chemical resistance with aggressive agents such as hexavalent chrome, chlorine, persulphate, etc (Mediterranean Action Plan, 2000). The summarized explanation of recovery/recycling technologies of rinsing water is given in Table 2.4.

Table 2.4. Overview of recovery/recycling technologies of rinsing water (UNEP, 1998b)

| Method | Advantages | Disadvantages | Successful Applications |
|---|---|---|---|
| Electrolytic Metal Recovery | -Recovers only metals<br>-Results in salable, non-hazardous products<br>-Energy efficient<br>-Low maintenance | -Solution concentration must be monitored<br>-Fumes can form and can require scrubbing system | Cadmium cyanide, copper cyanide, copper pre-etch, copper final etch, acid copper, electroless copper, gold, electroless nickel, silver, tin, and zinc |
| Reverse Osmosis | -Achieves modest concentration<br>-Small floor space requirement<br>-Less energy intensive than evaporation | - Fouled membranes because of feeds high in suspended solids<br>-Feed filtration essential<br>-Membrane sensitive to pH | Copper, nickel, and zinc |

### 2.3.2. Drag-out

Drag out is the amount of liquid that is extracted involuntarily from a bath with the performance of part extraction between two stages of any electroplating process (Mediterranean Action Plan, 2000). The amount of drag-out generated depends on many factors including the size and shape of the pieces being plated, the temperature, density and viscosity of the plating solution as well as the drainage time (UNEP, 1998a). Average standard drag-out value for rack plating is 1.5 $mL/dm^2$ in electroplating and PCB manufacture (Mediterranean Action Plan, 2000). Drag out reduction methods can be described as;

Controlling drip time (drainage time): In vertical process lines, allowing sufficient drip time above the process bath ensures effective drainage of the process solution from the boards. Studies have shown that a drip time of 30 seconds is a maximum level which minimal benefit is achieved. However, for most PCB manufacturers, a drip time of about 15 seconds provides an optimum level of drainage. If the drip time again reduced to only 8 seconds, the amount of drag-out increases by 50% (Luo and Huang, 1997; ENVIROWISE, 2001).

Increasing the drainage time after parts are removed from baths can significantly reduce the volume of drag-out. A trial in the United States showed that if the drainage time increases to 10 seconds from 5 seconds in metal plating, 50 % of drag-out reduction could be achieved (The Institute of Advanced Manufacturing Sciences). A trial in Hong Kong showed that drainage times of 15 seconds reduced drag-out by 75% without adversely affecting the quality or quantity of product (Hong Kong Government Industry Department) (UNEP, 1998a).

The speed with which work pieces are removed from a process solution also can have a major impact on drag-out volume. The withdrawal rate determines the amount of solution left on a workpiece. A slower withdrawal rate yields a much thinner film since it allows more time for viscosity forces to operate (Luo and Huang, 1997; Visvanathan., 1996). On automatic lines, a withdrawal rate of about 0.5 meter/second should be programmed into the controller unit (ENVIROWISE, 2001).

Viscosity and temperature control: The first factor that influences drag-out water volume is the viscosity of a plating process solution which can be described as its resistance to flow or removal by another liquid (in this case, rinsing water), caused by molecular attraction forces (EPA, 1995). The bath should be kept at the lowest concentration to reduce its viscosity since viscosity control is a key method for reducing drag-out from solution tanks. At higher viscosity, more solution adheres to parts and is removed from the process tank as drag-out (Mediterranean Action Plan, 2000).

As the chemical content of a solution is increased, its viscosity increased. Process chemicals should be kept at the lowest concentration consistent with effective operation to reduce both solution viscosity (and hence drag-out volume) and drag-out concentration. Increased viscosity contributes not only to a large volume of drag-out, but also to higher chemical concentration of drag-out. The consequent need for more rinsing water creates additional pollution control problems (EPA, 1998a). Since higher temperatures reduce solution viscosity, surface tension and consequently drag-out volume, baths should be operated at the highest temperature consistent with good process control (Mediterranean Action Plan, 2000).

A wetting agent, usually a surfactant, also reduces the surface tension of a liquid causing it to spread more readily on a solid surface (UNEP, 1998a; EPA 1998b; Luo and Huang, 1997; Allen and Rosselot, 1996). A typical plating bath solution has a surface tension of about 0.0074 kg/m at room temperature. The addition of very small amounts of surfactants can reduce surface tension considerably to as little as 0.0025 kg/m to 0.0036 kg/m. Further additions of the wetting agent will not lower the surface tension appreciably beyond this point (Mediterranean Action Plan, 2000). It is estimated that the use of wetting agents will reduce drag-out loss by as much as 50 %. For plating baths, the usage of non-ionic wetting agents such as alkyl poly(ethylene oxide),alkyl polyglucosides (octyll glucoside ,decyl maltoside),fatty alcohols( cetyl alcohol ,oleyl alcohol*)* is recommended (EPA 1998b).

Drag out recovery methods can be described as;

Drag-Out Tank: The drag out tank is a rinsing tank that initially is filled with process water. As the metal finishing chemical processing line is operated, the drag out rinsing tank remains stagnant and its chemical concentration increases as more work is processed. Air agitation is often used to aid the rinsing process because there is no water flow within the tank to cause turbulence. After a period of operation, the solution in the drag-out tank can be used to replenish the losses to the process bath (EPA, 1995).

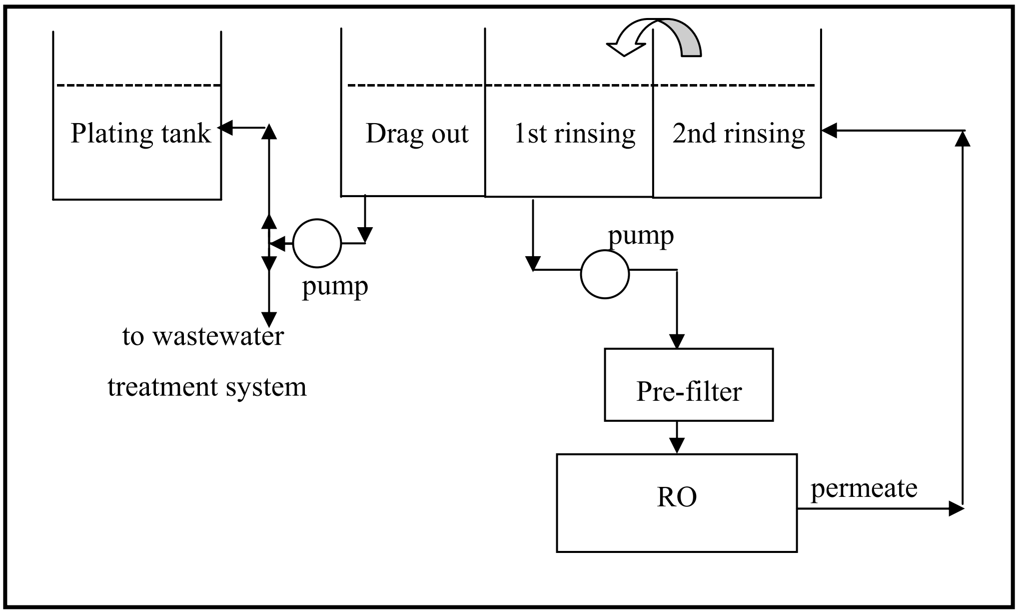


Figure 2.4. Reverse osmosis system utilizing drag out rinsing (Roy and Shapiro, 1999)

In automatic drag-out return system, chemical metering pumps were used to return drag-out from the rinsing tank to a plating tank. The pumps were controlled by a level sensor in the plating tank (Roy and Shapiro, 1999). It should be noted that drag-out tanks are used more frequently by metal finishing facilities than by PCB facilities (EPA, 1995). Depending upon the solution, up to 60 percent of the materials carried out of a plating tank by drag-out can be recovered for reuse (Visvanathan, 1996). It has been calculated that the chemical cost of losing 1 liter of plating solution will be at least \$2.20 (EPA, 1995).

Drain boards (Drip shields): The drain board consists of simple flat surfaces, installed between tanks and tipped toward the process tank for drainage. The drain board will catch all drag-out drainage during part movement from tank to tank. Solutions drip on the boards and drain back into their respective processing tanks. These systems have an angle to allow drag-out chemicals to collect and drain back into the tank (EPA, 1995; UNEP, 1998a; Luo and Huang, 1997; Mediterranean Action Plan, 2000). The schematic diagram of drain board application is given in Figure 2.5.

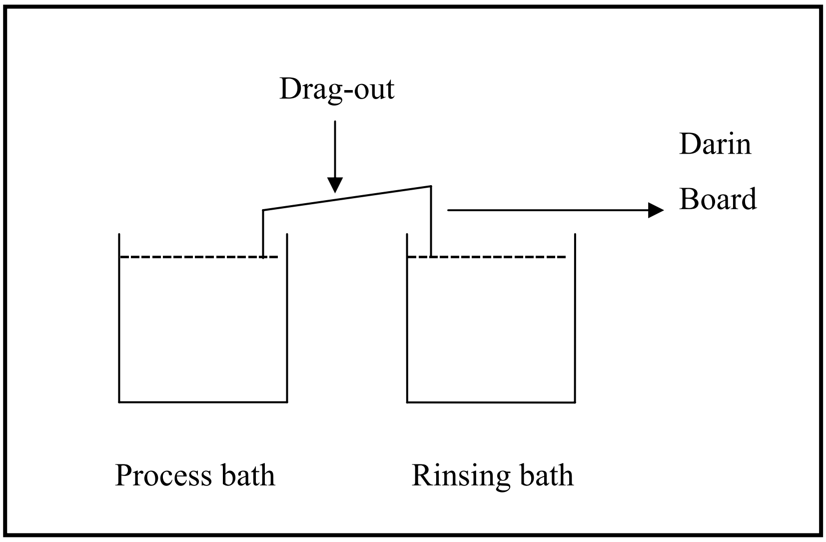


Figure 2.5. Application of drain board for drag-out recovery (EPA, 1993)

### 2.3.3. Plasma Desmear

Plasma can be defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles (Uner et al., 2000). Recent research has been indicated that plasma desmear, which eliminates water consumption at this process, can be used in cleaning circuit boards instead of permanganate desmear process. It has been discovered that radio frequency (RF) reactive cleaning with Oxygen ($O_2$), Nitrogen ($N_2$), Hydrogen ($H_2$) and carbon tetra fluoride ($CF_4$) can be used to remove epoxy-glass particle and copper drill smears in drilled through holes in printed circuit boards (Lee et al., 2002). The addition of relatively inert gases, such as nitrogen, stabilizes the plasma and controls the rate of ionization. Reactive oxygen species oxidize organic contaminants on the surface, creating volatile species that are pumped away. Etch rates are increased by providing more reactive species in the form of fluorine such as $CF_4$ (Fierr and Getty, 2003).

Located in Dayton, Ohio, Circuit Center Inc., manufactures approximately 34,875 $m^2$ of printed circuit board annually. The management of Circuit Center Inc. examined their desmear operations and realized that waste disposal costs related to this process were accounted for over 13% of the plant's environmental management costs. Costs associated with the permanganate process include wastewater treatment, chemical purchases, energy for the bath pumps and heaters, extensive labor for testing and maintaining the process baths within the required parameters and water costs. In some parts of the U.S., the costs of water used for the rinsing between baths can be a significant operating expense. For example, one larger facility (producing 197,400 $m^2$/year PCB) uses over 11,250 $m^3$ of water annually for their permanganate rinsing alone. CCI installed a plasma desmear unit and as soon as the system was in production, Circuit Center Inc. noticed a dramatic reduction in chemical consumption in both production processes and waste water treatment plant (EPA, 2006).

Plasma desmear is developed as a ‘dry’ and ‘clean’ method for removal of smear material. It was found to be an effective surface cleaning technique for PCBs to remove a very thin layer of contaminants from circuit surfaces. The application of plasma cleaning for circuit boards is widely exploited to improve wire bondability and interfacial adhesion. It can be seen that cost savings are resulted from the elimination of wastewater treatment, water use and off-site hazardous waste shipments associated with desmear. Additionally, operating costs were reduced. It is estimated that the energy used for the plasma desmear radio frequency generator is approximately the same as that used for permanganate bath pumps and heaters (Fierr and Getty, 2003).

## 2.4. Electroplating Industry in the World

### 2.4.1. Overall Production in Europe and Worldwide

The quantity of electronic equipment produced nowadays is very high and it has been constantly increasing due to the growth in the consumption of these goods by the population as well as the relatively short lifetime of this equipment (Veit et al., 2005).

In Europe, there are more than 10,000 firms in the surface treatment industry and 8300 companies with about 440,000 employees using so-called surface treatment equipment representing % 11 of all production in 2005 (Fresner et al., 2006). On the other hand, there are over 31,000 metal finishing facilities making up 18 % of all production industries in the United States according to a recent research carried out by Environmental

Protection Agency (EPA). According to EPA, automobile manufacturing, computers, electronics and metal finishing industries comprise over 11% of the US Gross National Product, employ over 4 million people and account for over 12% of the toxic releases. The US, Western Europe and Japan together accounted for 68.7% of world electronics production in 2001 (UNEP, 1998b).

Metal finishing, when taken as a whole, is one of the largest users of many toxic chemicals in the world. Electroplating alone is the second largest end user of nickel and nickel compounds and the third largest end user of cadmium and cadmium compounds. Electroplating also accounts for a substantial amount of chromium (hexavalent chromium; $Cr^{+6}$ and trivalent chromium; $Cr^{+3}$) use in the United States. In other words, this industry is responsible for managing large amounts of hazardous materials (ESCWA, 2001; Crama et al., 2002).

Copper is a metal of great importance for PCB and electronic industries. The large consumption of copper in these industries is due to his properties of electric conductivity and thermal conductibility. More than 50% of Cu world production is used in the electronic industries and about 30–40% of the copper world production is used for alloy production (Fornari and Abbruzzese, 1999).

Over the past two decades, the US domestic PCB industry has changed from being one in which US production dominated (with 42% of global revenue in 1984) to one in which the US production is largely irrelevant (less than 10% of global revenue in 2006) (La-Dou, 2006). China and Taiwan produced 220 million $m^2$ of PCBs and is estimated to supply about 20 percent of the world’s PCBs in 2004 (Glavič and Lukman, 2005). World PCB production rates divided by region are given in Figure 2.6.

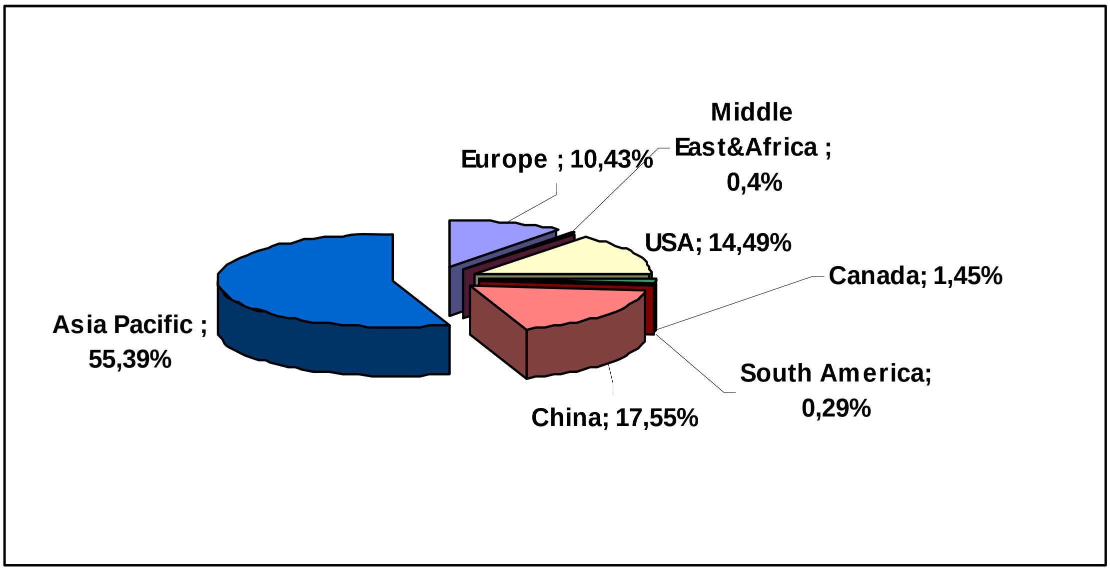


Figure 2.6. World PCB output divided by region in 2002 (DPPEA, 2002)

Today, Asia produces three-fourths of the world's PCBs, with over 1000 manufacturers in China alone. Only in the past 4 years, however, the US manufacturing has faced a serious decline. In 2003, the United States produced 15% of the world's PCBs, trailing Japan, the largest producer at 29% and China, the second largest at 17%. Taiwan was the fourth largest producer at 13%. Europe produced only 10% and South Korea 8%. For the time being, there isn't any US Company among the top ten manufacturers of PCBs. China will overtake Japan as the leader in PCB production in 2006. China is forecast to produce $10.6 billion worth of PCBs with 1,000 PCB production plant, accounting for 25% of the world total. According to The World Electronic Circuits Council Global PCB Production Report, the total PCB production in 2005 is estimated at just over 42.4 billion U.S. dollars with data from companies in the major producing countries/regions included (La-Dou, 2006). World PCB production value and production growth rates divided by region is given in Table 2.5.

Table 2.5. World PCB production value divided by region (CIRCUITREE, 2006)

| Region | Production Value (100M USD) | | | Percent in the World | |
|---|---|---|---|---|---|
| | 2002 | 2003 | Growth | 2002 | 2003 |
| North America | 53.67 | 55 | 2.48 % | 17.32 % | 15.94% |
| South America | 1.25 | 1 | - 20.00 % | 0.4 % | 0.29 % |
| West Europe | 34.62 | 36 | -3.46 % | 11.17% | 10.43% |
| East Europe | 1.23 | | | 0.40 % | |
| Russia | 1.44 | | | 0.46 % | |
| Middle East | 1.51 | 1.38 | -38.67 % | 0.49 % | 0.40% |
| Africa | 0.74 | | | 0.24 % | |
| Japan | 88.07 | 98.15 | 11.45 % | 28.42% | 28.45% |
| China | 44.99 | 60.54 | 34.56 % | 14.52% | 17.55% |
| Taiwan | 38.72 | 93.31 | 39.71 % | 12.49% | 26.94% |
| Korea | 22.58 | | | 7.29% | |
| Thailand | 5.49 | | | 1.77% | |
| Asia Total | 216 | 252 | 16.67 % | 69.70% | 72.94% |
| World Total | 316 | 345 | 9.18 % | 100.00% | 100.00% |

### 2.4.2 Electroplating Industry in Turkey

Production processes for the metal finishing includes automotive, electronics (including computers and semiconductor devices), telecommunications and mechanical parts fabrication industries in Turkey. Turkey PCB industry produces only $50 million worth of PCBs, accounting for 0.125 % of the world total production (ATOTECH, 2006).

Odak Inc.-İstanbul, Baskı Devre Inc-İstanbul, Ünal Elektronik Inc.-İstanbul, Beko Elektronik Inc.-İstanbul, Net Devre Inc.-Ankara, Bessan Inc,-Ankara, Beker Elektronik Inc.-Ankara, Aselsan Inc.-Ankara, Teknel Inc.-İzmir are the main electronic industries in Turkey. Canovate Inc. Co. was chosen for this study since it has a 15 % of Turkey’s total PCB and electroplated metal part production rate with being the second largest industry after Ünal Electronic Inc.

The selected industry, Canovate Inc. Co., aims to produce appropriate products for EU Directives such as RoHS (2002/95/EC), since they have a market in Israel, Germany, France and England. There isn't any production of Lead (Pb), Hexavalent chromium (Chromium VI or $Cr^{6+}$), Mercury (Hg), Cadmium (Cd), Polybrominated biphenyls (PBB), Polybrominated biphenyl ethers (PBBE) containing products because their usage are forbidden by RoHS Directive.

## 2.5. Environmental Relevance of Electroplating Industry

Electroplating industry has been generating a huge amount of waste in the forms of wastewater, waste solvent, waste process solutions and sludge. The industry has been labeled by the environmental regulators as handling many dangerous chemicals including cyanides, mineral acids (including nitric), heavy metals (including lead, hexavalent chromium, cadmium), EDTA (ethylenediaminetetraacetic acid) and organic solvents (toluene, xylene, chlorinated vapor degreasers) (Reeve , 2006).

In metal finishing industry, the major proportion of environmental management costs is spent on the wastewater treatment system. The cost of treatment chemicals can be over half the annual operating costs of the wastewater treatment systems and the total annual operating costs for wastewater treatment is often one half or more of the original capital cost of the system (UNEP, 1998a). To control waste disposal costs, metal finishers must focus on developing and implementing waste reduction programs.

In Western Europe, 8 million ton of electric and electronic waste was generated in 2004. The amount of this waste is expected to increase by at least 3–5% per annum. The generation of wastes from electrical and electronic equipment is around 7 kg/capita-year in Europe. In Taiwan, in terms of industries producing post consumer wastes, the top two are electronics and electrical engineering industries with 630.000 ton (43%) and metal industries with 200.000 ton (14%) in 2005 (Veit et al., 2005). Nowadays, approximately 1% of the hazardous waste in Europe is produced by the electroplating industry. The data in Table.2.6 show estimated world waste production of metals by different types of industries and it is possible to observe that the electronic industries play an important role in the emission of metals to the environment.

Table 2.6. World waste production of metals by different types of industries in 2002 (Veglio et al., 2005)

| Industries | Metals | Quantities (t/year) |
|---|---|---|
| Electronic | As, Pb, Cr, Hg, Se, Ni, Cu, Zn | 1,200 |
| Oil and Coal | As, Pb, Cd, Ni, Zn | 1,200 |
| Mining and metallurgy | Hg, Cr, Cu, As, Zn, Pb | 390 |
| Agriculture | Mg, As, Cu | 1,400 |
| Manufacturing | Cr, Co, Ni, Fe | 240 |

In particular, sources of metal finishing process wastewater include rinsing water, cooling water, blowdown water, exhaust scrubber solution, contaminated or spent electroplating or electroless plating baths, waste process baths such as etchants and cleaners that are contaminated, stripping and pickling baths containing nitric, sulfuric, hydrochloric and hydrofluoric acids.

Solid wastes caused by electronics industry include wastewater treatment sludge such as sludge containing cadmium, copper, chromium, nickel, tin or zinc. Moreover, other types of solid wastes including absorbents, filters, empty containers, contaminated solvents used for degreasing are of great importance. Also, vapors and mists both from degreasing and treatment processes and from solvents cleaning and plating operations lead to air emission generation (Veglio et al., 2005).

In metal finishing industry, plating process wastewater contains various kinds of toxic substances such as acid cyanide, alkaline cleaning agents, degreasing solvents, oil, fat and heavy metals such as Cr, Ni, Zn, Cu and Cd (Kentish and Stevens, 2001; Alvarez-Ayusoa et al., 2003; Hunsom et al., 2005). Table 2.7 shows the wastewater characteristics of acid zinc, cyanide zinc, chromium and nickel plating industries (EPA, 2006).

Table 2.7. Characteristics of the wastewaters (EPA, 2006)

| Wastewater | Parameter | |
|---|---|---|
| | Zinc, mg/L | pH |
| Acid zinc | 138 | 1.7 |
| Cyinide zinc | 40.5 | 12.8 |
| Chromium | 108 | 1.1 |
| Nickel | 50 | 6.0 |

In the zinc electroplating process, rinsing and disposal of waste plating solutions are at the origin of most harmful wastes. The waste materials resulting from the zinc plating process are mainly oils and greases in cleaning operations, alkalis from cleaner rinsing, dumped cleaners and alkaline plating baths, acids from pickling baths, plating bath rinsing, zinc metal and traces of cadmium metal from zinc plating rinsing water and dumped zinc plating baths (ESCWA, 2001). The types and volumes of hazardous wastewater generated from the metal finishing industry in Brisbane region of Australia are given in Table 2.7. It has been estimated that there are 130 electronics industry out of 100 is powder coating, 20 is electroplating, 5 is anodizing and 4 is galvanizing at this region. A relative scale of production, which is designed to 1-10, has been provided for these industries with the rate of 4, 10, 4 and 10, respectively (UNEP, 1998b).

Table 2.8. Types and volumes of hazardous wastewater generated by metal finishing industries in Brisbane region of Australia (UNEP, 1998b)

| Type of wastewater | Volume generated from metal finishing industry, $m^3$/year |
|---|---|
| Acid-Alkali-Metal wastes | 1,920 |
| Galvanising acids | 1,199 |
| Soluble heavy metal wastes | 321 |
| Solids requiring treatment | 219 |
| Soluble oils | 173 |
| Oil wastes containing phenol | 21 |

PCB composition is quite varied, containing polymers, ceramics and metals. The metal content is around 28% (copper: 10–20%, lead: 1–5%, nickel: 1–3%). The main concern is copper pollution from the many copper bearing chemistries consumed during PCB manufacture (EPA, 1995). As seen in Figure 2.8, waste etchant is the largest waste stream shipped off-site for most PCB industries. It also represents the most significant quantity of copper waste. Approximately 90-95 % of the total amount of copper discharged is from the inner layer and outer layer etching process (Hunsom et al., 2005).

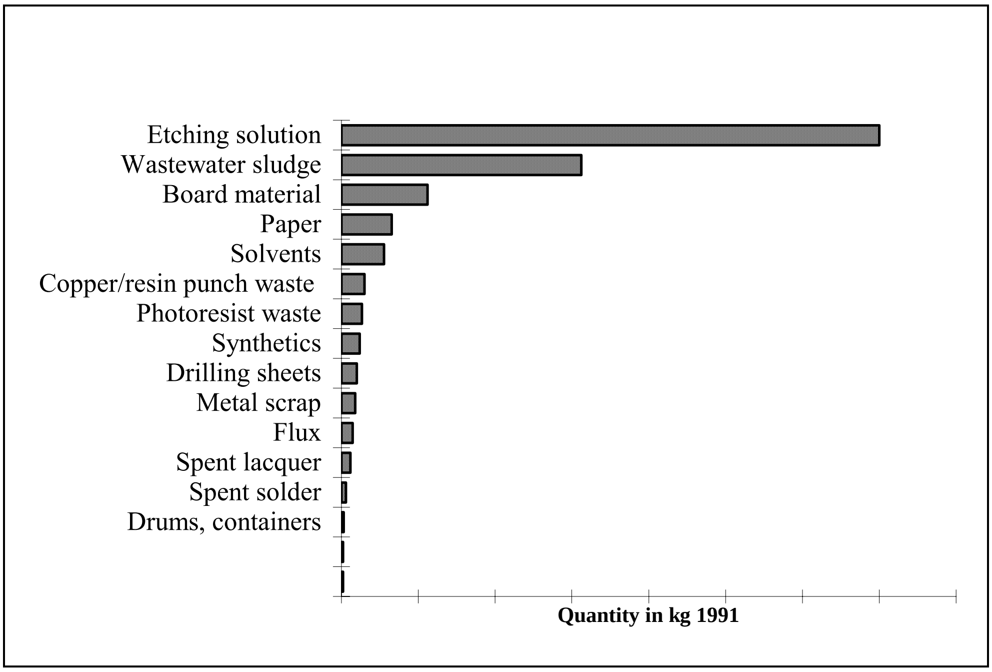


Figure 2.7. Waste streams in a PCB-Company (EPA, 1995)

It has been estimated that copper, lead and nickel concentrations in PCB production wastewater ranged from 0.4 mg/L to 100 mg/L, from 1 mg/L to 20 mg/L and from 1 mg/L to 7.5 mg/L, respectively according to the production rate (EPA, 1995). With the rapid growth of PCB industry, the total volume of generated spent etchant keeps increasing. Based on a market research in Singapore in 2002, it was estimated that 70,000 L/ month of spent ammoniacal etchant were produced by local PCBs industries (Yang and Kocherginsky, 2006).

In order to comply with effluent discharge regulations, the metal finishing industries prefer installation of end-of-pipe technologies, which generate toxic sludge that requires suitable disposal according to the local legislation (Viguri et al., 2000). The estimated amount of sludge from electroplating plants in 2004 is 80,000 tons for Germany and 4000 tons for Austria. Approximately 30% of the sludge is used as secondary raw material; the remainder is currently landfilled in Europe (Fresner et al., 2005).

It has been estimated that approximately 4000 and 150,000 tons/year of galvanic sludge were generated in Portugal and Europe countries, respectively in 2004. These sludge are generally classified as hazardous (European Waste Catalogue as adopted in Council Decision 2000/532/CE). It has been studied that the metal composition of non-cyanide zinc-plating sludge is 0.08 %, 0.33%, 0.03%, 0.78%, 6.93%, 0.01%, 37.5% for Al, Cd, Cu, Cr, Fe, Ni, Zn, respectively (Magalhaes et al., 2005). Air emissions from metal finishing activities mainly consist of two classes: volatile organic compounds which are produced by solvents used in degreasing and cleaning operations and fine dust mists that contain acids, metals and ammonia. These are also emissions of particulates from ovens and other processes (UNEP, 1998b). Volatilization of solvents during storage is another possible source of air emissions (Zufía et al., 2004). The types of waste generated from the metal finishing industry are summarized in Table 2.9.

According to the European Waste Code (EEC 200), the air emissions, which are associated with the use of electrolytic baths operated at high temperatures with the application of an electric direct current, classified as “code E”. These operating conditions result in the release of caustic emissions (E1) and acid emissions (E2) (Viguri et al., 2002). The air emissions from metal finishing processes must be controlled using air scrubbing equipment (Randal, 1998; Viguri et al., 2002).

The main sources of wastewater which is classified as “code L” are: (i) used cleaning and degreasing emulsions with oil, additives and dusts; (ii) the exhausted bath solutions discharged periodically when they lose their effectiveness due to the chemical depletion or contamination and acid pickling solutions with heavy metals and (iii) the rinsing water, to clean the drag-out from the pieces after removal from process baths (Viguri et al., 2002). More detailed classifications of electroplating wastes according to the Resource Conservation and Recovery Act (RCRA) code are given in Table 2.10.

Table 2.9. Summary of wastes generated from the metal finishing industry (UNEP, 1998a)

| **Waste Type** | **Source** |
|---|---|
| **Air emissions** | |
| Mists containing metals and acids | All finishing activities |
| Particulates | Metal polishing, powder coating |
| Fumes | Acids / alkalis |
| Volatile organic compounds (VOC) | Solvents, paint strippers |
| **Wastewater** | |
| Wastewater containing metals and process chemicals | Rinsing, equipment cleaning, spills |
| Acidic wastewater (nitric, sulphuric, hydrochloric, hydrofluoric) | Acid cleaners, pickling, etching |
| Alkali wastewater | Caustic cleaners, etching solutions |
| Plating solutions containing metals (cadmium, zinc, nickel, copper, chromium) | Contaminated plating solutions which are no longer efficient |
| **Solid waste & sludge** | |
| Precipitated metal sludge | Wastewater treatment |
| Filters and filter sludge | Filtering of cleaning and plating solutions |
| Oily / greasy rags | Pre-cleaning |
| Metal polishing residues | Polishing of metals prior to plating |
| Packaging and general wastes | |

Table 2.10. Classifications of the wastes in electroplating industry (Reeve, 2006)

| Waste category | Waste description | Process origin | Composition | EPA-RCRA code |
|---|---|---|---|---|
| Spent solvent | Spent alkaline cleaning solutions | Aqueous cleaning | NaOH, $Na_2CO_3$, $Na_2SiO_3$, $Na_3PO_4$, cyanide, EDTA +Mg/Ca, saponified and/or emulsified grease | D002 |
| | Spent acidic cleaning solutions | Acid pickling | HCl, $H_2SO_4$, $HNO_3$, $H_2CrO_4$, $H_3PO_4$, oils, soils | |
| Spent solutions | Spent plating solutions | Electroplating | Same as the compositions in relevant plating solution | D006 cadmium<br>D007 chromium<br>D008 lead<br>D009 mercury<br>D010 selenium<br>D011 silver |
| Treatment residue | Degreaser sludge | Pre-cleaning | Kerosene, naphtha, toluene, ketones, alcohols, ethers, halogenated hydrocarbons, oils, soil, water | F001<br>F002<br>F003<br>F005 |
| | Filter sludge | electroplating | Silica, silicides, carbides, ash, plating bath constituents | F008 |
| | Wastewater treatment sludge | Waste treatment | Metal hydroxides, sulfides, carbonates | F006 |

# 3. INTEGRATION OF POLLUTION PREVENTION STRATEGIES INTO THE COMPANY POLICY

## 3.1. Planning and Organization Phase of Cleaner Production Methodology

In this study, Electronics Industry is selected to implement UN-CP methodology in order to achieve waste minimization at source and resource conservation. The selected industry is concerned about Environmental Management Systems (EMS) which means that the company will be sure that it complies with all environmental regulatory requirements.

The aim of this phase is to obtain commitment of the enterprise about the advantages of Cleaner Production and to define the aim of the study for its successful implementation in the selected electroplating plant.

### 3.1.1. Involvement of the Enterprise within the Scope of the Project

Without sufficient commitment of the top management involvement, the Cleaner Production Assessment will be limited by a routine environmental management application. The management support was gained by giving information about the economic and environmental benefits of CP application through two meetings followed by one seminar.

During the meetings, it has been highlighted that CP assessment can be accompanied by significant reduction in the use of chemicals and water, improvement in process efficiency and product quality, decrease in the production cost and end off pipe treatment cost. It was concluded that CP application in electroplating companies was resulted in heavy metal elimination from effluents with recovery/reuse methods (99% Cu recovery has been achieved in PCB manufacturing) and it represents a significant benefit to the urban environment (Lee et al., 2003).

Also, special emphasize was given to the company image that will be renewed and market potentials on international base will increase in terms of obtaining external financing and adoption of Restriction of Hazardous Substances Directive (RoHS-2002/95/EC) and Waste Electrical and Electronic Equipment Directive (WEEE-2002/96/EC).

Information on eop treatment and CP implementation was made. It has been explained that eop treatment offers no new opportunities to the business development, while CP implementation provides optimization of the production processes, enhancement of the new trends towards process efficiency and finally facilitates the company's growth and competitiveness through operating condition improvement. Through the application of CP measures, savings can be made in the cost of waste treatment. At the same time, the optimization of production processes can lead to an increase in the business productivity due to time and labour savings. On the contrary, end of pipe treatment involves an additional cost that is dependent on regular production rate and it grows as production rate increases and has to be modified as updated or new regulation is put into use (Ministry of Environment Spain, 2000). At the end of these meetings, it was concluded that there will be continuous support by the top management of the company to the implementation of CP methodology.

### 3.1.2. Project Team

In order to get complete involvement of the enterprise, the leadership responsibilities are carried out by the product manager. The project team of this study has the following three members who are the representative of PCB production and metal finishing departments;

| | |
|---|---|
| Environmental Engineer, CP Expert | : Ms. Başak BÜYÜKBAY |
| Product Manager | : Mr. Erol YENİCİ |
| Production and Planning Manager | : Mr. Gün Evren GOREN, MSc |

### 3.1.3. Goal and Scope of the Project

The goal of this study is to implement Cleaner Production Assessment Methodology for the selected electroplating plant leading towards "Best Available Technology" application. Water and energy saving options are the prioritized issues of the cleaner production assessment. Together with pollution prevention, special emphasize is given to chemical substitution and its recovery. For the success of this study, cleaner production methodology developed by UN will be applied. After establishing the project team and goal & scope of the study, the fist step of the managerial roadmap is to define and overcome the barriers.

### 3.1.4. Barriers and Solutions

The input and output evolution and data collection is the primary step of the CP implementation (Barbiroli and Raggi, 2003). During planning and organization phase, raw material, chemical and water consumption amounts for each unit operation were measured and calculated since there isn't any recorded data in the company.

Measurement, collection and calculation of these data were achieved by considering the bath replacement periods and the concentration of chemicals in process baths. A project team consisting of product managers of the selected production processes was constituted for data collection. In cooperation with this project team, flow meters were established to the rinsing baths in order to identify process rinsing water consumption. Also, accountancy and purchasing department records about the amount of raw material, chemical and products on annual base for PCB production and metal finishing were investigated.

Organization barriers: As the selected enterprise has considerably attached importance to the sustainable production opportunities, the managers are easily convinced on determining both technical and managerial roadmaps for the success of pollution prevention. However, it has been impossible to overcome their interest in short term solutions for the reduction of their waste treatment.

Technical barriers: Since the plant was firstly constructed in 1966 in Ümraniye and moved to Alemdar in 2003, certain instruments are definitely old or not operated efficiently. There is also lack of flow meters especially in rinsing operations which creates problems in data collection. The insufficient records on water and energy consumption are also other technical barriers in the CP assessment audit focus determination.

Environmental barriers: Although the Company has not been certified for ISO 14001, they have been certificated for ISO 9001 since 2003. The wastewater treatment plant of the enterprise has been in service since 1972. Sufficient information about the process chemicals has been supplied through their Material Safety Data Sheet (MSDS) and the requirements of these sheets have been applied regularly. On the contrary, there exists the necessity of trainings to familiarize personnel with the MSDS. The trainings should cover the hazardous ingredients, health hazard data, first aid procedures and special precautions regarding each material used in production processes (Czech Cleaner Production Center, 2000). In general, the economic aspects of sustainability including environmental dimensions of the production processes and the interest of the company have been drawn.

## 3.2. General Information about the Selected Electroplating Industry "Canovate Electronic Inc. Co."

The aim of this phase is to provide general overview of the selected company's production and environmental aspects in order to define the CP focus points for assessment. The Company manufactures 6,000,000 $dm^2$/year electroplated metal parts and 140,000, 1,860,000, 83,000 $dm^2$/year single, double and multi layer circuit boards with the production rate of 6.7 %, 89.3% and 4.0%, respectively. In this phase, determination of all input-output quantities, raw materials, auxiliaries, energy and process water consumption, waste and emission generation, product and by-product given to the market on annual base and cost analysis have been carried out on the whole production plant basis.

The factory was firstly constructed in 1966 in Ümraniye and moved to Alemdar in 2003. It is located on 24,000 $m^2$ area in Alemdar-İstanbul. The enterprise is considered to be a small and medium-size plant (SME) with 220 personnel.

The selected electroplating industry, Canovate Inc. Co. designs, manufactures and markets 19" racks, cabinets, wall-mount enclosures, subracks, mechanical assemblies, structural cabling products, fiber optic products, multilayer and backplane printed circuit boards for industries of telecommunications, internet, networking and electronics.

Table 3.1. Summarized information about the Canovate Inc. Co.

| Summarized information about the Enterprise | |
|---|---|
| The name of the company | CANOVATE Electronic Industry Inc. Co. |
| Address | Turgut Özal Bulvarı No:4 Alemdar / İSTANBUL |
| Telephone | +90 216 484 22 22 |
| Telefax | +90 216 429 02 02 |
| Year for the reference for the data | 2005 & 2006 |
| Contact Person | Gün Evren GÖREN |
| Number of shifts | 2 shifts/24 hours |
| Working days/year | 230 day/ year for PCB<br>262 day/ year for metal finishing |

Total annual input-output and annual income cost evaluation of Canovate Inc. Co. is given in Table 3.2. The input-output evaluation method is based on material and energy flows and uses a set of profile indices, including water, chemical and wastewater unit index that describe all material flows related to the selected processes under investigation. The indices were used as a basis for determining an integrated index for overall environmental assessment of cleaner production technologies. This method was employed to evaluate environmental nuisance of implemented, modernized and modified technological processes as well to perform comparative analyses of alternative technologies (Fijał, 2007).

Table 3.2 depicts input-output analysis for each unit operation of the processes based mainly on the percentages of water and chemical consumed by selected processes. All the data given in Table 3.2 were measured/collected during the assessment phase with a continuous program for a duration of two months to identify the quality and quantity of raw material/water/chemical consumptions and wastewater production.

In determination of these inputs and outputs, chemical concentration and replacement periods of process baths were considered since there is lack of recorded data in the company. Flow meters were used in order to identify the amount of rinsing water consumption. Also, data records of accountancy and purchasing departments were evaluated within this scope. Alkaline zinc plating and double sided PCB production were chosen for the implementation of CP methodology as they have a great role;

a) on consumption of chemicals/ hazardous chemicals (91%)
b) on process rinsing water consumption rate (88 %) and,
c) on economic income of the plant with the highest production rate (91%).

In the production plant, 88 % of water is mainly used for process rinsing operation and the rest is used for chemical bath replacement and cleaning of the chemical baths. The raw water for the enterprise is supplied from a well and stored in 600 ton concrete basin (240 t/day) and has the characteristic of 700 µS/cm of conductivity, 32 Fr of hardness, and 0.05 mg/L of Fe. Raw water storage is followed by sand-carbon filter and reverse osmosis unit in order to produce process water with 85-90 µS/cm conductivity value. The rinsing water coming from zinc plating and PCB production rinsing operations also was passed through both sand and carbon filter and deionizer module which produce DI water with 5-6 µS/cm conductivity value. The 50 µS/cm conductivity value is achieved from the mixture of these two streams and is used in the production line. There are also two raw water tank with 20 ton capacity which was passed through only sand and carbon filter.

Table 3.2. The summarized total annual input-output and annual income cost evaluation of Canovate Inc. Co. (2005)

| **INPUTS/OUTPUTS** | **Amount** | **Amount (percent)** | **Cost (EUR/year)** | **Cost (per cent)** |
|---|---|---|---|---|
| **INPUTS** | | | | |
| **Raw material consumption** | | | | |
| PCB production | | | | |
| Epoxy plate for SS* dm$^2$/year | 318,500 | 7.6 | 45,036 | 3.0 |
| Epoxy plate for DS dm$^2$/year | 2,230,000 | 52.9 | 315,320 | 20.3 |
| Multi layer dm$^2$/year | | | | |
| - Pre-preg | 1,060,000 | 25.2 | 32,121 | |
| - middle layer | 200,000 | 4.7 | 27,273 | |
| - copper layer | 400,000 | 9.5 | 16,216 | 7.3 |
| | | | Total: 75,610 | |
| Zinc plating | | | | |
| Sheet steel (SS) dm$^2$/year | 6,000,000 | | 55,160 | 3.3 |
| **Chemical kg/year** | 126,481 | | 426,206 | 28.4 |
| **Water m$^3$/year** | | | | |
| - Raw water | 9,750 | 31.2 | 585 | |
| - DI water | 7,950 | 25.6 | 4,373 | |
| - Recycled water | 13,458 | 43.2 | 7,405 | |
| - Total | 31,158 | | 12,363 | 0.8 |
| **Electricity kWh/year** | 3,316,230 | | 250,153 | 16.9 |
| **Equipment maintenance and labor * EUR/year** | | | | |
| - Single sided PCB | | | 260,400 | |
| - Double sided PCB | | | 20,750 | |
| - Multi layer PCB | | | 14,000 | |
| | | | Total: 295,150 | 20.0 |
| **TOTAL INPUT COST EUR/year** | 1,475,234 | | | |

Table 3.2. The summarized total annual input-output and annual income cost evaluation of Canovate Inc. Co. (2005) (con't)

| **OUTPUTS** | Amount | Amount (per cent) | Income (EUR/year) | Cost (EUR/year) | Cost (per cent) |
|---|---|---|---|---|---|
| **Production** | | | | | |
| PCB production dm$^2$/year | | | | | |
| Single-sided | 140,000 | 6.7 | 112,000 | | 2.69 |
| double-sided | 1,860,000 | 89.3 | 2,232,000 | | 52.40 |
| multi layer | 83,000 | 4.0 | 249,000 | | 5.90 |
| Zinc plating | | | | | |
| Plated sheet steel dm$^2$/year | 6,000,000 | | 1,641,880 | | 38.50 |
| **Wastewater treatment m$^3$/year** | 17,609 | | 8,453 | | 0.24 |
| **Wastewater disposal m$^3$/year** | 17,609 | | 8,980 | | 0.26 |
| **Waste sludge kg/year** | 3,750 | | 397 | | 0.01 |
| **TOTAL OUTPUT COST EUR/year** | 4,256,364 | | | | |
| **NET INCOME EUR/year** | | | | | 3,161,882 |

* : Equipment maintenance and labor costs are 0.14 EUR/dm$^2$ for double sided, 0.25 EUR /dm$^2$ for multi layer and 0.1 EUR /dm$^2$ single sided PCB

SS*: single sided, DS: double sided, SS: sheet steel

The schematic diagram for preparation of process water and estimated costs of process water and wastewater are given in Figure 3.1 and Table 3.3, respectively. The Selected Company spends 17,609 € for wastewater treatment on annual base.

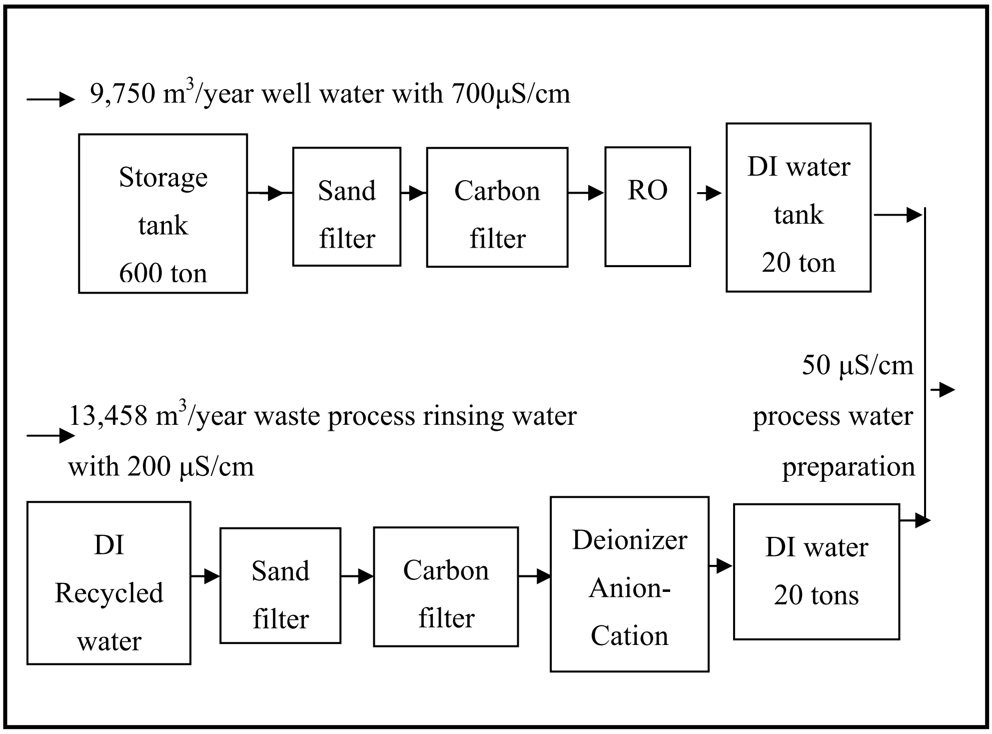


Figure 3.1. Preparation of process water

Table 3.3. The costs for water in Canovate Inc. Co.

| **Water** | **Cost ( €/$m^3$)** | **Zinc plating** | | **DS-PCB** | |
|---|---|---|---|---|---|
| | | **Amount $m^3$/year** | **Cost €/year** | **Amount $m^3$/year** | **Cost €/year** |
| - Well water<br>- Water from reverse osmosis application<br>Total | 0.06<br>0.49<br>0.55 | 1,800 | 990 | 6,150 | 3,383 |
| Raw water | 0.06 | - | - | 9,750 | 585 |
| Water from Deionizer module | 0.55 | 9,964 | 5,480 | 3,494 | 1,925 |
| **Total water consumption and costs** | | 11,764 | 6,490 | 19,394 | 5,893 |
| Wastewater treatment | 0.48 | 1,746 | 838 | 15,863 | 7,615 |
| Wastewater discharge | 0.51 | 1,746 | 890 | 15,863 | 8,090 |
| **Total cost for wastewater** | | | 1,708 | | 15,705 |

## 3.3. General Information about the Selected Production Lines

The production lines which will be evaluated in the electronics plant are Zinc Electroplating (Metal Finishing) and Printed Circuit Boards (PCB) Production.

### 3.3.1. Zinc Electroplating-Metal Finishing

This process consists of three main unit operations. These are;

Pre- treatment of metal parts: In metal preparation for finishing, the cleaning and degreasing are the most important processes. The contamination on hard surface which are films, particulates and oxidation products are removed by pre-treatment. Oil or grease lubricants and dust, soil matter, metal fines generate the composition of films and particulate matter, respectively (Randal, 1998). Cathodic cleaning with alkaline solution is the first step of the metal preparation and is consist of the application of “electrolytic oil cleaning agent”. Anodic cleaning is the second part of the cleaning and degreasing process and “hot oil cleaing agent” is used. Acid washing (pickling) is the last step of the pre-treatment process for the removal of metal oxides from the surface being plated. Sulphuric acid ($H_2SO_4$) is used as cleaning agent at this unit operation.

Zinc electroplating process: There are three basic ways of electrolytically plating zinc; acid zinc, alkaline zinc and cyanide zinc (Mediterranean Action Plan, 2000). The Selected Company uses alkaline zinc electroplating process. In this process, zinc reacts with the alkalis to give soluble zinc plating, according to the following reaction where hydrogen is also given off;

$$Zn + 2(OH)^- \rightleftarrows (ZnO_2)^{2-} + H_2 \qquad (3.1)$$

Table 3.4. Properties of the alkaline zinc electroplating process in the selected industry (Production Hand Book, 2001)

| Parameter | Range |
|---|---|
| Metallic Zinc | 4-16 g/L |
| Caustic Soda | 70-140 g/L (Caustic Soda provides conductivity of the bath and dissolution of the anode) |
| Voltage | 3-6 volt for rack, 9-18 volt for barrel |
| Temperature | 20-40 ºC (27 ºC optimum operating temperature) |
| Anode | Pure zinc in the steel baskets |
| Filtration | 20-30 micron permeability |
| Waste processes | Solution is neutralized with acid to pH 8.6-9.0 and zinc precipitate is filtrated. |

In Table 3.4, the operating parameters of zinc plating bath are given. Zinc plating provides a homogeneous surface and corrosion resistance to the metal object. In the selected company, if there is not any desired thickness by the customer, 5 µ zinc plating thickness is achieved, but 10 µ is also recommended for the life time of the plating object (Production Hand Book, 2001).

Post-treatment processes: Activation and pasivation processes (electropolishing) consists of hot concentrated acids to achieve a stainless steel mirror sheen parts. While nitric acid ($HNO_3$) is used as a cleaning agent in activation processes, trivalent chromium solution and nitric acid (($HNO_3$) are used for pasivation process. Passivation process also enhances the corrosion resistance of the finishing material. Each stage is fallowed by overflow rinsing.

### 3.3.2. Double Sided Printed Circuit Boards (PCB) Production

In the double sided PCB production process, laminated epoxy plate is cut and drilled. During drilling, the high temperature application leads to formation of melting resins (smear) at the edge of the holes. This smear constitutes a dielectric layer between the inner-layer copper surfaces and the plated copper.

For removal of this smear, permanganate desmear process is applied. At this unit, sweller as solvent (alkaline glycol ether), potassium permanganate ($KMnO_4$), M-alkali solution (sodium hydroxide based), reduction solution as a neutralizer and sulphuric acid ($H_2SO_4$) are used. Firstly, sweller and process water are used to soften the resin. After rinsing, oxidation of the swelled resin is achieved by the use of alkaline permanganate. A permanganate bath in an alkaline solution heated to 80 ºC removes the drill smear. This bath contains potassium permanganate ($KMnO_4$) in a sodium hydroxide (NaOH) based solution (M-alkali). During the oxidation process, the permanganate ion is reduced to manganate, which then reacts with water to form insoluble manganese dioxide (Goosey and Poole, 2005).

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^- \qquad (3.2)$$

After rinsing, the final bath is a neutralization step which is designed to remove all manganese residues, especially manganese dioxides from the board surface and through holes. Manganese dioxides residues can be sources of poor interconnect quality in micro-vias and poor hole wall adhesion problems through hole (Lee et al., 2002). Reduction solution and $H_2SO_4$ are used to stop the removal of resin and clean up the excess manganese (Goosey and Poole, 2005).

$$MnO_2 + H_2O_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + O_2 \qquad (3.3)$$

After drying, epoxy dust and cupper burs are removed from the epoxy plate in the deburring/brushing unit where a centrifuge system is used. The waste rinsing water which is collected separately in a “Cu wastewater tank” is filtered and recirculated continuously while waste cupper solution is sent to the wastewater treatment plant.

In direct metallization unit, holes, which will be plated electrolyte copper, are plated 0.5 μm conductive carbon. Shadow cleaner conditioner is a mildly alkaline aqueous solution which cleans both the copper and hole wall surfaces and conditions the hole wall to allow absorption of the shadow conductive colloid. Water rinsing removes excess conditioner from the material. Shadow conductive colloid which is a mildly alkaline aqueous dispersion of conductive graphite is used to provide a highly conductive coating on the copper and the hole wall surfaces. Fixer material is an acidic solution which causes a gel formation and renders the conductive coating semi-soluble in water. This solution also washes out excess colloid, leaving a very thin but highly conductive coating.

In microetch unit, sodium persulphate ($Na_2S_2O_8$) and sulfuric acid ($H_2SO_4$) solution penetrates into small micropores of colloidal coating. This process removes unwanted copper to protect the panels to oxidize prior to the subsequent process, such as soldermask application, direct metalization, pattern plating and hot-air-solder-leveling (Keskitalo et al., 2006). A slight etch of the copper surface will remove the graphite coating from this areas.

In the dry film unit, each surface of the panel is covered with 38 μm photographic film layer. Then, PCB is laminated with the heat and pressure. Pattern film is put on the panel surface and exposed on the surface of the panel using UV light. The parts of the film that are not exposed to UV light are developed by the sodium carbonate ($NaCO_3$) and then panel is rinsed.

Pattern plating, during which the circuit pattern and hole barrels are plated, starts with copper plating and is followed by a metallic tin-lead plating over the copper. At this unit, the plating thickness is 20 μm and 4-6 μm for copper and tin-lead coating, respectively. Acid cleaner, sodium persulphate ($Na_2S_2O_8$), sulphuric acid ($H_2SO_4$), tetra fluoroboric acid ($HBF_4$), tin tetra fluoroboricacid ($Sn(BF_4)_2$) and lead tetra fluoroboricacid ($Pb(BF_4)_2$) are used in pattern plating unit with 18 tanks capacity, hence high amount of chemical and water are consumed. Acid cleaner is used to remove the oil layer of the panel surface. Sodium persulfate and sulphuric acid are used to etch 0,5 μm Cu. Then, sulphuric acid baths are used to protect the cupper layer of the plate against the oxidation. PCB is plated with cupper, cleaned with tetra flouroboric acid bath and finally plated with tin-lead. At this unit, there are 9 rinsing tanks 6 of which are recycled rinsing. Each recycled rinsing bath has a capacity of 1.5 $m^3$/day. After this unit, the entire film layer is stripped by the resist stripper in the dry film stripping unit.

In the alkaline etching unit, the unwanted copper layer located under the stripped film is etched by the alkaline etch solution and ammonium hydroxide. 2.8 kg/hour copper is etched away from the panels at this unit (Production Hand Book, 2001). Therefore, waste alkaline etch solution contain high amount of copper which has economic value. When the copper content of the etchant increases beyond a certain level, the etchant can not continue to effectively remove the copper from the board and is considered as spent. Spent etchant is stored drums and is ultimately shipped off-site for reclamation. Then, the tin-lead layer located on copper layer of the panel is stripped by the tin-lead stripper.

The purpose of solder mask operation is to mask off and insulate physically and electrically those portions of the circuit to which no solder or soldering is required. At this unit, the panel surface is cleaned with pumice and water. Then, the panel is coated with solder resist (green die). This resist obtains electrical isolation to the plate. Then, parts of the solder resist surface that are not exposed to light is stripped from the panel by sodium carbonate and panel is dried at 150 ºC.

The HASL (the hot air solder leveling) process consists of a pre-clean, fluxing, hot air leveling and a post-clean. Pre-cleaning is done with a microetch process. At this unit, 0.5-0.6 µm copper is stripped by sodium persulphate ($Na_2S_2O_8$) and sulphuric acid ($H_2SO_4$) and coated with flux material which provides oxidation protection to the pre-cleaned surface. Hot air level machines consist of a panel transport mechanism that carries the panel into a reservoir of molten solder, then jets of hot air rapidly passes through the panel. All areas of exposed copper are coated with solder and masked areas remain solder-free. Boards are then cleaned in hot water and dried with hot air at 250 ºC.

The component names are written with solvent based die in screen printing unit and PCB is again dried in the position print unit. In the V-cutting unit, the edges of the plate are cut and the epoxy dust is vacuumed. Finally, PCB is rinsed with process water to remove epoxy dust and dried. After visual inspection and electrical test, PCBs are packed and shipped.

### 3.4. The Input and Output Evaluation of the Selected Processes

A framework of resource flow analysis through a product line is an emerging tool for quantifying and analyzing the economic and environmental impact of mass flows of a product as it moves from cradle-to-grave. These analyses can identify areas where a focus on practices could help promote more environmentally sustainable activity through reduced environmental impact, conservation of resources and improved economic performance. Water and chemical consumption and waste production audits are the proven tools to pinpoint water intensive operations in the production processes (Narayanaswamy et al., 2003).

Input and output evaluations of the production process were analyzed to comprehensively identify improvement CP opportunities. It concentrated on water and chemical usage in different production units, where the main sources of wastes and the major opportunities for improvement exist (Abbasi and Abbassi, 2004). These evaluations were also used to identify the costs associated with inputs, outputs and identified losses. Environmental performance indicators for the process were developed from the material balance data. This was achieved by dividing the quantity of a material input or waste stream by the production over the same period. Identification of overconsumed resources or excessive waste generation by performance indicators was achieved by comparing them with those of other companies or figures quoted in the literature (Fresner, 1998).

In the scope of these evaluations, site visits were performed and all process lines were examined. In identification of chemical consumption, bath replacement periods and chemical concentration of each process bath were taken into account. For water consumption determination, flow meters were established and production rates of the selected production lines were considered. Also, both raw material and chemical consumption and production records from related departments such as purchasing and accountancy were gathered and evaluated for PCB production and metal finishing departments. Since the required data about the energy consumption could not be obtained for each unit operation, information about the annual energy consumption and related cost calculations for the selected product groups are not included in this study.

The efficiency of the transformation of water and chemical consumption in the cycle were considered as water and chemical unit index. This was measured as the quantity of water and chemical used per both raw material and product. Besides, the wastewater intensity was evaluated as wastewater generation index. This was expressed as the quantity of wastewater per product unit (Barbiroli and Raggi, 2003). The examined water, chemical and wastewater unit index evaluations including cost analysis were given in Table 3.5 and Table 3.6 for each unit operation of the selected processes.

As it can be seen in Table 3.2, major production lines belong to double sided PCB and Alkaline Zinc Plating. Double Sided PCB production is responsible for the 89.3 % of the total PCB production while the only plating which is alkaline zinc has a production of 6,000,000 $dm^2$ for the year 2005. The water and chemical usage per unit production was calculated by utilizing data gathered in the preliminary investigation of the company. From Table 3.5 and Table 3.6, 12.36 kg water / $dm^2$ DS-PCB, 0.06 kg chemical/ $dm^2$ DS-PCB and 1.97 kg water / $dm^2$ SS, 0.004 chemical/ $dm^2$ SS values are calculated in terms of unit water and chemical consumption for double sided PCB and Alkaline Zinc Plating lines, respectively.

Also, unit chemical and water costs for producing 1 $dm^2$ double sided PCB and sheet steel were calculated for each unit operation. 0.2 EUR/ $dm^2$ DS-PCB and 0.008 EUR/ $dm^2$ SS are the unit chemical cost for double sided PCB and Alkaline Zinc Plating lines, respectively.

Table 3.5. Annual consumptions and cost analysis of raw material, product, waste and emissions of PCB production (2005)

| Product | | Desmear | De-burring | Direct Metallization | Micro Etching | Dry Film | Pattern Plating | Dry Film Stripping | Alkaline Etching | Tin-Lead Stripping | Solder Mask | Surface Finishing (HASL) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw Material | EP* $dm^2$/year | 2,230,000 | | | | | | | | | | |
| | kg/year | 780,500 | | | | | | | | | | |
| Chemicals | kg/year | Sweller: 361 | - | Cleaner: 927 | $H_2SO_4$: 300 | 38μPhotographic Film: 70,000 $m^2$/year | Acid cleaner: 665 | KOH: **1,150** | Etch solution :51,150 | Sn-Pb striper: **10,420** | Solder resist: 5,800 | $Na_2S_2O_8$: 750 |
| | | $KMnO_4$: 250 | | Colloid: 309 | $Na_2S_2O_8$: 750 | **$NaCO_3$: 2,200** | $Na_2S_2O_8$:750 | | $NH_4OH$: 25 | | $NaCO_3$: 800 | $H_2SO_4$: 1,200 |
| | | M-alkali: 230 | | Fixer: 254 | **Total: 1,050** | | $H_2SO_4$ : 300 | | **Total:51,175** | | **Total:6,600** | Flux : 1,595 |
| | | Neutralizer: 536 | | **Total:1,490** | | | $H_2SO_4$:800 | | | | | Sn-Pb: 2,900 |
| | | $H_2SO_4$:3,200 | | | | | $HBF_4$: 675 | | | | | **Total:6,445** |
| | | **Total: 4,577** | | | | | $Sn(BF_4)_2$: 180 | | | | | |
| | | | | | | | $Pb(BF_4)_2$: 120 | | | | | |
| | | | | | | | $BF_4$: 100 | | | | | |

Table 3.5. Annual consumptions and cost analysis of raw material, product, waste and emissions of PCB production (2005) (con't)

| Chemicals | | Desmear | De-burring | Direct Metallization | Micro Etching | Dry Film | Pattern Plating | Dry Film Stripping | Alkaline Etching | Tin-Lead Stripping | Solder Mask | Surface Finishing (HASL) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | kg/year | | | | | | Sn-Pb anode:1,825 | | | | | |
| | | | | | | | Cu anode:11,103 | | | | | |
| | | | | | | | **Total:16,518** | | | | | |
| | EUR/year | Sweller:1,473 | | Cleaner: 7,076 | $H_2SO_4$: 376 | 38µPhotographic Film: 119,000 | Acid cleaner:1,936 | KOH: **859** | Etch solution: 33,920 | Sn-Pb striper: 10,256 | Solder resist: 87 | $Na_2S_2O_8$: 2,106 |
| | | $KMnO_4$:1,371 | | Colloid: 20,900 | $Na_2S_2O_8$: 2,106 | $NaCO_3$: **443** | $Na_2S_2O_8$: 2,106 | | $NH_4OH$: 12 | **Total cost: 10,256** | $NaCO_3$: 161 | $H_2SO_4$: 1,507 |
| | | M-alkali :596 | | Fixer:999 | **Total cost:2,482** | | $H_2SO_4$ :376 | | **Total cost:33,932** | | **Total cost: 87,161** | Sn-Pb: 18,444 |
| | | Neutralizer: 2,123 | | **Total cost:28,975** | | | $H_2SO_4$:1,005 | | | | | Flux::4,446 |
| | | $H_2SO_4$:4,018 | | | | | $HBF_4$: 1,528 | | | | | **Total cost: 26,503** |
| | | **Total cost: 9,581** | | | | | | | | | | |

Table 3.5. Annual consumptions and cost analysis of raw material, product, waste and emissions of PCB production (2005) (con't)

| Chemicals | | Desmear | De-burring | Direct Metallization | Micro Etching | Dry Film | Pattern Plating | Dry Film Stripping | Alkaline Etching | Tin-Lead Stripping | Solder Mask | Surface Finishing (HASL) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EUR/year | | | | | | $Sn(BF_4)_2$: 1,157 | | | | | |
| | | | | | | | $Pb(BF_4)_2$: 278 | | | | | |
| | | | | | | | $HB_4$:48 | | | | | |
| | | | | | | | Cu anode: 42,192 | | | | | |
| | | | | | | | Sn-Pb anode: 9,526 | | | | | |
| | | | | | | | **Total cost:60,152** | | | | | |
| | kg chemical / kg raw EP | 0.00586 | | 0.00191 | 0.00135 | 0.00282 | 0.0212 | 0.00147 | 0.0656 | 0.0134 | 0.00846 | 0.0339 |
| | EUR chemical / kg raw EP | 0.0122 | | 0.0371 | 0.0032 | 0.153 | 0.0771 | 0.0011 | 0.0435 | 0.0131 | 0.0112 | 0.0339 |
| | kg chemical / kg DC-PCB*** | 0.00703 | | 0.00229 | 0.00161 | 0.00338 | 0.0254 | 0.00177 | 0.0786 | 0.016 | 0.0101 | 0.0099 |

Table 3.5. Annual consumptions and cost analysis of raw material, product, waste and emissions of PCB production (2005) (con't)

| Chemicals | | Desmear | De-burring | Direct Metallization | Micro Etching | Dry Film | Pattern Plating | Dry Film Stripping | Alkaline Etching | Tin-Lead Stripping | Solder Mask | Surface Finishing (HASL) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EUR chemical / kg DC-PCB | 0.0147 | | 0.0445 | 0.00381 | 0.00068 | 0.0924 | 0.00132 | 0.0521 | 0.0158 | 0.134 | 0.0407 |
| Water | kg/ year | 2,600,000 DI | 3,150,000 Raw Water | 1,200,000 DI | 850,000 DI | 1,000,000 Raw water<br>350,000 DI | 3,500,000 DI<br>500,000 Raw water | 800,000 Raw water | 900,000 Raw water | 800,000 Raw water | 2,600,000 Raw water | 1,150,000 DI |
| | EUR/ year | 1,430 | 189 | 660 | 468 | 253 | 1,955 | 48 | 54 | 48 | 156 | 633 |
| | kg water/ kg raw EP | 3.33 | 4.04 | 1.54 | 1.09 | 1.28 | 5.12 | 1.02 | 1.15 | 1.02 | 3.33 | 1.473 |
| | EUR water/ kg raw EP | 0.00183 | 0.00024 | 0.00085 | 0.00059 | 0.00033 | 0.0025 | 0.00006 | 0.00007 | 0.00006 | 0.00019 | 0.00081 |
| | kg water / kg DC-PCB | 3.99 | 4.34 | 1.84 | 1.31 | 1.54 | 6.15 | 1.23 | 1.38 | 1.23 | 3.99 | 1.77 |
| | EUR water/ kg DC-PCB | 0.0022 | 0.00029 | 0.001 | 0.00072 | 0.00039 | 0.003 | 0.000074 | 0.000083 | 0.000074 | 0.00024 | 0.00097 |
| | kg water / $dm^2$ DS-PCB | 1.39 | 1.69 | 0.65 | 0.46 | 0.54 | 1.88 | 0.43 | 0.48 | 0.43 | 1.39 | 0.62 |
| | EUR water/ $dm^2$ DS-PCB | 0.00077 | 0.0001 | 0.00035 | 0.00025 | 0.00014 | 0.0011 | 0.000026 | 0.000029 | 0.000026 | 0.00008 | 0.00034 |

Table 3.5. Annual consumptions and cost analysis of raw material, product, waste and emissions of PCB production (2005) (con't)

| Product | | Desmear | De-burring | Direct Metallization | Micro Etching | Dry Film | Pattern Plating | Dry Film Stripping | Alkaline Etching | Tin-Lead Stripping | Solder Mask | Surface Finishing (HASL) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $dm^2$/year | 1,860,000 | | | | | | | | | | |
| | kg / year | 651,000 | | | | | | | | | | |
| WW** treatment and disposal | kg / year | 2,596,655 | 3,146.655 | 1,196,655 | 846,655 | 1,346,655 | 3,996,655 | 796,655 | 896,655 | 796,655 | 2,596,655 | 1,146,655 |
| | EUR / year | 2,560 | 3,116 | 1,186 | 897 | 1,334 | 3,995 | 789 | 889 | 789 | 2,573 | 1,137 |
| | kg WW / kg raw EP | 1.159 | 1.411 | 0.537 | 0.379 | 0.604 | 1.791 | 0.357 | 0.402 | 0.357 | 1.165 | 0.514 |
| | kg WW / kg DS PCB | 3.973 | 4.834 | 1.838 | 1.3 | 2.069 | 6.139 | 1.224 | 1.377 | 1.224 | 3.989 | 1.761 |
| | kg WW / $dm^2$ DS PCB | 1.397 | 1.692 | 0.643 | 0.455 | 0.724 | 2.149 | 0.429 | 0.482 | 0.429 | 1.396 | 0.617 |

EP* : Epoxy plate
WW ** : Wastewater
DS PCB*** : Double sided printed circuit board

Table 3.6. Annual consumptions and cost analysis of raw material, product, waste and emissions of zinc plating production (2005)

| Product<br>By-Product | Unit | Cathodic Cleaning | Anodic Cleaning | Acid Washing | Zinc Plating ( 3 Bath) | Activation | Pasivation |
|---|---|---|---|---|---|---|---|
| sheet steel (SS*) dm$^2$/year | 6,000,000 | | | | | | |
| Chemicals | kg/year | Eloctrolytic oil cleaner: **260** | Hot oil cleaner: **420** | HCl(30-32%): **10,325** | Electrolytic Zn anode: 4,190 | $HNO_3$ (%56): **2,655** | Trivalent Chromium ($Cr^{+3}$) solution: 330 |
| | | | | | NaOH (96%): 2,550 | | $HNO_3$ (56%): 1,000 |
| | | | | | Zn-polisher 1,410 | | **Total:1,330** |
| | | | | | Booster: 1,140 | | |
| | | | | | **Total: 9,290** | | |
| | EUR/year | **279** | **434** | **1,423** | Electrolytic Zn anode: 24,570 | **493** | Trivalent Chromium ($Cr^{+3}$) solution: 1,259 |
| | | | | | NaOH (96%): 2,525 | | $HNO_3$ (56%): 186 |
| | | | | | Zn-polisher 8,672 | | **Total cost:1,455** |

Table 3.6. Annual consumptions and cost analysis of raw material, product, waste and emissions of zinc plating production (2005)$^{(con't)}$

| Chemicals | Unit | Cathodic Cleaning | Anodic Cleaning | Acid Washing | Zinc Plating ( 3 Bath) | Activation | Pasivation |
|---|---|---|---|---|---|---|---|
| | EUR/year | | | | Booster: 7,011 | | |
| | | | | | **Total cost:42,778** | | |
| | kg chemicals /dm$^2$ SS | 0.000043 | 0.00007 | 0.0017 | 0.0015 | 0.00044 | 0.00022 |
| | EUR chemicals /dm$^2$ SS | 0.000047 | 0.000072 | 0.00024 | 0.0071 | 0.000082 | 0.00024 |
| Water | kg/year | 400,000 Process bath<br>1,800,000 Rinsing bath No: 12<br>1,800,000 Rinsing bath No: 13 | 350,000 Process bath<br>1,600,000 Rinsing bath No: 8<br>1,600,000 Rinsing bath No: 9 | 350,000 Process bath<br>Rinsing bath No:9-8 | 50,000 Process bath<br>Rinsing bath No: 12-13 | 300,000 Process bath | 350,000 Process bath<br>1,600,000 Rinsing bath No:3<br>1,600,000 Rinsing bath No:4 |
| | EUR/year | 1,210 | 1,073 | 1,073 | 1,016 | 1,045 | 1,073 |
| | kg water/ dm$^2$ SS | 0.37 | 0.33 | 0.33 | 0.31 | 0.32 | 0.33 |
| | EUR/ dm$^2$ SS | 0.000202 | 0.000179 | 0.000179 | 0.000169 | 0.000174 | 0.000179 |

Table 3.6. Annual consumptions and cost analysis of raw material, product, waste and emissions of zinc plating production (2005)$^{\text{(con’t)}}$

| Product | dm$^2$/year | 6,000,000 | | | | | |
|---|---|---|---|---|---|---|---|
| Wastewater (WW**) (treatment + disposal) | kg/year | 391,000 | 341,000 | 341,000 | 41,000 | 291,000 | 341,000 |
| | EUR/year | 387 | 338 | 338 | 40.6 | 288 | 338 |
| | kg WW/dm$^2$ SS | 0.065 | 0.057 | 0.057 | 0.0068 | 0.049 | 0.057 |
| | EUR WW/dm$^2$ SS | 0.000065 | 0.000056 | 0.000056 | 0.0000068 | 0.000048 | 0.000056 |

SS* : Sheet Steel
WW ** : Wastewater

## 3.5. Generation of Cleaner Production (CP) Options

Synthesis, which is another tool in the waste audit, is used to determine the weak points in the system. After preparation of input and output evaluations for each unit operation, areas, where a focus on alternate CP Option could help promote more environmentally sustainable activity through conservation of resources and reduction of waste, were identified (Abbasi and Abbassi, 2004).

In evaluation of CP options, performance indicators was provided by dividing the quantity of a material input or waste stream by the production over the same period and used to identify overconsumption of resources or excessive waste generation by comparing them with those of other companies or figures quoted in the literature (Fresner, 1998).

The Cleaner Production options were identified according to the taken information from the company and literature survey made (Morina, 2000). The defined CP options categories, which are generated to reduce the environmental problems and to achieve economical benefits throughout resource conservation and recycling opportunists in the selected production plant, are (a) technology and process modification, (b) raw material change and conservation, (c) on site recycle/reuse/recovery, (d) goodhousekeeping practices. After identification of Cleaner Production options which were listed with the problems and their sources, prioritized CP opportunities were defined by holding a brainstorming session with the managers of the company.

Table 3.7. The generated CP options categories for the selected company

| **CP Option** | **Advantages** |
|---|---|
| **(A)Technology Modification** | |
| Plasma etch application in desmear process of Double Sided PCB production | Water consumption elimination and chemical consumption reduction in comparison with the permanganate desmear process. |
| Close loop cleaning system application in Pre-treatment of Zinc Plating | Reduction of water consumption and elimination of hazardous chemical consumption. |
| Longer drainage time implementation in zinc plating for drag-out minimization | More chemical drips back to process tank, which leads to chemical reduction in rinsing water. |
| Wetting agents application in general baths for drag-out minimization | Reduction of drag-out up to 50%, but in the meanwhile, foaming problems can occur. |
| Drag-out tanks application for drag-out minimization | Recovery of drag-out losses. |
| Drain board installation in zinc, copper and tin plating baths for drag-out minimization | Drag-out reduction up to 40 %. |
| Countercurrent rinsing application in rinsing baths of alkaline zinc plating line | Reduction of process water consumption. |
| Conductivity sensor and photo-sensor installation in rinsing baths of production lines | Monitoring and adjusting the quality and quantity of rinsing water. |
| Spray rinsing application in rinsing baths of production lines | Reduction in process water consumption. |
| Rinsing bath agitation | Increase in rinsing water quality. |
| Process wastewater segregation in production lines. | Water savings and increase in wastewater treatment plant efficiency. |

Table 3.7. The generated CP options categories for the selected company (con’t)

| | |
|---|---|
| (B**) Raw Material Substitution/Conservation** | |
| Consumption of non-chelated etchants such as sodium persulfate, potassium persulfate and hydrogen peroxide/sulfuric acid as substitutes for ammonium persulfate. | Increase in the metal precipitation in wastewater treatment plant. |
| Lead free solder substitution with tin-lead solder in HASL and Pattern Plating | Elimination of hazardous chemical consumption. |
| Trivalent chromium ($Cr^{3+}$) consumption instead of hexavalent chromium ($Cr^{6+}$), since hexavalent form is 500 times more toxic than the trivalent | Decrease in sludge and drag-out amount. On the top of this, elimination of hexavalent chromium which is more toxic. |
| **(C) On-site Recycle, Reuse and Recovery** | |
| Deionized rinsing water reuse in first rinsing baths | Reuse of first rinsing water in plating bath as evaporated water makeup. |
| Reverse osmosis application in rinsing water baths | Recovery and reuse of rinsing water up to 90-99% effectiveness. |
| Evaporation application in rinsing water baths | Reuse of condensate drag-out and water. |
| Electrowinning application in alkaline and micro etch of PCB production. | Recovery of metals from spent etching solution. |
| Particulate copper recovery in deburring unit of PCB production | Recovery of particulate copper using centrifuge filter and water reuse |
| Alkaline etchant recycling in alkaline etching process of PCB production | Recovery of pure copper metal, reuse of alkaline etchant and reuse of water. |
| Tin stripping solution recycling | Recovery of metals from tin stripping solution and recycle of tin etch solution. |
| Photoresist stripper recycling in resist stripper unit of PCB production. | Recovery of photoresist stripper. |

Table 3.7. The generated CP options categories for the selected company (con’t)

| **(D) Good House Keeping Measures** | |
|---|---|
| Deionized water consumption | Extension of plating bath life and minimization of sludge production. |
| Bath concentrations optimization | Reduction of chemical consumption |
| Bath filters installation | Extension of bath life. |
| Bath temperature increase | Minimization of drag-out losses. |

# 4. ASSESSMENT AND FEASIBILTY RESULTS OF CP OPTIONS

Assessment phase comprises collection of quantitative data, material and energy balances and identifying CP opportunities. In this phase, the mass balances of zinc plating and double sided printed circuit board production units were derived and checked. Appropriate CP options are proposed to reduce or prevent loss of materials. After CP options have been identified, they are evaluated following the same procedure used for evaluation of other investments or technical innovation options (Şişman, 2002).

In order to identify chemical consumption, bath replacement periods and concentration of chemicals in the preparation of baths were considered. Water consumption amount was measured by using flow meters and process bath replacement periods. In wastewater production, drag-out and evaporation lost which is 1.5 $mL/dm^2$ was taken into account. During the identification of raw materials and cost analysis, project team has been worked with many departments such as accountancy and purchasing department which provides the records of annual raw material and chemical purchase for PCB production and metal finishing production units.

According to the results of the pre-assessment phase, the audit focus points from the point of material balances were determined and derived during the assessment phase according to the taken information from the company and literature survey made. Hence CP options were generated and listed in order of priority through meetings which were held by company management (Gurbuz et al., 2004).

## 4.1. The Mass Balance Evaluation for the Selected Processes

A waste audit procedure is a systematic tool used to identify the opportunities of cleaner production. The information from a waste audit can be a starting point for investigating pollution prevention issues at any facility. Such an assessment of waste generation as well as raw material and energy consumption can provide a baseline for comparing subsequent increases or decreases in a specific waste stream (Avşar and Demirer, 2006). In order to conduct a descriptive audit which provides a detailed picture of all the relevant waste streams, a material balance approach was utilized for the Selected Electronics Industry.

The detailed flow chart of the production lines for “Double Sided Printed Circuit Board” and “Zinc Plating” are given in Figure 3.2 and Figure 3.3, respectively. A material balance makes it possible to identify and quantify previously unknown losses, wastes or emissions and provide an indication of their sources and causes. In order to make material balances more accurate, they were undertaken for individual unit operation. The results achieved from the evaluation of material balances will give concrete results about the contribution of these processes to the wastewater generation, chemical consumption which will support CP implementation (Fijał, 2007).

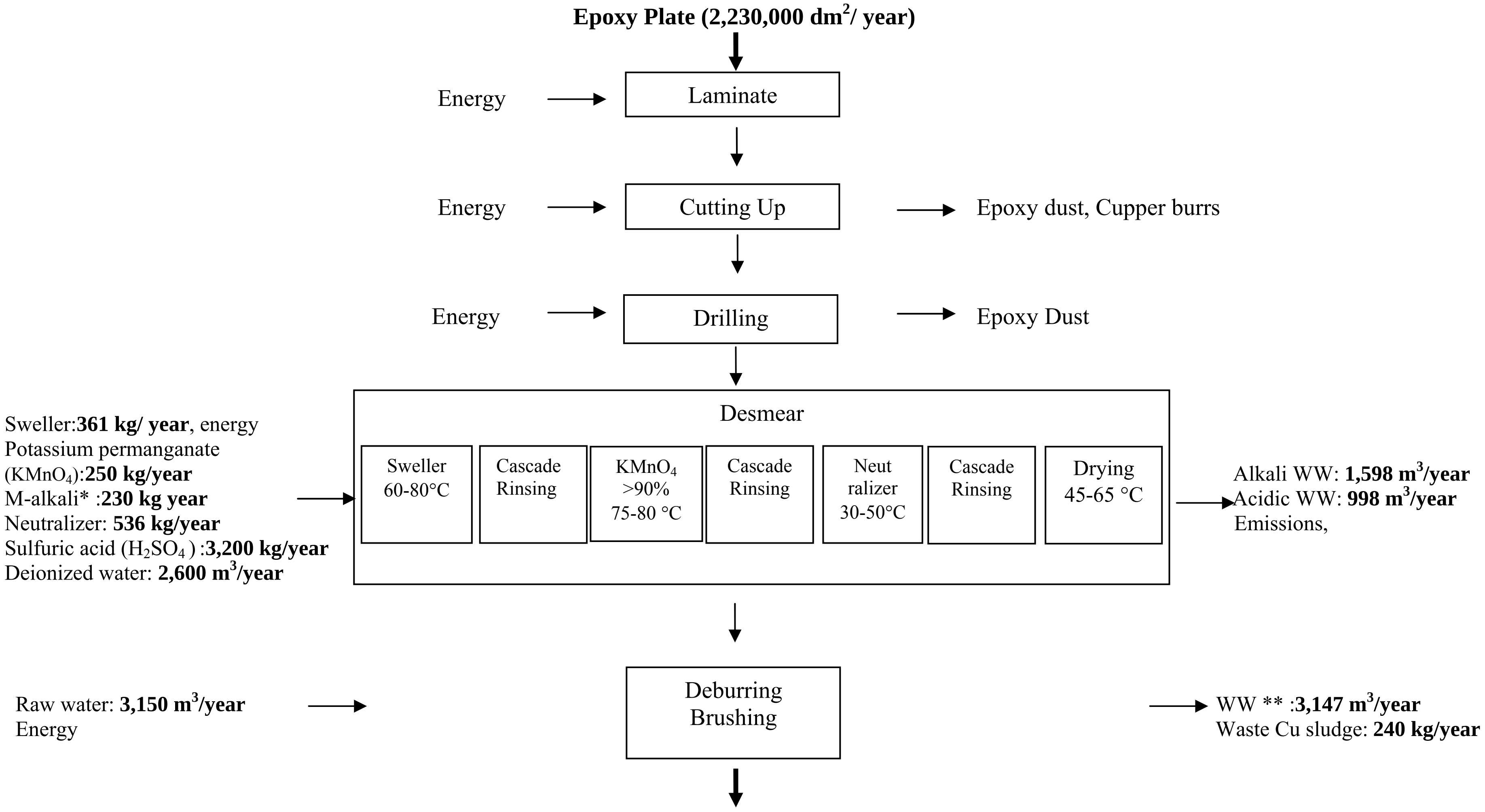
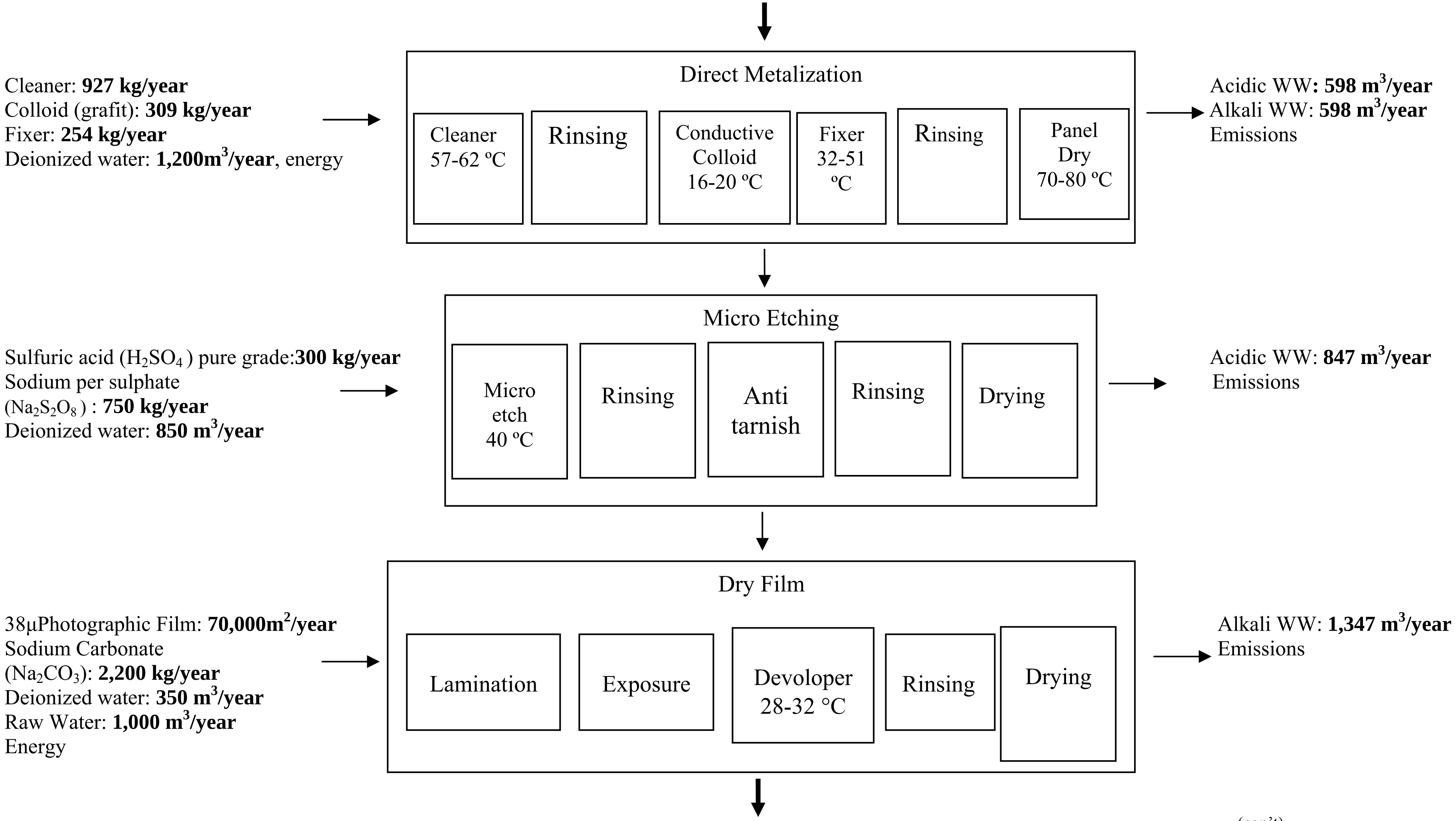


Figure 3.2. The detailed process flow chart of Canovate Inc. Co. for double sided PCB production line



Cleaner: **927 kg/year**
Colloid (grafit): **309 kg/year**
Fixer: **254 kg/year**
Deionized water: **1,200m$^3$/year**, energy

Acidic WW**: 598 m$^3$/year**
Alkali WW: **598 m$^3$/year**
Emissions

Sulfuric acid ($H_2SO_4$) pure grade:**300 kg/year**
Sodium per sulphate
($Na_2S_2O_8$) : **750 kg/year**
Deionized water: **850 m$^3$/year**

Acidic WW: **847 m$^3$/year**
Emissions

38μPhotographic Film: **70,000m$^2$/year**
Sodium Carbonate
($Na_2CO_3$): **2,200 kg/year**
Deionized water: **350 m$^3$/year**
Raw Water: **1,000 m$^3$/year**
Energy

Alkali WW: **1,347 m$^3$/year**
Emissions

Figure 3.2. The detailed process flow chart of Canovate Inc. Co. for double sided PCB production line $^{\text{(con't)}}$

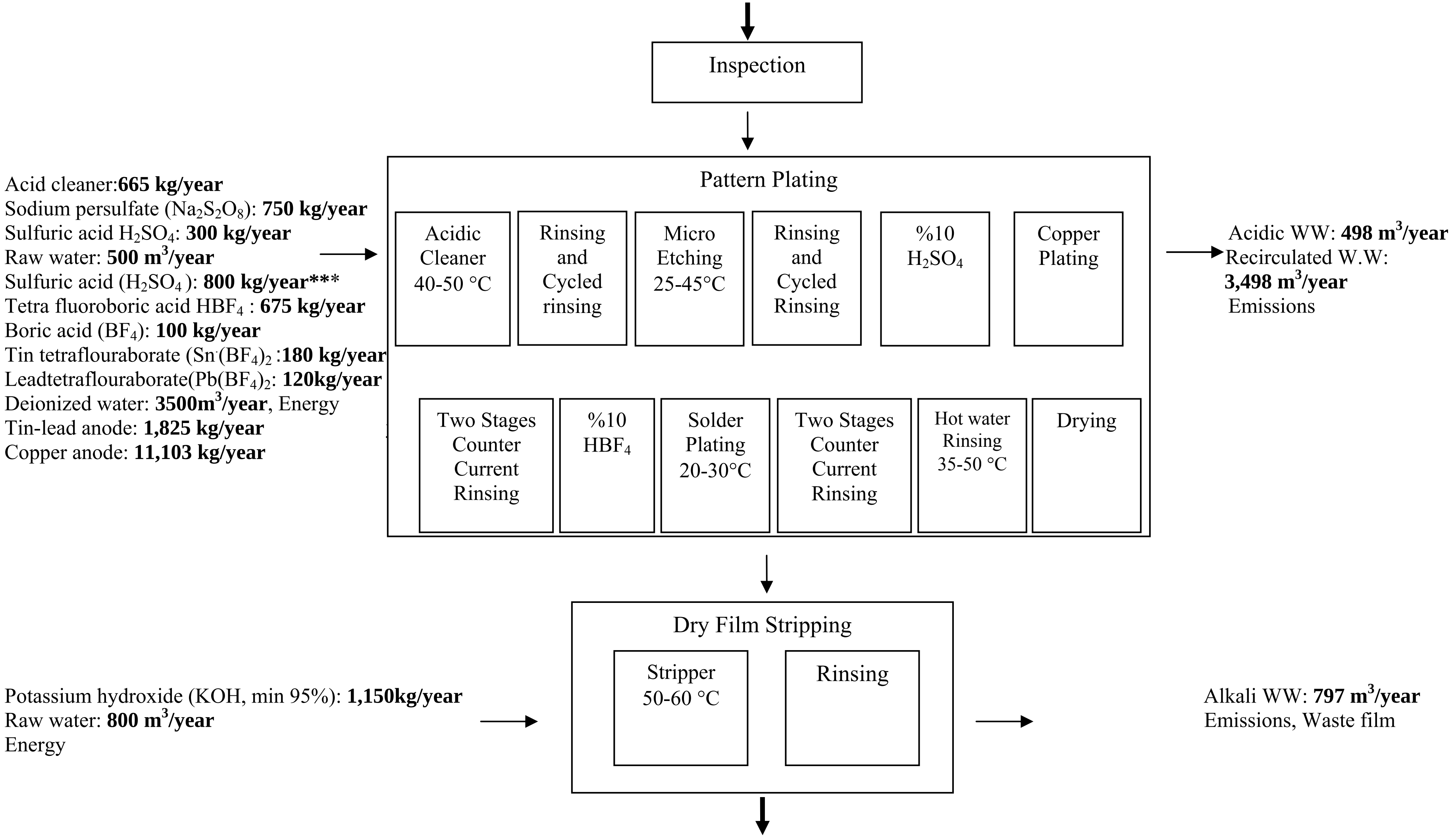


Figure 3.2. The detailed process flow chart of Canovate Inc. Co. for double sided PCB production line (con't)

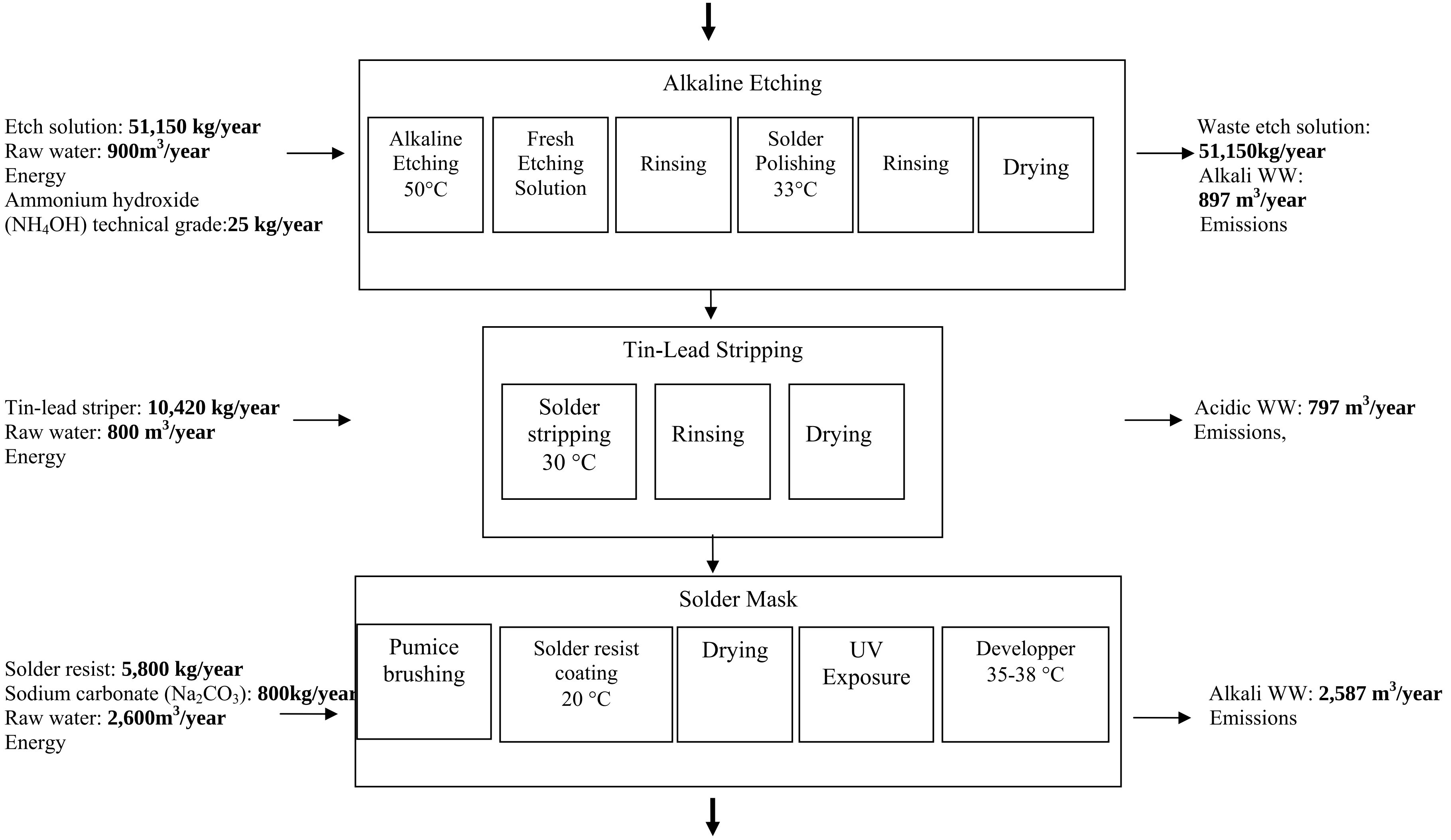


Figure 3.2. The detailed process flow chart of Canovate Inc. Co. for double sided PCB production line $^{\text{(con't)}}$

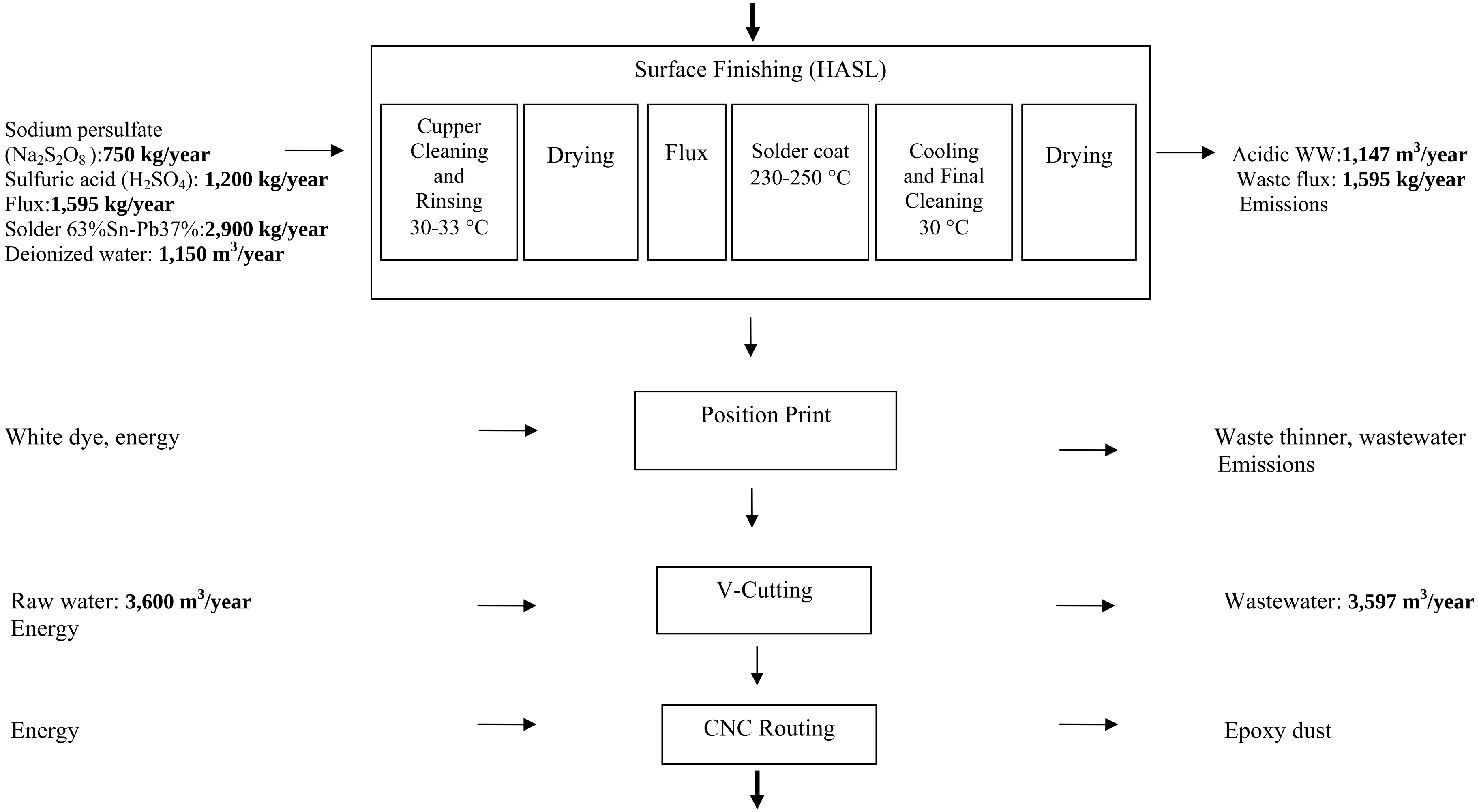
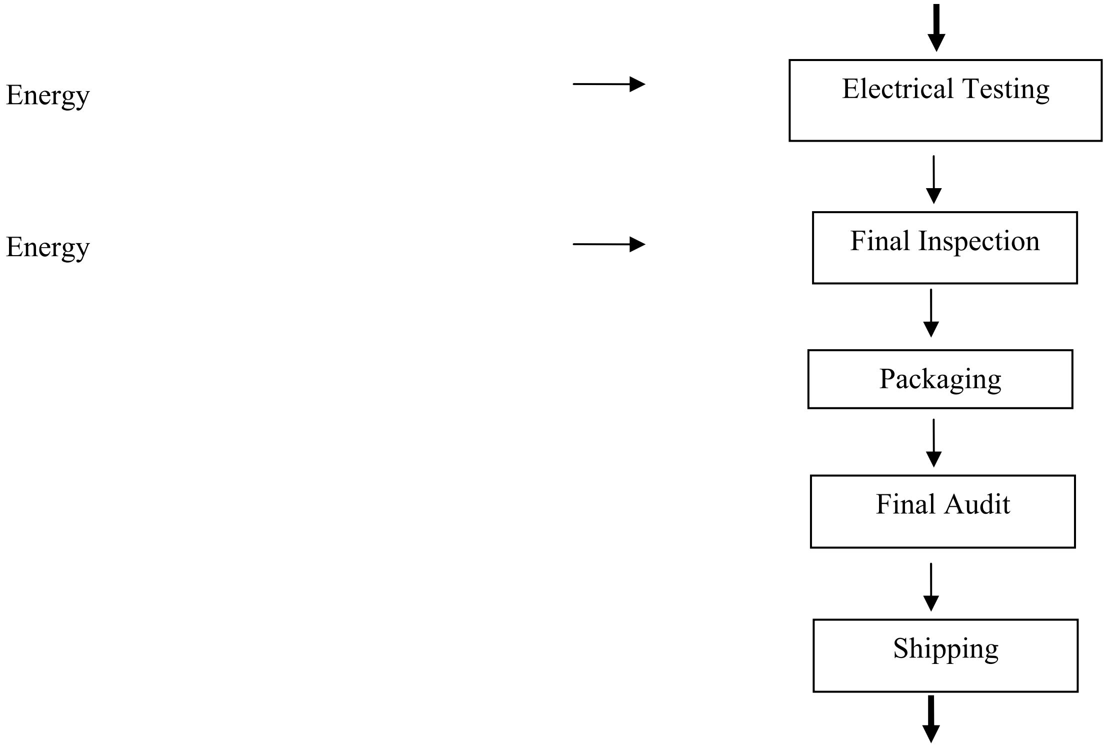


Figure 3.2. The detailed process flow chart of Canovate Inc. Co. for double sided PCB production line (con't)



**Double Sided Printed Circuit Board (1,860,000 dm$^2$/year)**

Figure 3.2. The detailed process flow chart of Canovate Inc. Co. for double sided PCB production line (con't)

* : NaOH based.
** : This wastewater is collected separately in a "Cu wastewater tank", filtered and recirculated continuously.
*** : Separate unit

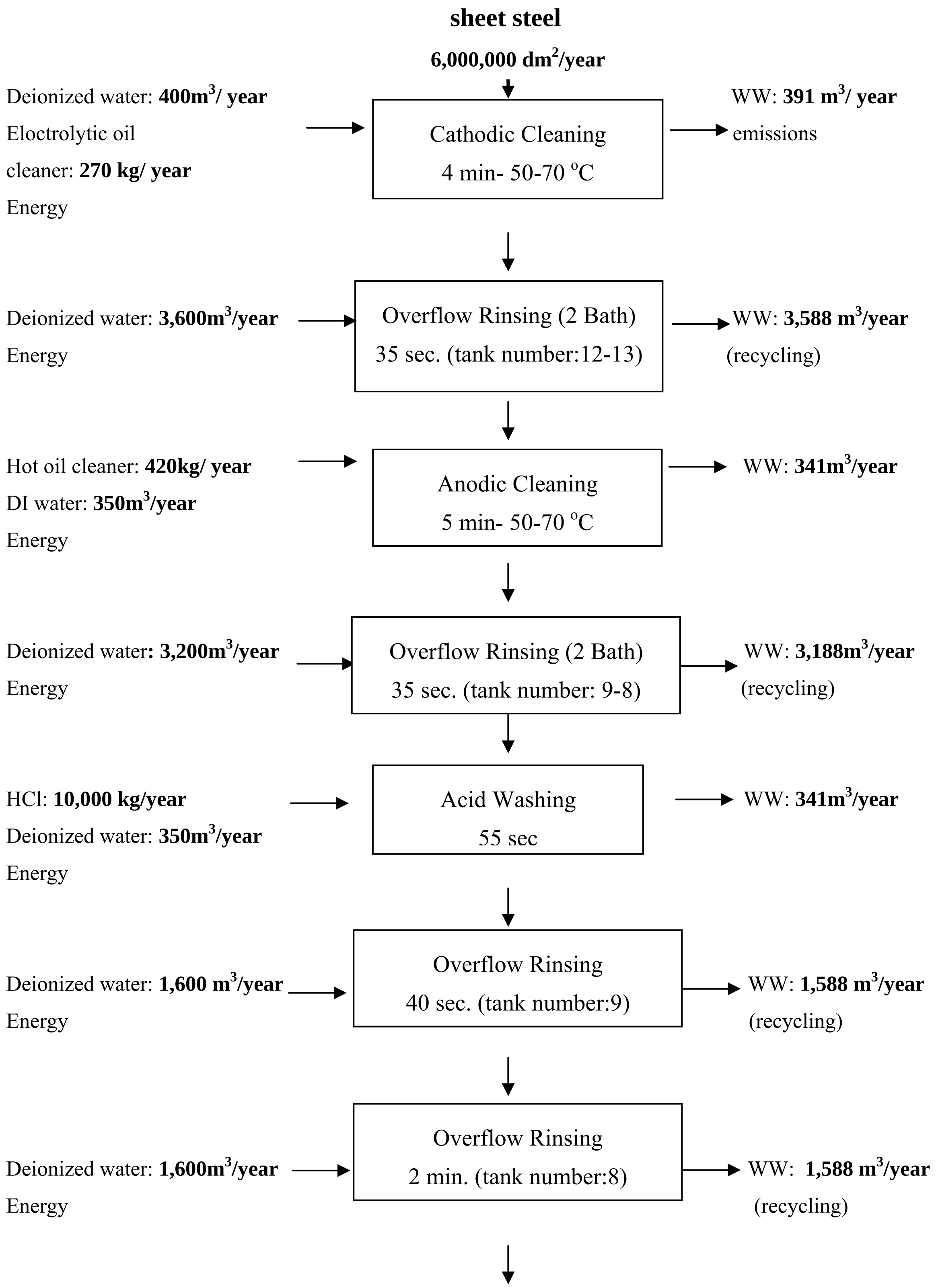


Figure 3.3. The detailed process flow chart of Canovate Inc. Co. for alkaline zinc plating

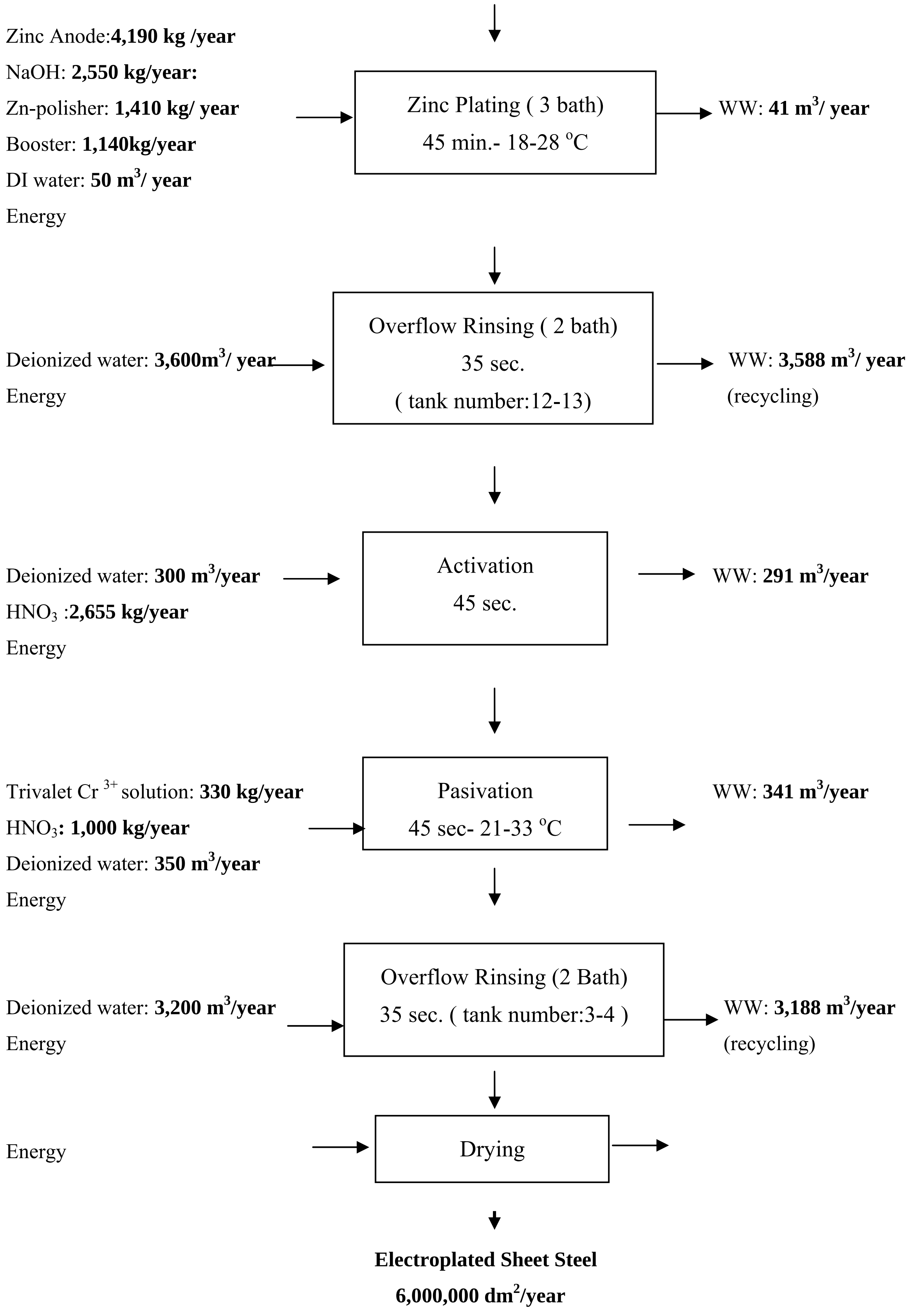


Figure 3.3.The detailed process flow chart of Canovate Inc.Co.for alkaline zinc plating
(cont'd)

## 4.2. Prioritization of Focus Points

The focus Cleaner Production opportunities were defined through meetings with related people from different departments and managers. In identification of focus points, product group that are responsible from the highest amount of production and that cause the most severe environmental pollution problems were considered. In determination of CP options, “technology modification”, “raw material substitution/conservation” and “on site recycle/reuse/recovery” options were considered.

The generated CP options were presented to the manager of the company and they were selected and prioritized by the manager. Among them, plasma desmear and closed loop cleaning system for pre-treatment of metal parts as technology modification, lead free coatings for HASL and pattern plating as raw material substitution/conservation and alkaline etchant regeneration system, continuous flow system for reusing of microetchant, drag-out recovery and counter current rinsing applications as on site recycle/reuse/recovery were selected since these options have a great effect on material recovery in terms of copper, etchant solution, plating chemicals and process rinsing water. These selected CP options which have been evaluated in detail in feasibility phase are summarized in Table 3.8.

Table 3.8. The selected and prioritized Cleaner Production options by the manager

| **Production Unit** | | **CP Option** | **Benefits** |
|---|---|---|---|
| **Technology Modification** | | | |
| Desmear | 1. | Substitution of permanganate desmear with plasma desmear | Elimination of an entire wet process line, reduction of chemical disposal, water consumption and treatment cost |
| Pre-treatment (anodic aleaning and cathodic cleaning) | 2. | Closed loop cleaning system for zinc plating | Elimination of solvent, recovery and reuse of the cleaning solution, sludge production minimization |
| **Raw Material Substitution/Conservation** | | | |
| Pattern plating | 3. | Lead free solder substitution | Adoption of EU Directive |
| Hot air solder leveling | 4. | Lead free solder substitution | Application of lead free HAL and Organic Solderability Preservative (OSP) which prevent lead containing solder. |
| **On-site Recycle/Reuse/Recovery** | | | |
| Alkaline etching | 5. | Etchant recovery process | Elimination of spent etchant generation, reduction of raw material consumption in terms of alkaline etchant chemical, recovery of copper metal from the spent etchant, rinsing water recycle and reuse. |
| OSP and direct metallization microetch unit | 6. | The continuous-flow system for reusing microetchant | Recovery of copper, reduction in copper load of wastewater treatment plant and treatment cost. |

Table 3.8. The selected and prioritized Cleaner Production options by the manager (con't)

| **On-site Recycle/Reuse/Recovery** (con't) | | | |
|---|---|---|---|
| Rinsing operations of zinc plating | 7. | -Two stage counter current rinsing and drain bath application<br>-Recycle/reuse of rinsing water by reverse osmosis | Minimization and recycle/reuse of rinsing water |
| Alkaline zinc and pattern plating | 8. | Drag-out recovery by<br>-Drainage time optimization<br>-Drain boards application | Drag-out reduction and minimization of plating chemical lost by drag-out |

Cost estimation and economic assessment of the proposed CP options were evaluated in order to estimate the feasibility of the option. The cost estimate and assessment for all equipment needed for the proposed CP options were based on tentative market survey. The economic assessment was based on the expected capital cost for each recommended solution in addition to the operation costs for the different components (Abou-Elela et al., 2006). The capital cost, which was based on the current prevailing prices for year 2006, was estimated. The running cost covers operation costs which comprise water and chemical consumption and wastewater treatment and discharge costs.

At a technical level, after having identified a number of environmentally relevant technical aspects for the various stages of the production processes, these were quantified both before and after the adoption of recommended CP option and the relative improvements (in terms of percentage changes) were computed. Besides the technical assessment, measures are taken of some typical performance indicators at an economic level in order to obtain a more comprehensive assessment of a given innovation. The aggregation of the calculated annual saving gives a global score which is a measure of the environmental improvement brought by the recommended CP option for each unit operation analyzed (Barbiroli and Raggi, 2003).

For measuring CP results, the comparison of the company's environmental and economic performance before and after implementation of a CP project was made. This would typically lead to the use of pollution intensity indicators, expressed as net environmental impact (e.g. kilogram of waste, water and chemical used) per unit of raw material and production. (Howgrave-Graham and Berkel, 2007).

## 4.3.Technology and Process Modification

### 4.3.1. Substitution of Permanganate Desmear with Plasma Desmear

Plasma is an electrically neutral mixture of physically and chemically active gas phase species including ions, radicals and reaction by-products. These active gas phase species can perform numerous surface modification processes including contamination removal and etching (Luo and Huang, 1997; CIRCUITREE, 2006).

The recommended plasma process consists of four major components: the vacuum chamber, electrodes, vacuum pump and a RF power supply and requires the use of Oxygen ($O_2$), Nitrogen ($N_2$), Hydrogen ($H_2$) and tetrafluoromethane ($CF_4$). The panels are suspended between electrodes. Unlike the permanganate series of wet chemical tanks, the plasma desmear process takes place in a compact, sealed chamber. In plasma desmear, the PCB panels are suspended between a pair of electrodes located within the vacuum chamber. A vacuum pumping system is utilized to maintain a plasma process pressure. Source gases are introduced through mass flow controllers at a specified flow rate. Once the desired process pressure is achieved, RF power is applied to the electrodes thereby initiating the plasma process. The typical frequency for the RF discharge is 13.56 MHz (Randal, 1998). The schematic diagram of recommended system is given in Figure 3.4.

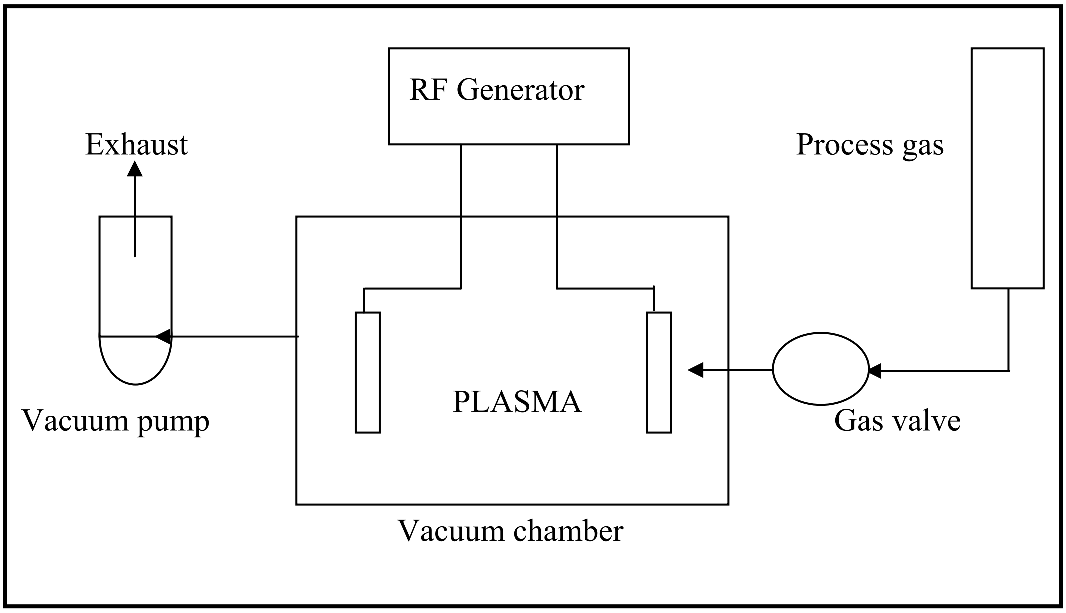


Figure 3.4. The recommended plasma system configuration (PLASMA-ETCH, 2005)

The radicals react with the polymer smear on the board, breaking the polymer into water vapor, carbon dioxide and hydrofluoric acid, all of which are volatile and vaporize at the low pressure. At this process, only small amounts of process gases are needed to get efficient reaction rates, because the reaction takes place in a vacuum (Crama et al., 2002). In contrast to the open, heated baths of the permanganate process, occupational health and safety issues associated with the enclosed plasma process are greatly reduced. The small amount of hydrofluoric acid (HF) generated by the process is toxic by inhalation and ingestion and is highly corrosive. An alkaline wet scrubber was recommended to neutralize the hydrofluoric acid gas produced. The scrubber is equipped with a pH meter to indicate to the operator when additional alkaline solution should be added (EPA, 2006).

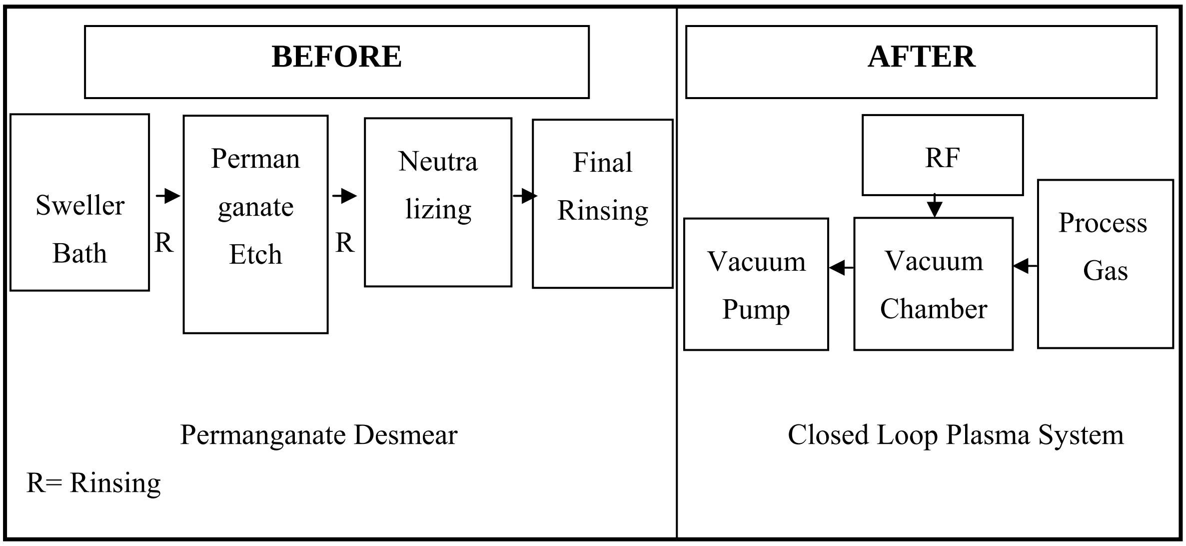


Figure 3.5. The schematic diagram for the comparison of the process before and after "plasma desmear"

Table 3.9 gives the recommended plasma desmear system specificaions. In the recommended system, the flow rate of the gasses (375 $CF_4$ /375 $O_2$ $cm^3$/minute) for desmear process which requires 10 minutes is 3750 $cm^3$ /cycle for $CF_4$ and $O_2$. Etchback is typically 20 minutes with the same gas flow of 375/375 $cm^3$/minute and the consumption amounts of $CF_4$ and $O_2$ are 7500 $cm^3$ /cycle. In surface activation, the recipe for 25 minutes at 1500 watts is 700 $N_2$ / 300 $H_2$ $cm^3$ /minute and the consumption amounts of $N_2$ and $H_2$ are 17,500 $cm^3$/cycle and 7500 $cm^3$ /cycle, respectively (PLASMA-ETCH, 2005). In one cycle, 335 $dm^2$ boards can be processed so; the required process gases for 1,860,000 $dm^2$ printed circuit board are calculated as follows;

Required cycle for annual production: 1,860,000 $dm^2$ / 335 $dm^2$/cycle= 5552.24 cycle

Required process gasses: $CF_4$= (5,552.24 x 3750) + (5,552.24x 7,500) = 62.46 $m^3$

$O_2$= (5,552.24 x 3,750) + (5,552.24x 7,500) = 62.46 $m^3$

$N_2$ = 5,552.24 x 17,500 = 97.16 $m^3$

$H_2$= 5,552.24 x 7,500 =41.64 $m^3$

Table 3.9. The recommended plasma desmear specifications (PLASMA-ETCH, 2005)

| Standard system features | Specifications |
|---|---|
| Electrodes, horizontal planar | 12 level, 457mm X 610 mm |
| Temperature control | 52 $^{o}$C- 149 $^{o}$C |
| RF generator | 3000 W-13,56 MHz |
| Mass flow controller, 2 channels | 0-2000 cm$^{3}$/min |
| Oil mist eliminator, vacuum pump | Included |
| Fume scrubber | Included |
| Chilled water recirculator, closed loop | 20 $^{o}$C |
| Fume scrubber | Included |
| Facility requirements | |
| Water service (2-4 bar pressure, closed loop) | 226 L/hour |
| Air service (5.5-8.6 bar pressure) | <0.85 m$^{3}$/hour |

As seen in Table 3.10, although system has a long pay-back period time, 2,600 m$^{3}$/year water consumption and 4,577 kg/year hazardous chemical consumption containing alkalis, acids and solvents are totally prevented. Also, the recommended plasma desmear system eliminated the end-of-pipe treatment and sludge disposal cost since there isn't any wastewater production. While the environmental performance indicators for the existing system are 3.99 kg water / kg DC-PCB and 0.0022 EUR water/ kg DC-PCB as water consumption index and  3.973 kg WW / kg DS PCB and 0.0039 EUR WW/ kg DC-PCB for wastewater index, these indices decreased to zero since water consumption was eliminated in the recommended system.

Table 3.10. Summary of the economic evaluation of “plasma desmear”

| **Parameter** | **Old process** | **New process** | **Savings** |
|---|---|---|---|
| **Amount and cost of resource and chemical consumption** | | | |
| **Raw material** | | | |
| Epoxy resin dm$^2$/year | 2,230,000 | 2,230,000 | - |
| kg/year | 780,500 | 780,500 | |
| % | 89.30 | 89.30 | - |
| **Water m$^3$/year** | 2,600 | - | 2,600 |
| % | 8.43 | - | - |
| EUR/year | 1,430 | | 1,430 |
| **Chemicals kg / year** | Sweller : 361<br>$KMnO_4$: 250<br>M-alkali : 230<br>Neutralizer: 536<br>$H_2SO_4$:3,200<br>Total: 4,577 | $CF_4$ : 62.46 m$^3$<br>$O_2$: 62.46 m$^3$<br>$N_2$: 97.16 m$^3$<br>$H_2$: 41.64 m$^3$<br>Total: 263.72 m$^3$ | |
| % | 4.49 | - | - |
| EUR/year | Sweller: 1,473<br>$KMnO_4$: 1,371<br>M-alkali : 596<br>Neutralizer: 2,123<br>Total cost: 5,563 | $CF_4$ : 2,199<br>$O_2$: 131<br>$N_2$: 378<br>$H_2$: 707<br>Total cost:3,415 | 2,148 |
| **End of pipe treatment cost** | | | |
| Wastewater produced m$^3$/year | 2,597 | - | 2,597 |
| Cost of treatment and disposal EUR/year | 2,574 | - | 2,574 |
| **Annual savings EUR/year** | | | **6,152** |
| **Investment cost** | | | |
| Plasma system (second hand) EUR/piece | | | 43,230 |
| Fume scrubber (second hand) EUR/piece | | | 1,530 |
| **Total** | | | 47,760 |
| **Pay-back period year** | | | 7.2 |

### 4.3.2. Closed Loop Cleaning System for Zinc Plating

The recommended "Closed Loop Cleaning Systems" needs aqueous cleaning solutions instead of solvents to achieve high-quality cleaning. This technology prevents the hazardous solvent wastewater production in pre-treatment unit and reduces hazardous solvent content of wastewater generated and total amount of hazardous sludge generation. The closed loop cleaning system combines the time-tested elements of natural bioremediation and aqueous cleaning technology in terms of greater efficiency and costs savings. BIO Soak Cleaner which is used as cleaning agent in the system contains hydroxide ($OH^-$) and silicate ($SiO_4$) to saponify fatty acids/oils, anionic and nonionic surfactants as emulsifying agent and gluconate ($C_6H_{12}O_7$) to remove metallic oxides. It is an alkaline liquid which is operated at pH 12, very suitable for rapid growth of new microorganisms; it can be easily installed into the existing lines and operated at lower temperature (40-50 ºC). Air agitation is required, since it contains aerobic microorganisms for bioremediation (ATOTECH, 2006).

In this system, the self-contained, closed-loop BIO filter unit removes sludge and monitors and maintains the temperature, pH and surfactant levels in the working soak cleaner. BIO filter unit has three metering pump for BIO cleaner, BIO minus and BIO Plus which are used for pH adjustment and two magnetic drive pump to feed the solution from the cleaner tank to the filter unit and return the solution to the cleaner tank (ATOTECH, 2006). Thus the process is constantly working under optimum conditions for 1-1.5 year. The benefits of the system are energy saving with low operating temperature, closed loop system with low waste treatment costs, minimal tank residue generation which eliminates costly hazardous sludge disposal, continuous replenishment, bioremediation technology which is environmentally friendly, moderate pH and simple operation.

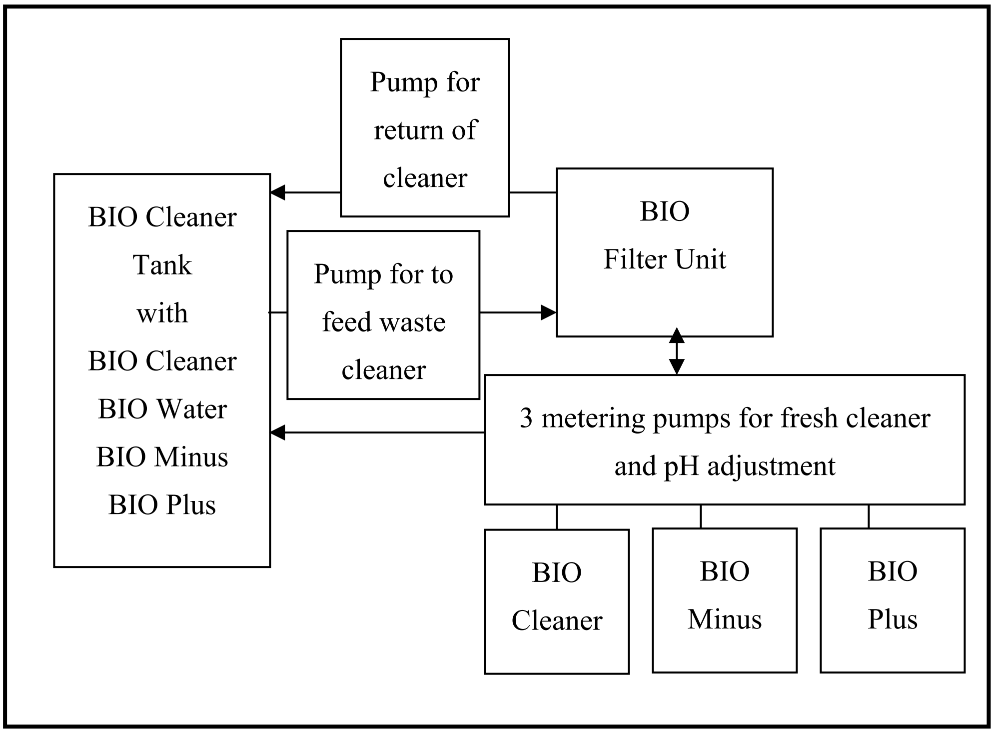


Figure 3.6. The recommended system for pre-treatment of the zinc plating (ATOTECH, 2006)

Bioremediation is a simple and natural process. BIO Cleaner is a highly emulsifying soak cleaner. The surfactant system displaces and emulsifies oils and greases from the surfaces of metal parts. Naturally occurring microorganisms then digest and metabolize the oils and greases by enzyme action and convert them into carbon dioxide and water (Groudeva et al., 2001; Timian and Connolly, 2000). The cleaner is constantly replenished and returned back to the tank in optimum condition for a steady-state. This system is designed to provide and maintain ideal environmental conditions for the naturally introduced microorganisms to thrive. The count should be $10^3$-$10^8$ microorganisms/mL in the BIO Cleaner tank (Veglio et al., 2003).

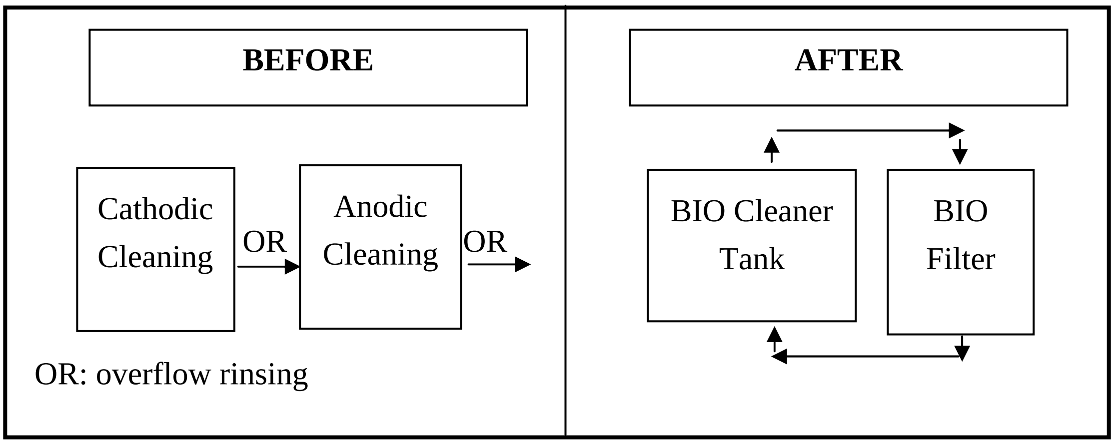


Figure 3.7. The schematic diagram for the comparison of the process application for "closed loop cleaning system"

The summarized economic evaluation of the recommended system is given in Table 3.11. The chemical consumption amounts for the existing system were calculated by the chemical concentration and replacement periods of baths. This technology eliminates 680 kg/year solvent consumption leading to substitution of acidic anodic and cathodic cleaning baths with bioremediation technology which consumes aqueous cleaner. The consumption amounts of aqueous cleaner solution were calculated according to the recommended system configurations which were provided by the supplier company of the recommended system. The closed loop system not only reduces wastewater generation but also allows for recovery and reuse opportunities for the cleaning solution which provides 1 to 1.5 years cleaner bath life. As a result of this fact, the consumption of cleaning chemicals (and their loss through wastewater) will be definitely lower with the rate of 14.7%.

Table 3.11. Summary of the economic evaluation of “the closed loop cleaning system”

| **Amount and cost of resource and chemical consumption before the implementation** | | **Amount** |
|---|---|---|
| **Raw material** | | |
| Electroplated sheet steel (SS) | $dm^2$/year | 6,000,000 |
| **Cathodic cleaning** | | |
| **Water** | **$m^3$/year** | 4,000 |
| | % | 33.90 |
| **Chemicals** | **kg/year** | Electrolitic Oil Cleaner: 260 |
| | % | 1.07 |
| | EUR/year | 279 |
| **Anodic cleaning** | | |
| **Water** | **$m^3$/year** | 3,550 |
| | % | 30.10 |
| **Chemicals** | **kg/year** | Hot oil cleaner: 420 |
| | % | 1.73 |
| | EUR/year | 434 |
| **En-of pipe treatment costs** | | |
| Wastewater | $m^3$/year | 732 |
| Recycled water | $m^3$/year | 6,776 |
| Cost of treatment | EUR/year | 772 |
| Cost of recycled water | EUR/year | 4,140 |
| **Total cost** | **EUR/year** | 5,625 |
| **Amount and cost of resource and chemical consumption after the implementation** | | **Amount** |
| **BIO cleaner tank** | | |
| **Raw material** | | |
| Electroplated sheet steel | $dm^2$/year | |
| **Water** | **$m^3$/year** | 1,263 |
| | % | 10.70 |

Table 3.11. Summary of the economic evaluation of “the closed loop cleaning system”$^{(con't)}$

| | | |
|---|---|---|
| **Chemicals** | **kg/year** | BIO Soak Cleaner: 430<br>BIO water: 80<br>BIO Plus: 35<br>BIO Minus: 35<br>Total: 580 |
| | % | 2.59 |
| | EUR/year * | 1,152 |
| **End-of-pipe treatment costs** | | |
| Wastewater | $m^3$/year | - |
| Recycled wastewater | $m^3$/year | 1,247 |
| Cost of recycled water | EUR/year | 618 |
| **Investment cost for BIO filter unit** | **EUR** | 13,000 |
| Total annual revenue | EUR | 5,625 |
| Total annual consumption cost | EUR | 1,770 |
| **Total annual savings** | **EUR** | 3,855 |
| **Pay-back time** | **year** | 3.3 |
| * : Designated total chemical cost is $8.5.10^{-4}$ EUR/$dm^2$ for the recommended system.<br>**: Unit prices are BIO soak: 2 € /kg, BIO water: 5 € /kg, BIO plus: 2 € /kg and BIO minus: 2 € /kg. | | |

In the selected company, overflow rinsing 8, 9, 12 and 13 tanks are used with the 6,800 $m^3$/year water consumption after anodic and cathodic cleaning tanks. In the recommended system, two stages counter current rinsing system with a flow rate of 200 L/hour fresh water will be applied after BIO clean tank. This will result in 1,263 $m^3$/year water consumption which corresponds to 80% of rinsing water savings. This system is also suitable for worker’s environment since it prevents hazardous solvent consumption and air mist generation with a closed loop system. The water consumption index was decreased to 0.2 kg water/ $dm^2$ SS from 0.7 kg water/ $dm^2$ SS.

## 4.4. Raw Material Substitution/Conservation

### 4.4.1. Substitution of Lead Free Surface Finishing Alternatives for Hot Air Solder Leveling (HASL)

In hot air solder leveling (HASL), solder (Pb-Sn) as coating material has been applied in the company. According to the RoHS Directive, starting from 1 July 2006 electrical and electronic equipment must not contain lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBBs) or polybrominated diphenyl ethers (PBDEs) (EC Directive 2002/95/EC, 2002) . Within the scope of this obligatory, the recommended lead free hot air leveling CP options are;

Lead free HAL (Hot air leveling): Among all the lead free finish processes which provide the preservation of the solderability of bare PCBs, lead free hot air leveling is the most cost effective process and produces a product with excellent shelf life. A major cost of the hot air leveling process is the solder. There have been numerous lead-free alloys such as Tin/Silver/Copper (SAC), Tin/Copper and Tin/Nickel (SN) SN100 (Tin-Nickel) is the recommended lead free alloy for the selected industry. The lead free solder SN100 is a nickel based alloy which is excellently suitable for mechanical coating processes. It has a melting point of 227 $^{o}$C and the bath temperature is ranges between 250-300 $^{o}$C. Also the flux material substituted with a lead free flux material (CIRCUITREE, 2006).

Organic solder preservative (OSP): Organic Solder Preservative (OSP) is designed to produce a thin, uniform, protective layer on the copper surface of the PCBs. Most of the commercially available coatings are azole related compounds such as imidazole, benzotriazole (thin films) and benzimidazole (thick films). Thick OSP provides a significant improvement in protection against copper oxidation at elevated temperature and humidity and this is important when the PCB goes through the complex assembly process (UNEP, 1998a). In the recommended OSP line, while acidic cleaner is used for pre-cleaned unit, sulfuric acid, sodium persulfate are used for microetching implementation and “imidazole derivatives acetic acid aqueous solution” is used as OSP material. OSPs offer lead free alternative, low capital equipment, lower maintenance cost compare to HASL and are safer for employees to handle. The OSP process costs approximately one-third that of HASL, however, recommended OSP material has the highest cost in comparison with other azole related compounds, hence it cost more than HASL.

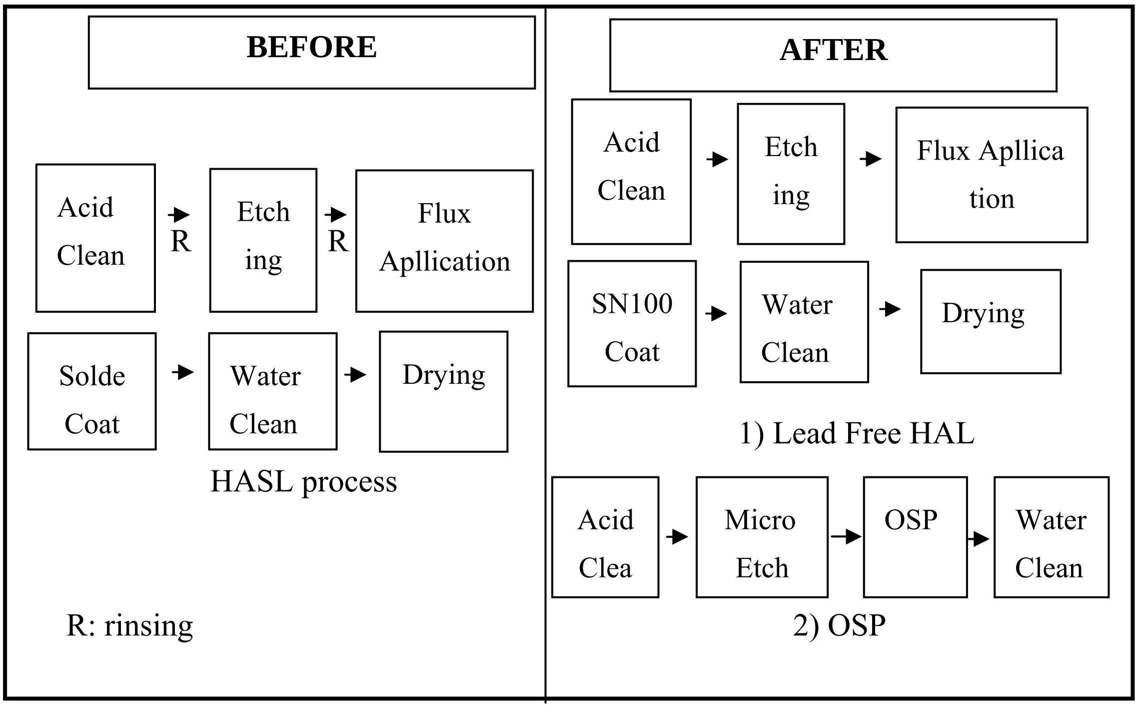


Figure 3.8. The schematic diagram for the comparison of the process application for “lead free surface finishes alternative”

### 4.4.2. Lead Free Solder for Pattern Plating

In pattern plating, the hole walls are plated with copper and tin-lead in order to gain electrical conductivity to hole walls. However, RoHS Directive is forbidden the usage of tin-lead etch resist because new electrical and electronic equipment do not contain lead (EC Directive 2002/95/EC, 2002). Within this scope, tin-lead resist, tin tetraflouraborate and lead tetraflouraborate are substituted with acid tin plating agent. Also tin-lead stripping agent is substituted with tin stripping agent .The economic evaluation of substitution of lead free surface finishes is given in Table 3.12.

Table 3.12. The summary of the economic evaluation of “lead free surface finishes alternative”

| **Old process for HASL** | **Chemical consumption** | | |
|---|---|---|---|
| | **Consumption kg/year** | **EUR/kg** | **EUR/year** |
| Sn-Pb | 2,900 | 6,36 | 18,444 |
| **Lead free alternative for HASL** | | | |
| Lead free HAL Sn-Ni | 2,900 | 11.8 | 34,220 |
| OSP- imidazole derivatives acetic acid solution | 5,357 | 16.89 | 90,480 |
| **Old process for pattern plating** | | | |
| Tin-Lead anode | 1,825 | 5.22 | 9,526 |
| **Lead free alternative for pattern plating** | | | |
| Tin anode | 1,280 | 9.15 | 11,712 |

## 4.5. On-Site Recycle/Reuse/Recovery

### 4.5.1. Alkaline Etchant Recovery Process

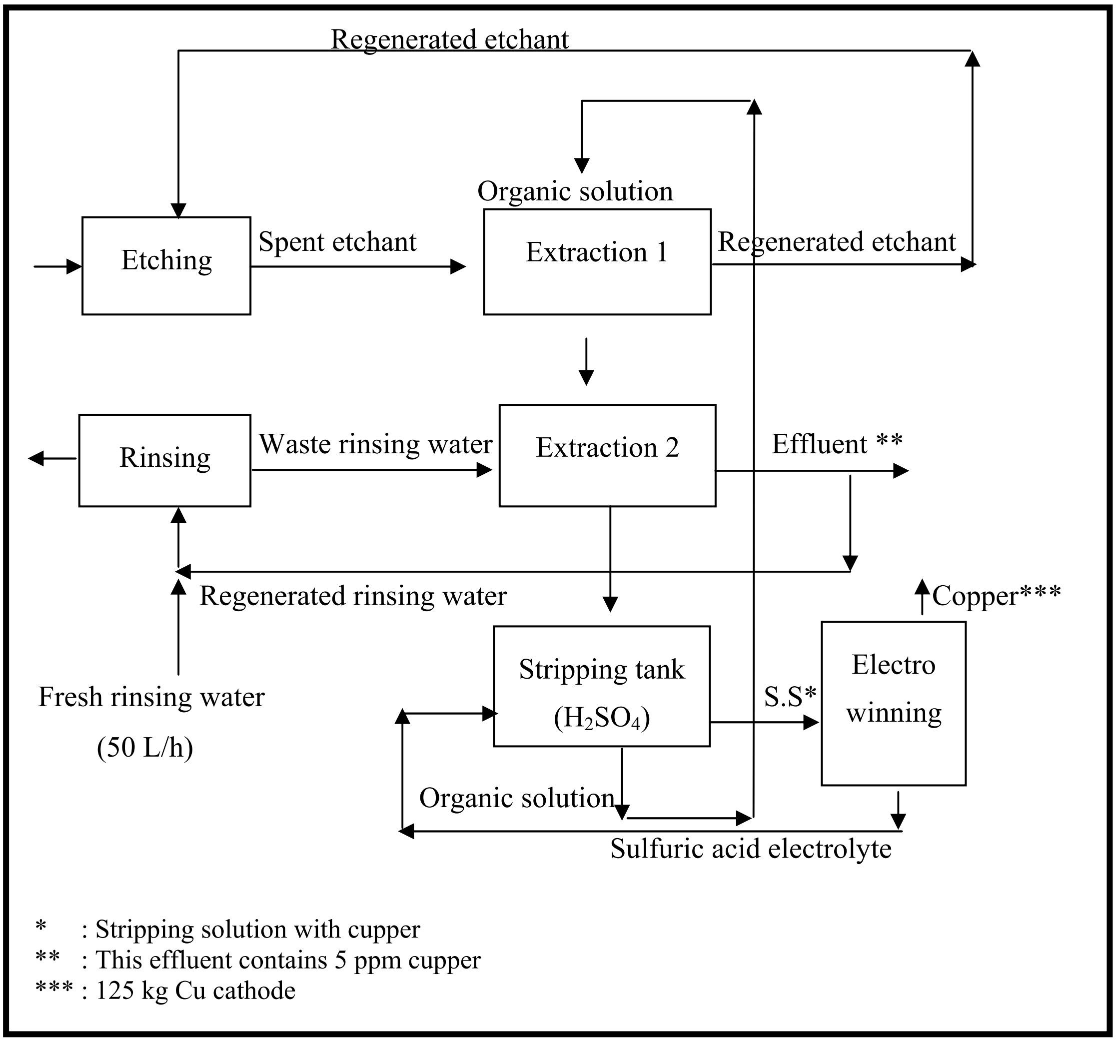
It has been estimated that alkaline etchant can be regenerated with an electrochemical cell divided by solvent extraction technique in the printed circuit boards manufacturing. With this technique, copper recovery can be achieved, as well (EPA, 1999; Sage and Schnitzer, 1994; Melling, 1986; Yang and Kocherginsky, 2006). In the selected industry, etching efficiency starts to declines when copper concentration reaches values above 110 to 130 g/L. This etchant must be restored once as the copper has concentration of 150 to 170 g/L (Melling, 1986). In the recommended system, as the etcher density increases and it requires fresh material, regenerated etchant containing approximately 100 g/L copper is added to the etcher module. Spent etching material is removed from the module and stored in a buffer tank. Also this system needs ammonia for pH adjustment, chlorides to compensate for drag-out and etchant additive to control etch speed.

When enough spent etchant has accumulated in the spent buffer tank, the system automatically turns on and begins to regenerate etchant. Using a process known as solvent extraction, a portion of the copper is transferred out of the etchant into an organic extractant. The regenerated etchant is then sent back to storage for reuse in the etcher. The organic is passed on to the next step in the solvent extraction process. As regenerated etchant is added to the etching module, regenerated rinsing water is added to the flood rinsing module. Regenerated rinsing water that contains approximately 7 g/L ammonium chloride, 5 ppm copper and free ammonia can be recycled. As the rinsing water cascades through the flood rinsing module it becomes contaminated and is sent to a buffer tank for storage before processing by the system (SIGMA-MECER, 2005).

Waste process rinsing water is fed into the second extraction stage of the system where the copper is reduced from ~2 g/L to 5 ppm. The regenerated rinsing water is sent back to a buffer tank for storage and reuse by the etching machine. A small portion of this material is also bled off to waste treatment to balance the volume of water being added to the process through the fresh rinsing module. Typically, DI water is added to this module at a rate of 50 L/h. Therefore it reduces rinsing water consumption for a typical etcher by 90%. After the organic material has contacted with the spent rinsing water, it is completely loaded with copper. This copper needs to be removed before the organic material can be passed through the system again. This is done by contacting the organic material with sulfuric acid. Under this pH condition, the organic material releases its copper to the acid and is regenerated for reuse. It is then stored in a buffer tank (SIGMA-MECER, 2005).

The copper loaded acid (electrolyte) travels from the third extraction stage to the electrowinning cell where the copper is plated onto copper starter sheets. When a cathode’s weight reaches ~125 kg it is removed from the system and sold as electrolytic grade copper. The process of plating the copper regenerates the acid in the electrolyte so that is ready to be used again to strip the copper from the organic material (SIGMA-MECER, 2005).

In summary, there are four recycling loops in this system: (a) extraction 1: the etchant recycling loop, (b) extraction 2: the rinsing water recycling loop, (c) stripping tank: the organic recycling loop, ( d) electrowinning: the electrolyte recycling loop.



* : Stripping solution with cupper
** : This effluent contains 5 ppm cupper
*** : 125 kg Cu cathode

Figure.3.9 Ammoniacal etchant regeneration system (SIGMA-MECER, 2005)

- Etching copper metal from printed circuit boards:

$$Cu^o + Cu(NH_3)_4Cl_2 \longrightarrow 2\ Cu(NH_3)_2Cl \text{ (dissolution)} \qquad (3.4)$$

$$2\ Cu(NH_3)_2Cl + \tfrac{1}{2}\ 0_2 + 2\ NH_3 + 2\ NH_4Cl \longrightarrow 2\ Cu(NH_3)_4Cl_2 + H_2O \text{ (oxidation)} \qquad (3.5)$$

- These two equations can be summarized in one equation:

$$Cu^o + 2\ NH_3 + 2\ NH_4Cl + \tfrac{1}{2}\ O_2 \longrightarrow Cu(NH_3)_4Cl_2 + H_2O \qquad (3.6)$$

- Extracting copper from spent etchant or spent rinsing water:

$$Cu(NH_3)_4Cl_2 + 2\ RH(org) \longrightarrow CuR_2(org) + 2\ NH_3 + 2\ NH_4Cl \qquad (3.7)$$

- Stripping copper from the organic solution to the electrolyte:

$$CuR_2(org) + H_2SO_4 \longrightarrow CuSO_4 + 2\ RH(org) \qquad (3.8)$$

- Electrowinning copper metal from the electrolyte:

$$CuSO_4 + H_2O \longrightarrow Cu^o + H_2SO_4 + \tfrac{1}{2}\ O_2 \qquad (3.9)$$

The final product from this recycling process is 99.9% pure copper, which can be sold to the metal market. Table 3.13 gives the suitable data for sizing an ammoniacal etchant regeneration system (SIGMA-MECER, 2005). The design capacity of the recommended regeneration system corresponds to the production of 1.6 kg/hours of copper metal or the discharge of 10 L/hours of waste etchant at 150 g/L cupper content.

Table 3.13. Suitable data for sizing an ammoniacal etchant regeneration system in the selected industry (SIGMA-MECER, 2005)

| Section | | Rate |
|---|---|---:|
| Operation time | hour/year (22 h/d, 5 d/w, 49w/y*) | 5,400 |
| Number of etchers | | 1 |
| Copper concentration in etcher | g/L | 150 |
| Earlier replenisher consumption rate | kg/year | 51,000 |
| Production of copper metal rate | kg/year | 9,100 |
| Rinsing water flow | $m^3$/year | 900 |
| Wastewater treatment cost | EUR/$m^3$ | 0.48 |
| Water rinsing stages | | 3 |
| *: h/d: hour/day, d/w: day/week, w/y: week/year | | |

Table 3.14. Summary of the economic evaluation of "alkaline etchant recovery process"

| **Annual consumption cost before the regeneration system** | | **Amount** | **Unit price EUR** | **Value** |
|---|---|---|---|---|
| Earlier replenisher cost | kg/year | 58,000 | 0.70 | 40,600 |
| Lost of recovered copper cost | kg/year | 9,100 | 3.70 | 33,700 |
| Raw water | $m^3$/year | 900 | 0.06 | 54 |
| Wastewater treatment and disposal cost | $m^3$/year | 897 | 0.99 | 890 |
| **Total annual consumption cost** | **EUR** | | | 75,245 |
| **Annual consumption cost after the regeneration system** | | | | |
| Ammonia as 100% | kg/year | 1,044 | 1.10 | 1,200 |
| Replenisher make-up | kg/year | 348 | 10.50 | 3,700 |
| Reagent MX 80 make-up | kg/year | 60 | 66.200 | 3,900 |
| Other chemicals, including spare parts ( % of total cost) | EUR | - | - | 820 |
| - sulphuric acid (ca. 2.2 % of the Cu prod.) | kg/year | 200 | - | - |
| - deionized water (ca. 50 % of the Cu prod.) | $m^3$/year | 4.4 | - | - |
| Copper starter-sheets | pieces/year | 70 | 51.60 | 3,600 |
| Change of DSA anodes each 5th year | pieces/5year | 6 | 1,500.00 | 1,800 |
| **Total annual consumption cost** | **EUR** | | | 15,100 |
| **Total investment for SX Unit SX10-1.6** | **EUR** | 134,100 | | |
| Total annual revenue | EUR | 75,245 | | |
| Total annual consumption cost | EUR | 15,100 | | |
| **Total annual savings** | **EUR** | 60,145 | | |
| **Pay-back time** | **year** | 2.2 years | | |

Waste etchant causes manufacturing costs such as purchase of fresh replenishment, storage of chemicals for replenishment, hazardous chemicals storage, wastewater treatment cost, cost of transport for hazardous chemicals and giving away valuable metal (Luo and Huang, 1997; Lee et al., 2003; Alanso et al., 2005). With the application of this system, consumption of alkaline etchant chemical as replenisher is reduced by about 90%. Spent etchant generation which contains valuable copper metal is totally eliminated, thus storage and shipping of hazardous spent etchant is also eliminated. After the copper is recovered, the alkaline etching solution is recycled and the only replenisher is needed for drag-out and evaporation losses. 9,100 kg/year copper is recovered from the spent etchant and can be sold as pure copper which provides 33,700 €/year savings. Water consumption is definitely reduced to 4.4 $m^3$/year with the rate of 99.5% and the copper concentration in the discharged rinsing water is less than 5 ppm as seen in Table 3.14.

### 4.5.2. The Continuous-Flow System for Reusing Microetchant and Copper Recovery

For the selected industry, microetching is a common process used as a pre-clean step at many stages of PCB manufacturing. OSP and direct metallization microetch units were used as closed loop systems in order to use microetchant effectively. The Continuous-Flow System (cascading reuse) is a potential method of reducing the quantity of microetchant used in PCB manufacturing. In the recommended method, microetchant is used in one process until its efficiency is reduced; it is then reused in another process that has a lower chemical requirement. In designing a continuous-flow system, microetch rates, tank location and floor layout should be considered (EPA, 1996).

Table 3.15. The amount of copper etching rate for each microetching unit

| Microetching Unit | Etch rate of copper (μm) | The amount of Copper etched away (g/day) |
|---|---:|---:|
| Direct metallization micro etching | 0.3 | 250 |
| OSP micro etching | 1-1.2 | 750 |
| Total | | 1,000 |

The sulfuric acid-potassium persulfate microetchant cannot be regenerated due to the buildup of sulfates that results from the breakdown of the microetch chemistry (EPA, 1995). Therefore, electrolytic recovery serves to minimize the usage of microetchant and remove copper before the solution goes to the wastewater treatment unit, but not to regenerate microetchant. The recommended continuous-flow system begins with a single tank of microetch solution, prepared daily. This day tank is formulated according to the specifications for OSP micro etch step during which 1 to 1.2 μm of copper must be removed from the panels. This bath contains 16 kg $Na_2S_2O_8$, 4.4 L $H_2SO_4$ and DI water with the rate of 230 liter.

There is an aerometer/sensor which measures copper ion concentration in the microetch bath of OSP and automatically feeds fresh microetchant from the day tank to the bath when the copper concentration reaches a threshold of 10 g/L. The autofeed arrangement maintains copper concentration between 9 to 11 g/L, allowing for better process control and a more stable etch rate of 1 to 1.2 µm. The excess spent etchant is fed to the microetch bath of direct metallization unit. This pre-clean process needs to remove only 0.3 µm of copper; therefore, a weaker solution that has 750 g/day copper concentration and less oxygen available can be used. After these microetching applications, spent etch solution contains 1 kg/day Cu. The amount of Cu etching rate for each microetching unit is given in Table 3.15.

The waste microetchant is pumped to the electrolytic plate-out cell, where copper is plated out and sold. Electrolytic recovery is the oldest metal recovery technique. At this system, metal ions are plated-out of solution electrochemically by reduction at the cathode (EPA, 1993; EPA, 1999; Sage and Schnitzer, 1994; Lee et al., 2003). The remaining waste microetchant, consisting of residual copper, water and microetchant chemicals, is sent to wastewater treatment (EPA, 1996).

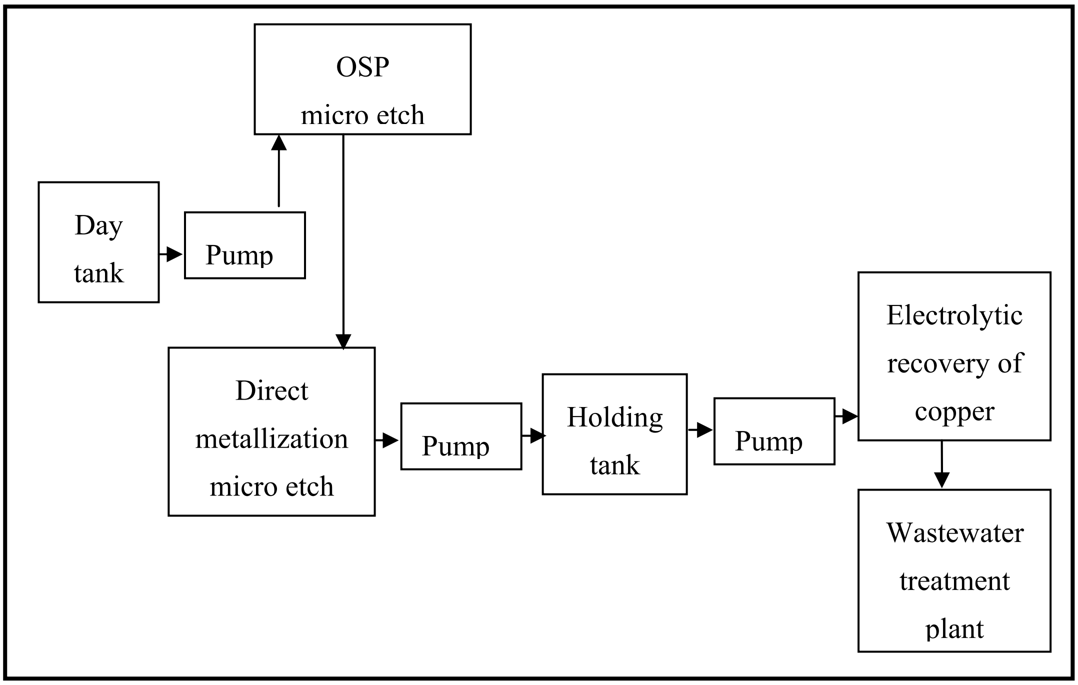


Figure.3.10 The recommended continuous-flow system (EPA, 1996)

Table 3.16. The summary of the economic evaluation of “the continuous-flow system for reusing microetchant”

| Parameter | Old process | New process | Savings |
|---|---|---|---|
| **Amount and cost of raw material, water, and chemical consumption** | | | |
| **Direct metallization micro etch unit** | | | |
| **Raw material** | | | |
| Epoxy resin dm$^2$/year | 2,230,000 | 2,230,000 | - |
| **Water m$^3$/year** | 850 | 850 | - |
| % | 4.5 | 4.5 | |
| EUR/year | 468 | 468 | - |
| **Chemicals kg/year** | | | |
| | $H_2SO_4$ : 300<br>$Na_2S_2O_8$ :750<br>Total: 1,050 | - | 1,050 |
| % | 1.03 | - | |
| EUR/year | $H_2SO_4$ :711<br>$Na_2S_2O_8$: 3,975<br>Total: 4,886 | - | 4,886 |
| **Total annual cost EUR/year** | 5,354 | 468 | 4,686 |
| Etch solution consumption m$^3$/yaer | 4.5 | - | 4.5 |
| **OSP micro etch unit** | | | |
| **Raw material** | | | |
| Epoxy resin dm$^2$/year | 2,230,000 | 2,230,000 | - |
| **Water m$^3$/year** | 950 | 950 | - |
| % | 5.04 | 5.04 | |
| EUR/year | 523 | 523 | - |
| **Chemicals kg/year** | | | |
| | $H_2SO_4$ : 1,200<br>$Na_2S_2O_8$ : 3,000<br>Total: 4,200 | $H_2SO_4$ : 960*<br>$Na_2S_2O_8$ : 2,400*<br>Total:3,360 | 840 |
| % | 4.1 | 3.3 | - |
| EUR/year | $H_2SO_4$ :2,844<br>$Na_2S_2O_8$: 15,900<br>Total: 18,744 | $H_2SO_4$ :2,275<br>$Na_2S_2O_8$: 12,720<br>Total: 14,995 | 3,749 |

Table 3.16. The summary of the economic evaluation of "the continuous-flow system for reusing microetchant" (con't)

| | | | |
|---|---|---|---|
| **Total annual cost EUR/year** | 19,267 | 15,518 | 3,749 |
| Etch solution consumption $m^3$/year | 9.5 | 7.5 | 2.5 |
| **Copper recovery kg/year** | - | 250 | |
| EUR/year | | 925 | 925 |
| **End of pipe treatment cost** | | | |
| Wastewater produced $m^3$/year | 1,809 | 1,809 | - |
| Cost of treatment EUR/year | 1,790 | 1,790 | - |
| Pay-back period | | | |
| **Annual savings EUR/year** | 9,560 | | |
| **Investment cost** | | | |
| Aerometer EUR/ piece | 102 | | |
| Sensor (3 pieces) EUR/ piece | 628 | | |
| Dosage pump for fresh microetch EUR/piece | 1947 | | |
| Dosage pump for waste microetch EUR/ 2 pieces | 690 | | |
| Electrolytic recovery system EUR | 11,700 | | |
| **Total EUR** | 15,067 | | |
| **Pay-back period year** | 1.6 | | |
| *: It was assumed that after etchant sensor usage, the chemical consumptions were decreased by the rate of 20 % | | | |

The economic evaluation of the continuous flow system for reusing micro etchant is given in Table 3.16. Savings are seen in 1,890 kg/year hazardous acidic etch solution consumption which corresponds to 8,435 €/year. Also, 250 kg/year copper can be recovered and sold as pure metal. With this recovery options, system also considerably, reduces the hazardous chemical and copper load of wastewater treatment plant. This option can be considered as short term implementation as it has a payback period time of 1.6 years.

### 4.5.3. Drag-out Recovery in Zinc Plating and Pattern Plating

One of the factors that have the greatest influence in the rinsing volumes is drag-out. Parts and their support mechanisms need to be rinsed to avoid cross-contamination between processing tanks.

Both the part and its rack carry part of the aqueous solution where they were submerged and they are covered with a fine liquid film when removed from the tank. Part of the liquid thus gets transferred from one tank to another and contaminates it. By reducing the volume of drag-out that enters the rinsing water system, valuable process chemicals can be saved, water consumption and wastewater generation can be reduced and sludge generation and disposal can be minimized (EPA, 1998a).

<u>Drainage time optimization:</u> In zinc plating line, the drainage time of zinc plating chemical bath is 5 seconds. 10 seconds drainage time is recommended for this unit because longer drainage time allows reducing the drag-out amount by % 50 (UNEP, 1998a).

In zinc plating bath, the estimated drag out value for rack plating is 1.5 mL/dm$^2$ (Mediterranean Action Plan, 2000) and the water and chemical lost from the zinc plating is; 1.5 mL/m$^2$ drag out x 6,000,000 dm$^2$ /year =9 m$^3$/year solution. As seen Table 3.4, Zn plating solution contains 4-16 g/L metallic zinc. According to this, maximum 9000 L/year x 16 g/L = 144 kg /year metallic zinc and minimum 9000 L/year x 4 g/L = 36 kg /year metallic zinc are carried with metal parts.

In average, 90 kg Metallic Zinc were lost due to the drag out annually. If the drainage time is increased to 10 seconds, the drag out value is decreased with the amount of 50% and the process solution and metallic zinc lost will be 4,500 L/year, 45 kg/year, respectively. With this simple adjustment, 45 kg/year zinc lost can be prevented without any investment. Economic evaluation of the system is given in Table 3.17.

Table 3.17. The summary of the economic evaluation of "drainage time optimization"

| Parameter | | Old process | New process | Savings |
|---|---|---|---|---|
| Solution lost | $m^3$/year | 9 | 4.5 | 4.5 |
| Metallic Zinc lost | kg/year | 90 | 45 | 45 |
| Metallic Zinc lost | EUR/year | 528 | 264 | 264 |
| Total saving | EUR/year | | | 264 |

Drain board application: Installing drain board after process baths returns the drag-out to the chemical baths. Drain boards are recommended for metal plating baths which comprise the zinc plating, copper (Cu) plating and tin (Sn) plating bath and as a result, both zinc and pattern plating chemical lost is reduced by 40 % (EPA, 1993).

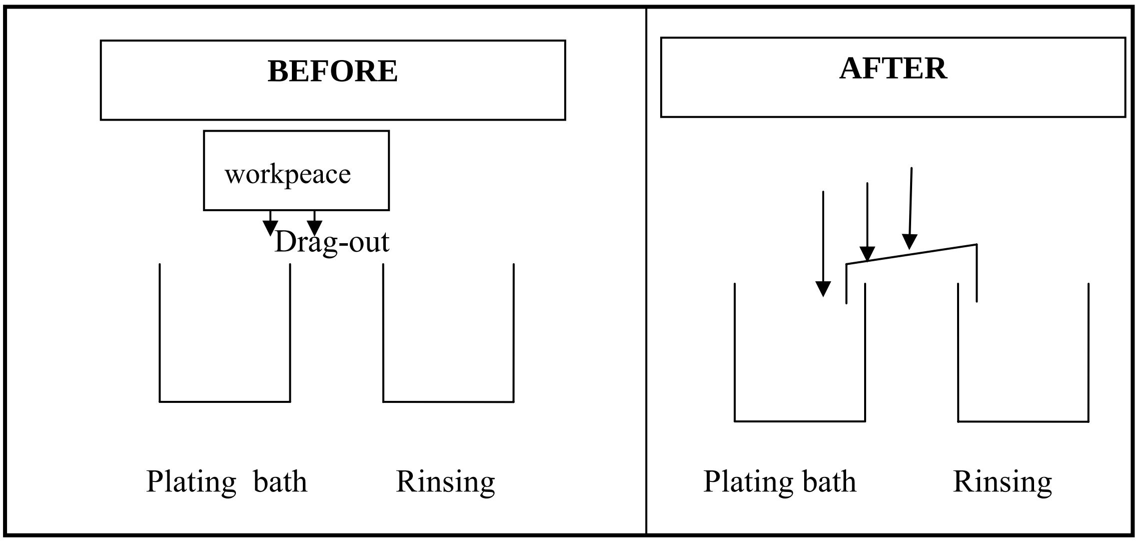


Figure 3.11 The schematic diagram for the comparison of the process application "drain board usage" in zinc plating

In Cu and Sn plating; 1.5 mL/$dm^2$ drag out x 2,230,000 $dm^2$ /year =3.345 $m^3$/year solution was lost which contains 154 kg Cu (plating solution contains 46 gr/L Cu) and 45 kg Sn (plating solution contains 13.5 gr/L Sn), respectively due to the drag-out. With drain board application, drag-out value is decreased to 2 $m^3$/year.

As seen in Table 3.18, application of drain board to route drippings back to process tanks is a cost-effective technique since system has a low capital investment with 300 € and provides 98 kg/year metal consumption saving. As a result, valuable process chemicals such as zinc, tin and copper can be prevented from reaching the rinsing water bath. Sludge generation is also reduced since the process chemicals are prevented from entering the rinsing system (Visvanathan, 1996). 454 €/year chemical consumption saving can be achieved leading to 8 months pay-back period time which is consider as short term option for the enterprise .

Table 3.18. The summary of the economic evaluation of “drain board application”

| **Parameter** | **Old process** | **New process** | **Savings** |
|---|---|---|---|
| **Drag out lost m$^3$/year** | | | |
| Zinc plating | 4.5 | 2.7 | 1.8 |
| Cu plating in pattern plating | 3.4 | 2.0 | 1.4 |
| Sn plating in pattern plating | 3.4 | 2.0 | 1.4 |
| **Chemical lost kg/year** | | | |
| Zn plating | 45 | 27 | 18 |
| Cu plating in pattern plating | 154 | 92 | 62 |
| Sn plating in pattern plating | 45 | 27 | 18 |
| **Chemical cost EUR/year** | | | |
| | Zn: 264<br>Cu: 416<br>Sn:450 | Zn: 158<br>Cu: 248<br>Sn:270 | Zn: 106<br>Cu:168<br>Sn:180 |
| **Total annual cost EUR/year** | 1,130 | 676 | 454 |
| Investment cost<br>3 piece x 100 EUR/piece | | | 300 |
| **Pay-back period months** | | | 8 |

### 4.5.4. Application of Counter Current Rinsing and Drag-out Tank in Zinc Plating and Recycle-Reuse of Rinsing Water by Reverse Osmosis

The selected company uses skip technique which consists of using the same rinsing in different stages that are chemically compatible (Mediterranean Action Plan, 2000).

Overflow rinsing 8 and 9 are applied after both anodic cleaning and acid washing and overflow rinsing 12 and 13 are used after both cathodic cleaning and zinc plating. With this application, the number of rinsing tanks and water consumption are reduced but the hazardous waste load of rinsing water increases to an extent. The quantity of sludge is usually proportional to the metal concentration in the waste rinsing water. Therefore, the reduction of rinsing water consumption is always the first step towards sludge reduction (Luo and Huang, 1997).

In zinc plating line, two stage rinsing is applied. All waste rinsing water is recycled and each tank has own inlet point which has a capacity of 200 L/hour of fresh water. Counter current rinsing system is recommended for zinc plating line. In counter current rinsing, only the last rinsing bath has an inlet point for fresh water and the excess water goes to preceding rinsing bath. Also, a drag out tank which is filled with DI water is recommended for zinc plating and pasivation tanks. A chemical metering pump will be used to return drag-out from this tank to the plating tank. The pumps will be controlled by a level sensor in the plating tank (Roy and Shapiro, 1999). The excess waste DI water from first rinsing bath is sent to the RO system and recycled through rinsing system.

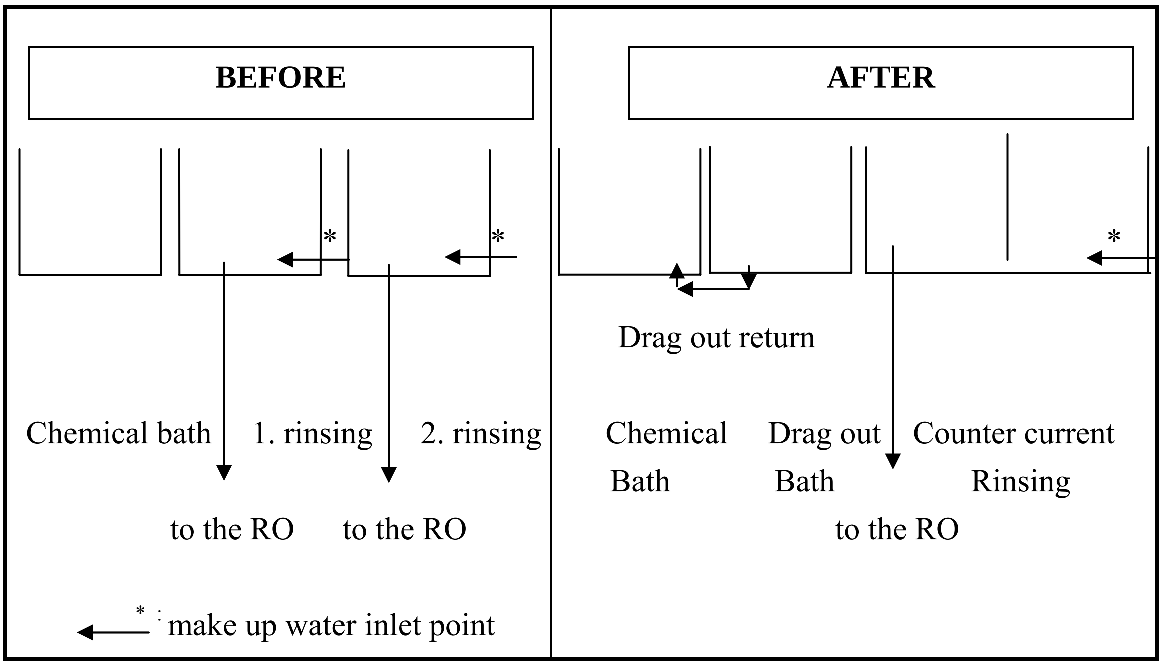


Figure 3.12. The schematic diagram for the comparison of the process application of "counter current rinsing and drag out bath"

Table 3.19. The summary of the economic evaluation of "counter current rinsing and drag-out tank"

| **Parameter** | | **Old process** | **New process** | **Savings** |
|---|---|---|---|---|
| **Amount and cost of water, and chemical consumption** | | | | |
| **Water** | | | | |
| **Rinsing baths** | | | | |
| Recycled rinsing bath 3- 4 | $m^3$/year | 3,200 | 1,263 | 1,937 |
| | % | 32 | 33.3 | - |
| | EUR/year | 1,760 | 695 | 1,065 |
| Recycled rinsing bath 8- 9 | $m^3$/year | 3,200 | 1,263 | 1,937 |
| | % | 32 | 33.3 | - |
| | EUR/year | 1,760 | 695 | 1,065 |
| Recycled rinsing bath 12- 13 | $m^3$/year | 3,600 | 1,263 | 2,337 |
| | % | 36 | 33.3 | - |
| | EUR/year | 1,980 | 695 | 1,285 |
| **Zinc plating bath** | | | | |
| Drag-out return | $m^3$/year | - | 2.7 | 2.7 |
| Zn recovery | kg/year | - | 27 | 27 |
| | EUR/year | - | 158 | 158 |
| **Pasivation bath** | | | | |
| Drag-out return | $m^3$/year | - | 2.7 | 2.7 |
| Trivalent solution recovery | kg/year | - | 102 | 102 |
| | EUR/year | - | 387 | 387 |
| Pay-back period | | | | |
| Annual savings | EUR/year | 4,181 | | |
| **Investment cost** | **EUR** | | | |
| Level sensor | EUR/ 2 pieces | 60 | | |
| Pump | EUR/ 2 pieces | 260 | | |
| Control panel for drag-out return | EUR/ 2pieces | 20 | | |
| **Total investment cost** | **EUR** | 340 | | |
| **Pay-back period** | **month** | 1 | | |

As seen in Table 3.19, counter current rinsing in metal plating provides 6,200 $m^3$/year saving in terms of water consumption. The recommended option leads to 4,181 € saving on annual base with very short term pay back period of 1 month. Moreover, drag-out bath application obtains 515 €/year process chemical recovery.

## 4.6. The General Evaluation of Selected CP Options

The feasibility results of prioritized CP options, which comprise technology modification for “desmear process” and “pre-treatment of metal parts” and on site recovery/reuse/recycle for “ammoniacal etchant”, “microetchant” and “rinsing water”, are given in Table 3.20. In terms of the whole plant, none of the recommended CP options interfere with each other, for that, all of them can be implemented in the selected production plant.

In metal finishing, recycled rinsing water consumption reduced to 3,789 $m^3$/year from 9,964 $m^3$/year after counter current rinsing application leading to 3,823 €/year saving. 5,798 €/year saving was also achieved in terms of recycled water production and wastewater treatment and disposal for total production lines of metal finishing and PCB production after recommended CP options implementation.

680 kg/year hazardous solvent consumption was eliminated and recovery and reuse of BIO cleaner bath solution was accomplished by BIO filter unit for 1 to 1.5 years with application of closed loop cleaning system. Process rinsing water consumption was also reduced by about 81%.

With alkaline/micro etchant recovery processes, 9,350 kg/year total copper which has market value with 34,625 €/year was recovered. Also, 51,000 kg/year ammoniacal etchant consumption as replenisher was reduced by about 90%. Rinsing water consumption was decreased to 4.4 $m^3$/year since the only need for process rinsing water is due to the evaporation and drag-out losses. The payback period of this system can be considered as short term period with 2.2 years.

Adaptation of RoHS Directive (2002/95/EC) to the electroplated products with lead-free coating has a great importance in terms of obtaining international market share for the selected electronics industry.

Substitution of permanganate desmear with plasma desmear eliminated both 2,600 $m^3$/year process rinsing water and 4,577 kg/year hazardous chemical consumption. Although this system has a long term pay back period time with 7.2 years, it is definitely adjusted with sustainable production concept since all waste emissions are eliminated at source.

Drag-out minimization provided 272 kg/year valuable metals recovery with 1,263 €/year saving leading to 8 month payback period time. Implementation of counter current rinsing in zinc electroplating line obtained 62 % water consumption reduction which provides very short payback period time with 1 month.

Table 3.20. The evaluation of CP options

| CP Option | Parameter | Before | After | Saving |
|---|---|---|---|---|
| Technology modification<br>(Substitution of the pre-treatment of zinc plating with the closed loop cleaning system) | | Anodic-cathodic cleaning | Closed loop cleaning | |
| | Water consumption | 7,550 m$^3$/year | 1,263 m$^3$/year | 6,287 m$^3$/year |
| | Chemical consumption | 680 kg/year | 630 kg/year | 50 kg/year |
| | Wastewater production | 732 m$^3$/year | - | 732 m$^3$/year |
| | Recycled water production | 6,776 m$^3$/year | 1,260 m$^3$/year | 5516 m$^3$/year |
| | Running costs | 5,625 EUR/year | 1,770 EUR/year | Total annual saving:<br>3,855 €/year |
| | Capital investment cost | 13,000 € | | |
| | Payback period | 3.3 years | | |

| Technology modification<br>(Substitution of permanganate desmear with the plasma desmear system) | Parameter | Before | After | Saving |
|---|---|---|---|---|
| | | Anodic-cathodic cleaning | Closed loop cleaning | |
| | Water consumption | 2,600 m$^3$/year | - | 2,600 m$^3$/year |
| | Chemical consumption | 4,577 kg/year | 263.72 m$^3$ | - |
| | Wastewater production | 2,597 m$^3$/year | - | 2,597 m$^3$/year |
| | Running costs | 9,567 EUR/year | 3,415 EUR/year | Total annual saving:<br>6,152 €/year |
| | Capital investment cost | 57,760 € | | |
| | Payback period | 7.2 years | | |

Table 3.20. The evaluation of CP options (con't)

| On-site recycle/reuse/recovery<br>(Recovery and reuse of alkaline etchant and rinsing water of alkaline etchant process) | Parameter | Before | After | Saving |
|---|---|---|---|---|
| | | Alkaline etchant process | Ammoniacal etchant regeneration system | |
| | Water consumption | 900 $m^3$/year | 4.4 $m^3$/year | 895.6 $m^3$/year |
| | Chemical consumption | 51,000 kg/year | 348 kg/year | - |
| | Copper recovery | - | 9,100 kg/year | 9,100 kg/year |
| | Wastewater production | 897 $m^3$/year | - | 897 $m^3$/year |
| | Running costs | 75,245 EUR/year | 15,100 EUR/year | Total annual saving: 60,145 €/year |
| | Capital investment cost | 134,100€ | | |
| | Payback period | 2.2 year | | |

| On-site recycle/reuse/recovery<br>(reusing of microetchant and copper recovery in OSP and direct metallization ) | Parameter | Before | After | Saving |
|---|---|---|---|---|
| | | Micro etch process | The continuous-flow system | |
| | Chemical consumption | 22,944 kg/year | 18,355 kg/year | 4,589 kg/year |
| | Copper recovery | - | 250 kg/year | 250 kg/year |
| | Running costs | 24,555 EUR/year | 14,995 EUR/year | Total annual saving: 9,560 €/year |
| | Capital investment cost | 15,067 € | | |
| | Payback period | 1.6 years | | |

Table 3.20. The evaluation of CP options $^{(con't)}$

| On-site recycle/reuse/recovery (metallic zinc recovery by drainage time optimization ) | Parameter | Before | After | Saving | Comment |
|---|---|---|---|---|---|
| | | | | | Zinc which was transferred from plating tank to rinsing tank was reduced by 50 % |
| | Zinc lost | 90 kg/year | 45 kg/year | 45 kg/year | |
| | Total annual saving | 264 €/year | | | |

| On-site recycle/reuse/recovery (Zinc, Tin and Copper recovery by drain board application ) | Parameter | Before | After | Saving |
|---|---|---|---|---|
| | | | Drain board application | |
| | Zinc lost | 45 kg/year | 27 kg/year | 18 kg/year |
| | Tin lost | 154 kg/year | 92 kg/year | 62 kg/year |
| | Copper lost | 45 kg/year | 27 kg/year | 18 kg/year |
| | Total annual saving | 454 €/year | | |
| | Capital investment cost | 300 € | | |
| | Payback period | 8 months | | |

Table 3.20. The evaluation of CP options (con't)

| On-site recycle/reuse/recovery | Parameter | Before | After | Saving |
|---|---|---|---|---|
| | | Two-stage rinsing | Two stage counter current rinsing | |
| (Application of counter current rinsing and drag out tank in zinc plating and recycle-reuse of rinsing water by reverse osmosis ) | Recycled rinsing water consumption | 10,000 $m^3$/year | 3,789 $m^3$/year | 4,411 $m^3$/year |
| | Zinc recovery | - | 27 kg/year | 27 kg/year |
| | Trivalent solution recovery | - | 102 kg/year | 102 kg/year |
| | Total annual saving | 4,181 €/year | | |
| | Capital investment cost | 340 € | | |
| | Payback period | 1 month | | |

# 5. CONCLUSION

In this study, the explanation of the process flow sheets and the definition of the main characteristics and quantity of the generated wastes were determined for Canovate Inc. Co. Additionally, annual consumptions and cost analysis of raw material, product, waste and emissions of zinc plating and PCB production were carried out.

Canovate Inc. Co. has been chosen as a case study for the implementation of CP methodology since it is the second largest electronic industry in İstanbul and produces 15 % of PCB and electroplated products in Turkey. Production processes of the selected electronic industry created high amount of wastewater, thus, it has been essential to provide the minimum amount of process rinsing water consumption which resulted in reduced volume of wastewater and waste sludge. With this respect, special emphasize was given to both water consumption minimization and recovery and recycling methods of rinsing water.

Technical barriers such as lack of recorded data about raw material/water/chemical consumption and wastewater production were overcome during Planning and Organization and Assessment Phases of the study. Within a duration of two months, data collection assessment including measurement and calculation was completed. Rinsing water consumption in double sided PCB production and zinc plating lines was measured by flow meters. In the scope of commitment of the enterprise, sustainable production in electronics sector and its importance to the human health, safety and production quality were emphasized with seminars and meetings to the company manager and employees throughout the study.

In the assessment phase, the input-output evaluation method which was based on flow charts with material balances was conducted. A set of profile indices, including water/chemical/wastewater unit index, were determined using material flows related to the selected processes. Also, cost evaluations in terms of material and waste cost unit index were considered. The assessment of CP methodology allowed overall evaluation of environmental and economic impacts resulting from PCB manufacturing and metal finishing. The CP assessment method was employed for modification of the technological process by providing comparative analyses of alternative technologies leading to the manufacture of the same product quality.

In the feasibility phase, technical, environmental and economical evaluations of prioritized CP options were evaluated. Technology modifications for “plasma desmear” and “closed loop cleaning system”, raw material substitution/conservation for “lead free coatings” and on-site recycle/reuse/recovery of “ammoniacal etchant/microetchant”, “rinsing water” and “drag-out” have been constituted the focus point of the Cleaner Production assessment in Canovate Inc. Co.

With implementation of alkaline etchant recovery process, 9,100 kg/year (33,700 €/year) of copper which can be sold as pure copper was recovered. Also, ammoniacal etchant consumption as replenisher was reduced by about 90%. With these recovery methods, copper and hazardous chemical load sent to the wastewater treatment plant is decreased since all process chemicals and copper metal were recovered and reused. Process rinsing water consumption decreased to 4.4 m$^3$/year for only evaporation and drag-out losses because all rinsing water was recycled and reused.

In closed loop cleaning system, 680 kg/year hazardous solvent consumption was eliminated and application of aqueous cleaning solution which is suitable for rapid growth of microorganisms was achieved for pre-treatment of metal part. Process rinsing water consumption was reduced by about 81%. Also, hazardous chemical load of wastewater treatment plant is also reduced since cleaner bath solution was recovered and reused with BIO filter unit for 1 to 1.5 year. System has 3.3 years payback period time and considered long term CP option implementation by the selected enterprise.

Technology modification of permanganate desmear process was seen as plasma desmear process eliminating both 2,600 m$^3$/year process rinsing water and 4,577 kg/year hazardous chemical consumption in an entire wet process which promotes sustainable production with minimum waste production. The only waste emission from plasma desmear is a small amount of hydrofluoric acid and it was eliminated by an alkaline wet scrubber. Although it has a long payback period time with 7.2 years, this system has future for sustainable production which is the most important element of CP implementation.

Drag-out recovery which prevents the carrying of process chemicals to the rinsing bath was achieved with 1,263 €/year chemical consumption savings. Implementation of counter current rinsing in zinc electroplating line provides 62 % water consumption reduction leading to very short payback period time with 1 month. This correspond to 3,823 €/year saving in the production of DI water. Adaptation of RoHS Directive (2002/95/EC) to the electroplated products has a great importance for Canovate Inc. Co. since they have a market in Europe. With this respect, special emphasize was given to production of lead free PCBs which provides lead free coating at their production processes. This chemical substitution method doesn't provide any economic advantage but sustainable production concept which is of utmost importance can be achieved with the implementation of recommended option.

The feasibility results showed that the payback periods for economic evaluations concluded variations between 1 month to 7.2 years. CP options are planned to the realized at two different time periods that are decided as short term (1 month-2.5 years) and long term (2.5-8 years) applications. Within this frame, managers have started to develop an organizational procedure for implementation of CP options with a payback period less then 2.5 years. On the top of this, as the product market is of utmost importance for the manufacturers, the priority is given to the product quality during the CP Assessment.

The results of this study showed that the implementation of CP options which were recommended in this study provide definite decrease in the end-of-pipe treatment cost. Also, technical, environmental and economical evaluation of CP options indicated that recommended CP options obtain feasible investment for the production processes which lead to minimum etchant chemical, electroplating metal and rinsing water consumption.

The information of this study, which comprises preventive business strategy designed to conserve resources and promote greater overall efficiency through improved production technologies will be useful to the companies in order to obtain a better knowledge of the electronic process which could be a decision making tool in order to improve economical performance and environmental safety.

# REFERENCES

Abbasi, G.Y., Abbassi, B.E., 2004. Environmental assessment for paper and cardboard industry in Jordan - a cleaner production concept. Journal of Cleaner Production, 12, 321-326.

Abou-Elela, S.I., Abdel Haleem, H., Abou-Taleb, E., Ibrahim, H.S., 2006. Application of cleaner production technology in chemical industry: a near zero emission. Journal of Cleaner production, 12, 102-118.

Adhoum, N., Monser, L., Bellakhal, N., Belgaied, J.E., 2004. Treatment of electroplating wastewater containing $Cu^{2+}$, $Zn^{2+}$ and Cr (VI) by electro coagulation. Journal of Hazardous Materials, 30, 207-213.

Alanso, C.J., Garvin, J., Juanmartin X., 2005. Life Cycle Thinking to Reduce the Waste Generated During the Printed Circuit Board Manufacturing Process, International Conference on Life Cycle Assessment Publication, 5-7 September 2005, Barcelona.

Allen, T.D., Rosselot, S.K., 1996. Pollution Prevention for Chemical Processes, Wiley-Interscience Publication, John Willey&Sons Inc., U.S.A.

Alvarez-Ayusoa, E., Garcia-Sancheza, A., Querol, X., 2003. Purification of metal electroplating waste waters using zeolites. Water Research, 37, 4855-4862.

Arnaiz, S., Miguel, R., Larrauri, E., 2004. Eco-efficiency at Electric and Electronic Equipment from Concept to Case Studies http://www.erscp2004.net/downloads/papers/sixtoarnaiz.pdf.

ATOTECH, 2006. Annual Report of Atotech GmbH, Closed Loop Cleaning System for Economy and Ecology. http://www.atotech.com/.

Avşar, E., Demirer, G.N., 2006. Cleaner production opportunity assessment study in SEKA Balikesir pulp and paper mill. Journal of Cleaner Production, 18, 111-120.

Baban, A., Yediler, A., Kiran Ciliz, N., Kettrup, A., 2004. Biodegradability oriented treatability studies on high strength segregated wastewater of a woolen textile dyeing plant, Chemosphere, 57, 731-738.

Barbiroli, G., Raggi, A., 2003. A method for evaluating the overall technical and economic performance of environmental innovations in production cycles. Journal of Cleaner Production, 11, 365-374.

Benito, Y., Ruiz, M.L., 2002. Reverse osmosis applied to metal finishing wastewater, Desalination, 142, 229-234.

Berkel, R.V., 1999. Building a Cleaner World: Cleaner Production, its Role in Australia, Lessons from Overseas, and Its Future Applications. http://www.p2pays.org/ref/13/12032.pdf.

Bingham, P.A., Hand, R.J., 2005. Vitrified metal finishing wastes composition, density and chemical durability. Journal of Hazardous Materials, 119, 125-133.

CCPIC (Canadian Pollution Prevention Information Clearinghouse), 1996. A Cleaner Production Handbook for Local Government, Australian National University and Deni Green Consulting Services Publication, ISBN, Australia.

Chmielewski, A.G., Urbtiski, T.S., Migdal, W., 1997. Separation technologies for metals recovery from industrial wastes. Hydrometallurgy, 45, 333-344.

CIRCUITREE, 2006. Hot Air Leveling in the Lead-Free Environment. http://www.circuitree.com/CDA/Articles/Feature_Article/c3b03763c4409010VgnVCM100000f932a8c0.

Crama, Y., Klundert, J., Spieksma, F.C.R., 2002. Production planning problems in printed circuit board assembly. Discrete Applied Mathematics, 123, 339-361.

Czech Cleaner Production Center, 2000. Production through EMS-Achieving Cleaner Production using EMS, Czech Cleaner Production Center Publication, Prague.

DEP (Florida Department of Environmental Protection), 1997. A guide on Hazardous Waste Management for Florida's Printed Circuit Board Manufactures. http://www.dep.state.fl.us/waste/quicktopics/publications/shw/hazardous/wiringboard.PDF

DPPEA (North Carolina Division of Pollution Prevention and Environmental Assistance), 2000. Striving for Zero Water Waste in a Metal Finishing Facility in Spain. http://www.p2pays.org/ref/10/09287.htm.

DPPEA (North Carolina Division of Pollution Prevention and Environmental Assistance), 2002. PWB Industry and use Cluster Profile, http://www.owr.ehnr.state.nc.us/ref/13/12023/pr_pt1-1.htm.

EC Directive 2002/95/EC, 2002. Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic equipment. Official Journal of the European Union, 19-23.

ENVIROWISE (Practical Environmental Advice for Business), 2001. Reducing Water and Effluent Costs in PCB Manufacture, http://www.envirowise.gov.uk/page.aspx?o=117459.

EPA (Environmental Protection Agency), 1993. Fact Sheet: Metal Recovery Technologies for the Metal Finishing Industry. http://es.epa.gov/techinfo/facts/michigan/michfs20.html.

EPA (Environmental Protection Agency), 1995. Printed Wiring Board Pollution Prevention and Control Technology: Analysis of Updated Survey Results. http://www.epa.gov/dfe/pubs/pwb/pdf/p2tech.pdf.

EPA (Environmental Protection Agency), 1996. Case Study 5: A Continuous-Flow System for Reusing Microetchant. http://www.epa.gov/dfe/pubs/pwb/case_stu/case5/index.html.

EPA (Environmental Protection Agency), 1998a. Case Study 1: Pollution Prevention Work Practices. http://www.epa.gov/dfe/pubs/pwb/case_stu/case1/index.html#dragout.

EPA (Environmental Protection Agency), 1998b. Profile of the Metal Fabrication Industry. http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/fabric.html.

EPA (Environmental Protection Agency), 1999. On-Site Etchant Regeneration. http://www.epa.gov/dfe/pubs/pwb/casestu/case2/.

EPA (Environmental Protection Agency), 2006. Case Study 4: Plasma Desmear. http://www.epa.gov/dfe/pubs/pwb/case_stu/case4/index.htm.

Erol, P., Thming, J., 2006. ECO-optimization of pre-treatment processes in metal finishing. Computers & Chemical Engineering, 30, 587-598.

ESCWA (Economic and Social Commission for Western Asia), 2001. Environmentally Sound Technologies in the Metal Finishing Industry. http://www.escwa.org.lb/information/publications/edit/upload/tech-01-6-e.pdf.

Fierr, L., Getty, J.-D., 2003. Plasma Process for PCB Manufacturing. http://www.marchplasma.com/pdf/Plasma_4_PCB.pdf.

Fijał, T., 2007**.** An environmental assessment method for cleaner production technologies**.** Journal of Cleaner production, 15, 914-919.

Fornari, P., Abbruzzese, C., 1999. Copper and nickel selective recovery by electrowinning from electronic and galvanic industrial solutions. Hydrometallurgy, 52, 209-222.

Fresner, J., 1998. Cleaner production as a means for effective environmental management. Journal of Cleaner Production, 6, 171-179.

Fresner J., Schnitzer H., Gwehenberger G., Planasch M. , Brunner C., Taferner K., Mair J., 2006. Practical experiences with the implementation of the concept of zero emissions in the surface treatment industry in Austria. Journal of Cleaner Production, 24,198-209.

Glavič, P., Lukman, R., 2005. Sustainability Terms and their Definitions, http://www.vito.be/erscp2005/documents/papers/PAPER117.PDF.

Goosey, M., Poole, M., 2005. Chemical Processes in PCB Fabrication, http://www.rohmhaas.com/electronicmaterials/CBT/vol5/papers/HighPerfLamimates.pdf.

Groudeva**,** V.I., Groudev**,** S.N, Doycheva**,** A.S. 2001. Bioremediation of waters contaminated with crude oil and toxic heavy metals. International Journal of Mineral Processing, 62, 293-299.

Gurbuz, S., Kiran-Ciliz, N., Yenigun, O., 2004. Cleaner production implementation through process modifications for selected SMEs in Turkish olive oil production , Journal of Cleaner Production, 12, 613-621

Howgrave-Graham, A., Berkel, R., 2007. Assessment of cleaner production uptake: method development and trial with small businesses in Western Australia**.** Journal of Cleaner Production, 15, 787-797.

Hunsom, M., Pruksathorn, K., Damronglerd, S., Vergnes, H., Duverneuil, P., 2005. Electrochemical treatment of heavy metals ($Cu^{2+}$, $Cr^{6+}$, $Ni^{2+}$) from industrial effluent and modeling of copper reduction. Water Research, 39, 610-616.

Janssen, L.J., Koene, L., 2002. The role of electrochemistry and electrochemical technology in environmental protection. Chemical Engineering Journal, 85, 137-146.

Joseph, D., 2004. Conserve Water with Conductivity Meters. http://www.metalfinishing.com/editors_choice/articles/041129_Joseph.html.

Juang, R.S., Wang, S.W., 2000. Electrolytic recovery of binary metals and EDTA from strong complexed solutions. Water Research, 34, 3179-3185.

Kentish, S.E., Stevens, G.W., 2001. Innovations in separations technology for the recycling and re-use of liquid waste streams. Chemical Engineering Journal, 84, 149-159.

Keskitalo, T., Tanskanen, J., Kuokkanen, T., 2006. Analysis of key patents of the regeneration of acidic cupric chloride etchant waste and tin stripping waste. Resources, Conservation and Recycling, 18, 1847-1874.

Kjær, T., Dirckinck-Holmfelcd, K.R., Braun, C.S., Andersen, J.B., 2005. Are the European directives WEEE and RoHS Fostering Cleaner Production among the Chinese Industry? http://www.vito.be/erscp2005/documents/papers/PAPER050.PDF.

La-Dou, J., 2006. Printed circuit board industry. International Journal of Hygiene and Environmental Health, 209, 211-219.

Lee, M.S., Ahn, JG., Ahn, J.W., 2003. Recovery of copper, tin and lead from the spent nitric etching solutions of printed circuit board and regeneration of the etching solution. Hydrometallurgy, 70, 23-29.

Lee, E.S., Park, H., Baik, H.K., Lee S.J., Song, K.M., Hwang, M.K., Huh, C.S., 2002. Air mesh plasma for PCB Desmear process. Surface and Coatings Technology, 171, 328-332.

Lemos, F.A., Sobral, L.G.S., Dutra, A.J.B., 2006. Copper electrowinning from gold plant waste streams. Minerals Engineering, 19, 388-398.

Luo, K.Q., Huang, Y.L., 1997. Intelligent decision support for waste minimization in electroplating plants. Engineering Applications of Artificial Intelligence, 10, 321-334.

Magalhães, J.M., Silva, J.E., Castro, F.P., Labrincha, J.A., 2005. Physical and chemical characterization of metal finishing industrial wastes. Journal of Environmental Management, 75, 157-166.

Mediterranean Action Plan, 2000. Alternatives for Preventing Pollution in the Surface Treatment Industry, Regional Activity Centre for Cleaner Production (RAC/CP) Publication, Spain.

Melling, J., 1986. Treatment of ammoniacal copper etchants. Resources and Conservation, 12, 113-124.

Milad, G., 2002. Surface Finishing for Lead-Free Products. Uyemura International Corporation Southington CT, http://www.uyemura.com/library-4.htm.

Ministry of Environment Spain, 2000. Minimization Opportunities Environmental Diagnosis (MOED), Altes Publications, Spain.

Morina, E., 2000. Application of Cleaner Production Methodology in Dairy Industry, M.S. Thesis, Boğaziçi University.

Narayanaswamy, V., Scott, J.A., Ness, J.N., Lochead, M.L., 2003. Resource glow and product chain analysis as practical tools to promote cleaner production initiatives. Journal of Cleaner Production, 11, 375-387.

NMFRC (National Metal Finishing Resource Center), 1995. Reverse Osmosis Applications for Metal Finishing Operations, P2 Project for Metal Finishers. http://www.nmfrc.org/pdf/ro.htm.

PLASMA-ETCH (Plasma Etch, Inc.), 2005. Industrial Plasma System Annual Report. http://www.plasmaetch.com/.

Qin, J.J., Oo, M.H., Wai, M.N., Ang, C.M., Wong, F.S., Lee, H., 2003. A dual membrane UF/RO process for reclamation of spent rinses from a nickel-plating operation-a case study. Water Research, 37, 3269-3278.

Qin, J.J., Wai, M.-N., Oo, M.H., Wong, F.S., 2002. A feasibility study on the treatment and recycling of a wastewater from metal plating. Journal of Membrane Science, 208, 213-221.

Randal, P.M., 1998. Engineers' Guide to Cleaner Production Technologies, Technomic Publishing Company, Inc., U.S.A.

Reeve, D. J., 2006. Environmental improvements in the metal finishing industry in Australasia. Journal of Cleaner Production, 22, 1-8.

Roy, C., Shapiro, M., 1999. Automated direct drag-out recovery: A novel approach to reclamation of metals from electroplating rinse water. Plating and Surface Finishing, 34, 112-119.

Sage, J., Schnitzer, H., 1994. Waste Minimization and its ecological evaluation-A case study in the printed circuit boards. Journal of Cleaner Production, 2, 185-195.

Scott, K., Chen, X., Atkinson, J.W., Todd, M., Armstrong, R.D., 1997. Electrochemical recycling of tin, lead and copper from stripping solution in the manufacture of circuit boards. Resources, Conservation and Recycling, 20, 43-55.

SIGMA-MECER, 2005 Annual Report of Sigma Metallextarktion AB, Mecer™ Process for the Recycle of Ammoniacal Etchant. http://www.sigma-mecer.com/.

Solisio, C., Panizza, M., Paganelli, P., Cerisola, G., 1999. Electrochemical remediation of copper (II) from an industrial effluent, Part I: Monopolar plate electrodes. Resources, Conservation and Recycling, 26, 115-124.

Sullivan, G.P., Hyner, R., Masella, P., 2000. The NICE$^3$-Whyco technologies partnership: Saving energy, dollars, and the environment in the metal plating industry. Resources, Conservation and Recycling, 28,199-205.

Şişman, F., 2002. Cleaner Production Implementation for Integrated Tannery in Turkey, M.S. Thesis, Boğaziçi University.

Telukdarie, A., Brouckaert, Haung, Y., 2006a. A case study on artificial intelligence based cleaner production evaluation system for surface treatment facilities. Journal of Cleaner Production, 14, 1622-1634.

Telukdarie, A., Buckley, C., Koefoed, M., 2006b. The importance of assessment tools in promoting cleaner production in the metal finishing industry. Journal of Cleaner Production, 14, 1612-1621.

Timian, S.J., Connolly, D.M., 2000. The Regulation and Development of Bioremediation. http://www.fplc.edu/risk/vol7/summer/Timian.htm.

UNEP-UNIDO (United Nations Environment Programme- United Nations Industrial Development Organization), 1991. Audit and Reduction Manual for Industrial Emissions and Wastes, First Edition, United Nation Publications.

UNEP (United Nations Environment Programme), 1995. Cleaner Production Assessment Manual, Cleaner Production Program/NCPC Project Publication.

UNEP (United Nations Environment Programme), 1998a. Cleaner Production Manual for Queensland's Metal Finishing Industry. http://geosp.uq.edu.au/emc/cp/res/Metal%20Finish/Metal%20Finish_manual.htm.

UNEP (United Nations Environment Programme), 1998b. A Cleaner Production Manual for the Metal Finishing Industry, UNEP Working Group for Cleaner Production. http://www.p2pays.org/ref/22/21983.pdf.

Uner, J., Theriault, M., Carsac, C., 2000. The application of atmospheric pressure plasma to various steps in integrated circuit packaging, 3rd. Annual Semiconductor Packaging Symposium/Session III, http://www.airliquide.com/file/paragraphtranslation/pdf-tech-paper/plasma_2000.pdf.

Unnikrishnan, S., Hegde, D.S., 2006. An analysis of cleaner production and its impact on health hazards in the workplace. Environment International, 32, 87-94

Veglio, F., Quaresima, R., Fornari, P., Ubaldini, S., 2003. Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning. Waste Management, 23, 245-252.

Veit, H.M., Diehl, T.R., Salami, A.P., Rodrigues, J.S., Bernardes, A.M., Tenório, J.A.S., 2005. Utilization of magnetic and electrostatic separation in the recycling of printed circuit boards scrap. Waste Management, 25, 67-74.

Viguri, J.R., Andrés, A., Puente, C.R., Irabien, A., 2000. Characterization of metal finishing sludges: Influence of the pH. Journal of Hazardous Materials, 79, 63-75.

Viguri, J.R., Andrés, A., Irabien, A., 2002. Waste minimizations in a hard chromium plating small medium enterprise (SME). Waste Management, 22, 931-936.

Visvanathan, C., 1996. Profitability of in plant modifications in pollution control. Resource, Conservation and Recycling, 16, 135-143.

Visvanathan, C., Parasnis, M., Janesiripanich, A., 1998. Multimedia environmental audit in a rice cracker factory in Thailand: A model case study. Journal of Cleaner Production, 6, 93-101.

Wong, F.S., Qin, J.J., Wai, M.N., Lim, A.L., Adiga, M., 2002. A pilot study on a membrane process for the treatment and recycling of spent final rinse water from electroless plating, Separation and Purification Technology, 29, 41-51.

Yang, Y.H., Lou, H.H., Huang, Y.L., 2000. Synthesis of an optimal wastewater reuse network**.** Waste Management, 20, 311-319.

Yang, Q., Kocherginsky, N.M, 2006. Copper recovery and spent ammoniacal etchant regeneration based on hollow fiber supported liquid membrane technology: From bench-scale to pilot-scale tests. Journal of Membrane Science, 286, 301-309.

Zhao, M., Duncan, J.R., Hile, V.P., 1999. Removal and recovery of zinc from solution and electroplating effluent using Azolla filiculoides. Water Research 33, 1516-1522.

Zufía, J., Duch, A., Esturo, A., Buruaga, M.S., 2004. Innovative Method for Cleaner Production Transfer to Developing Countries. http://www.erscp2004.net/downloads/papers/jaime%20zufia.pdf.