Australian Sustainable Industry Research Centre Ltd

Milestone 2 Report
For
Swart Water Fund

Metal Recovery From Wash Waters and Treatment Plant Sludges

'An assessment of the technology options available for minimising water usage and maximising the recovery of valuable heavy metals from Metal Plating operations'

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Executive Summary

This report is the second Milestone Report and deliverable as part of the Smart Water Fund Project, Metal Recovery from Wash Waters and Treatment Plant Sludges.

The report is a review of available literature in best practice operations in the metal finishing industry. The majority of available literature on best practice in Metal finishing operations has been generated and developed to its current form over the 1980's and 1990's. This material is easily accessed from a number of sources. Guides such as the Metal finishing guidebook & directory, updated annually, and in particular, web based sites of Government agencies and Industry groups and partnerships set up as clearing houses to promulgate cleaner production, pollution prevention and resource exchange principles, metal finishing being one of the subject areas covered in these sites.

The Metal Finishing Industry Guide cites the major benefits arising from pollution prevention programs as including:

- Reduced manufacturing and waste disposal costs (reduced materials, water costs and anode loss, waste water treatment and reduced solid waste),
- Product quality improvements (with improved process control/rinsing comes improved predictability/performance of plating systems, leading to decreased rejection rates from spotting, staining and imperfections in work pieces),
- Environmental risk reduction (decreased spill frequency, site contamination or non-compliance risk, improved OHS performance).

The DPPEA in a recent publication stated that "Improving rinsing efficiency represents the greatest water reduction option for metal finishing" and that a rinsing efficiency improvement program is the first step necessary to enable metal finishers to implement further pollution prevention techniques such as chemical recovery and in developing the potential to achieve closed looping for water usage in the electroplating process.

It has been acknowledged that a successful pollution prevention program requires management support and involvement. An in-house team should be set up to manage the process and develop company wide involvement. Such a strategy should be based on the facility's current issues (e.g. effluent compliance, material costs, product rejection rates etc) and the team needs to work with management to:

- Set preliminary short term and long term goals,
- Gather and analyse existing information, develop process flow sheets and mass balances and identify information gaps relevant to the design and implementation of the program,

- Act to promote the program with staff, indicating how members can take part, and

- Monitor and report progress to management and company members

The above process exemplifies the fact that cleaner production is not just limited to environmental consideration, and can actually be an effective business tool. The following literature review will demonstrate this, as well as highlighting the main tools that can be used to bring an element of best practice in cleaner production to the metal finishing industry.

Substantial savings can often be made in these areas with very little investment, while further savings can be made with comparatively simple techniques. The use of excess water to dilute the effluent is now an unacceptable practice. European studies suggest that it is rarely necessary to use sophisticated technology to cut water costs. These areas are outlined in more detail within this chapter, as they relate directly to achieving waste minimisation and pollution prevention.

The literature has broadly identified 5 main areas where waste minimisation and pollution reduction practises have been most successful. These areas are:

- Product Changes and Process Substitution – Improved operating procedures

- General Waste Reduction – Reduced dragout losses and rinse water discharges

- Process Solution maintenance

- Chemical Recovery, and

- Treatment / Off-site Recycling

The report provides a summary of initiatives undertaken in Australia and overseas and provides examples of case studies documented in the USA.

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1. Introduction

1.1. Intent of the Paper

As a part of the Smart Water Fund Part A project “An assessment of the technology options available for minimising water usage and maximising the recovery of valuable heavy metals from Metal Plating operations’, a literature survey of best practice in water usage and management was undertaken. A widespread exposition of common theme was present throughout the literature surveyed which will be presented in summary as part of this report.

Recently Chalmers (2008) reviewed from an American perspective the economic, regulatory and technology trends for the future of the surface finishing industry. Similarly, a recent review by Reeve (2007) discussed environmental improvements in the Australasian context and focused on specific issues including new technologies being adopted, research projects and responses to government legislation and education.

The majority of available literature on best practice in Metal finishing operations has been generated and developed to its current form over the 1980’s and 1990’s. This material is easily accessed from a number of sources. Guides such as the Metal finishing guidebook & directory, updated annually, and in particular, web based sites of Government agencies and Industry groups and partnerships set up as clearing houses to promulgate cleaner production, pollution prevention and resource exchange principles, metal finishing being one of the subject areas covered in these sites. ILLEPA, (WRRC. 2008), (USAID.2007) ISTC 2008.

One US site alone (DPPEA, 2000) has over 700 articles on pollution prevention, many of which are available through web access (WRRC, 2008). The North Carolina Department of Environment and Natural resources (NCDENR) for instance is part of the Strategic Goals program of Commonsense Initiatives, a program developed as a joint effort between the USEPA and the Surface Finishing Industry Council (with support of several trade associations and stakeholders). These initiatives provide a wide range of information in the area of surface finishing including ‘General Guides’, ‘Guides on Bath Life and Metal Recovery’ and ‘Water and Wastewater Issues’.

1.2. A Definition of Metal Finishing

The term “Metal finishing” includes both electroplating and coating operations as well as their supporting processes (polishing, cleaning, degreasing, pickling, etching etc) (USAID, 2007).

Metal finishing consists of three main unit operations (EPA 1995a):

- Surface preparation - cleaning and surface activation typically using detergents, solvents or caustic materials;

- Surface Treatment/Plating - such as electroplating, electroless plating, mechanical plating, anodising etc modifying the work piece surface, and

- Post - treatment processes - such as chromating, passivating, phosphating etc… used to enhance the appearance or add to the properties of the work.

Each of the operations involve a post operation draining and/or rinsing step that results in loss of process fluid and the generation of wash waters contaminated primarily with heavy metals and other inorganic contaminants. The wastes resulting from end of pipe treatment of these streams include the primary source of the treated waste waters (generally disposed of to sewer), and the prescribed waste solid residues arising from metal finishing (generally disposed to landfill).

This type of ‘classical’ end of pipe treatment approach is wasteful of both water and feed chemical resources. With the rising costs of the feed plating solutions, potable water and the increasing disposal costs for treated waste water and solid residuals, the inherent profitability of metal finishing operations is being impacted.

1.3. A summary of the benefits realised by cleaner production programs

The Metal Finishing Industry Guide (WRRC, 2008) cites the major benefits arising from pollution prevention programs as including:

- Reduced manufacturing and waste disposal costs (reduced materials, water costs and anode loss, waste water treatment and reduced solid waste),

- Product quality improvements (with improved process control/rinsing comes improved predictability/performance of plating systems, leading to decreased rejection rates from spotting, staining and imperfections in work pieces),

- Environmental risk reduction (decreased spill frequency, site contamination or non-compliance risk, improved OHS performance).

The DPPEA in a recent publication stated that “Improving rinsing efficiency represents the greatest water reduction option for metal finishing” (DPPEA, 1999), and that a rinsing efficiency improvement program is the first step necessary to enable metal finishers to implement further pollution prevention techniques such as chemical recovery and in developing the potential to achieve closed looping for water usage in the electroplating process (Heller, 1999).

It has been acknowledged that a successful pollution prevention program requires management support and involvement (Dennison, 1996). An in-house team should be set up to manage the process and develop company wide involvement. According to Dennison such a strategy should be based on the facility’s current issues (e.g. effluent compliance, material costs, product rejection rates etc) and the team needs to work with management to:

- Set preliminary short term and long term goals,
- Gather and analyse existing information, develop process flow sheets and mass balances (Viguri, 2002) (identify information gaps) relevant to the design and implementation of the program,
- Act to promote the program with staff, indicating how members can take part, and
- Monitor and report progress to management and company members

The above process exemplifies the fact that cleaner production is not just limited to environmental consideration, and can actually be an effective business tool. The following literature review will demonstrate this, as well as highlighting the main tools that can be used to bring an element of best practice in cleaner production to the metal finishing industry.

2. Best Practice Waste Minimisation and Pollution Prevention

2.1. Introduction

Pollution prevention, cleaner production and waste minimisation are terms often used interchangeably to refer to the practice of reducing business waste and being generally more efficient with resources. It is widely acknowledged that this practice can be a valuable business tool, and much of the literature reviewed in this paper exemplifies this. The literature survey was undertaken to identify waste minimisation initiatives implemented around the world in the metal finishing industry. A wealth of information is available from countries such as Canada (The Metal Finishing Pollution Prevention Task Force, 2001), USA (National Metal Finishing Resource Centre (NMFRC), Iowa Pollution Prevention Initiative, USEPA), South Africa (Thambiran (2002)), UK, (TIMF (1999) (Envirowise) as well as from Australia (Centre of Excellence in Cleaner Production, Uniquest). Most of these studies were undertaken in the 1990's and are generally organised through industry based organisations.

Perhaps the most extensive reference found in this review was the 'Metal Finishing Topic Hub (WRRC, 2008). Within this 'topic hub' was a comprehensive 'Metal finishing Industry Guide', and although much of the information contained within this guide is somewhat dated now, it still remains an extensive tool for cleaner production concepts and practices in the metal finishing industry.

Along with useful guidelines and information sheets, a number of fact sheets are available that espouse simple options for cleaner production in the area of water savings. These are readily available on the World Wide Web, on sites like the 'p2pays' website (DPPEA, 2000). The DPPEA states that substantial reductions in water usage can be achieved through the application of pollution prevention or cleaner production techniques (DPPEA, 1999) and that improved rinsing efficiencies represent the greatest waste reduction opportunity for metal finishing. Similarly, other groups list general water saving tips. Curtin University with funding from Environment Australia, and the Australian Industry Group (AiG) in Australia recently promoted the good business sense that efficient water use entails with fact sheets offering simple tips CUT (2002), (AIG, 2006) and websites such as Cleanerproduction.com and FINISHING.COM list the top 10 and 20 generic water saving suggestions.

Despite this information, and the apparent benefits to the metal finishing industry, the Centre of Excellence in Cleaner Production (Uniquest), based at Curtain University, has reported that the uptake of new technologies in Australia has been poor. They have reported that the likely causes for this are:

- A lack of basic awareness by businesses of the environmental impacts and risks of their operations

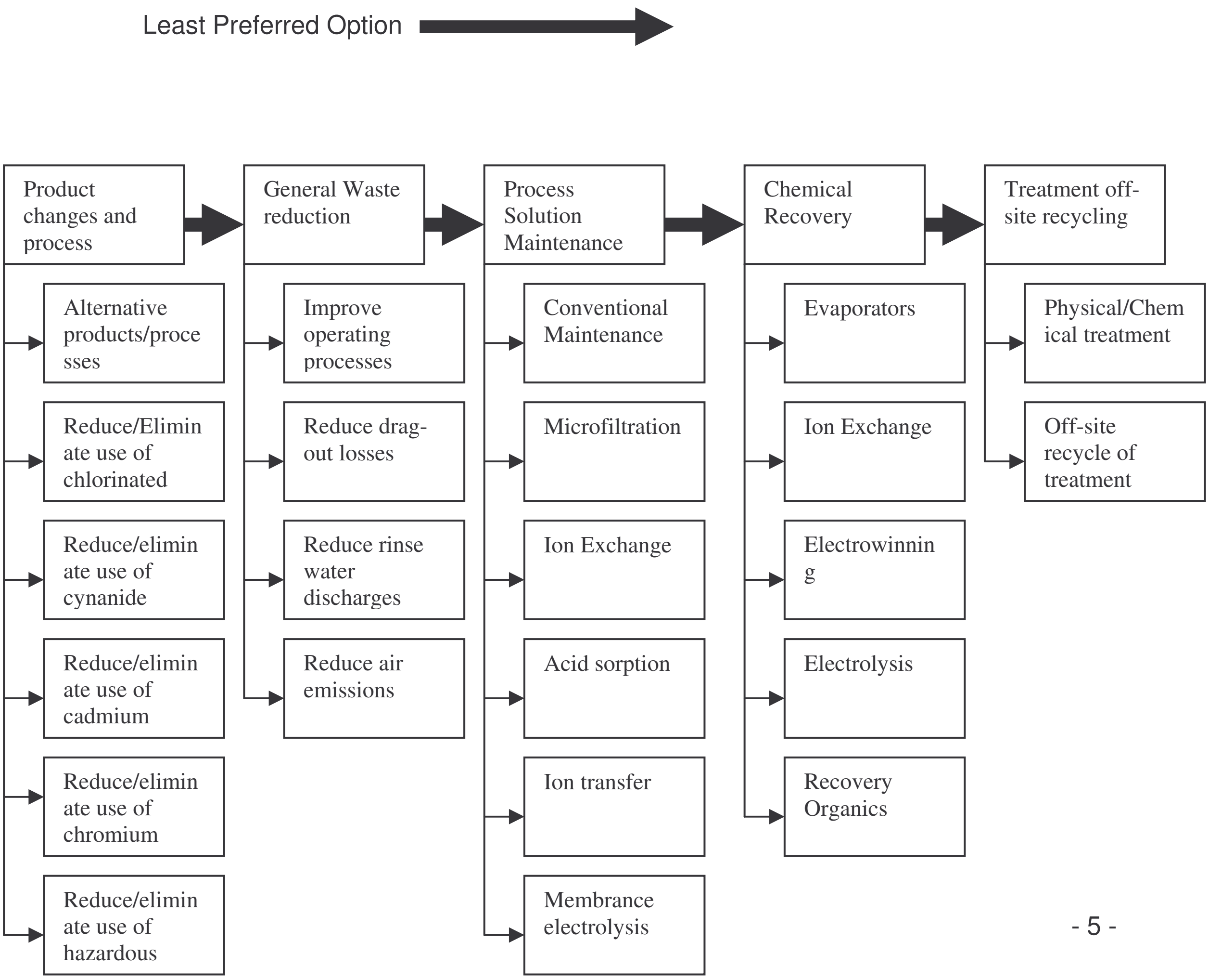
- A lack of understanding of the business benefits of cleaner production and eco-efficiency
- Real or Perceived barriers to implementation. These real and perceived barriers tend to be common across small to medium sized enterprises.

Schwartz (1997) indicated that costs, in particular for hardware additions could cause an obstacle to adoption of additional water reduction opportunities. The four main obstacles sited were:

- Cost is too high,
- Waste reduction could slow down production,
- Waste reduction could hurt quality of the product, and
- Inability to recover costs of waste reduction measure where non-complying shops can undercut their prices

The literature has broadly identified 5 main areas where waste minimisation and pollution reduction practises have been most successful. These areas are summarised by the US EPA in their 'Profile of the Fabricated Metal Products Industry' document (EPA, 1995b). Figure 1 below outlines these methods and technologies.

Figure 1 – Waste Minimisation/Pollution Prevention Methods and Technologies (EPA, 1995b)



The main principles, in order of preference, shown in Figure 1 are:

- Product Changes and Process Substitution – Improved operating procedures
- General Waste Reduction – Reduced dragout losses and rinse water discharges
- Process Solution maintenance
- Chemical Recovery, and
- Treatment / Off-site Recycling

As the focus of this review is best practice water management, a full review of 'Product Changes and Process Substitution' is outside the scope of this review (for example, the detailed discussions related to changes to process design to coating systems such as vapour deposition or moving from cyanide to non cyanide process to eliminate toxicity are outside the scope of this review). However, each of the other principles ('General Waste Reduction, 'Process Solution Maintenance' etc…) will be included in subsequent chapters. Interestingly, the order of these topics reflects in general the increasing costs of application.

Substantial savings can often be made in these areas with very little investment, while further savings can be made with comparatively simple techniques. The use of excess water to dilute the effluent is now an unacceptable practice. Studies by the Environmental Technology Best Practice Program (UK) and industrial experience, especially in Germany, suggests that it is rarely necessary to use sophisticated technology to cut water costs. These areas are outlined in more detail within this chapter, as they relate directly to achieving waste minimisation and pollution prevention.

In terms of quantifying improvements, this can be measured against the overall chemical usage figure per unit of production and the maintenance/improvement of product quality (for example overall rejection levels, adherence, plating thickness etc) (Telukdarie, 2006).

It is critical to understand the sources of contaminants in metal cleaning and plating baths, to then look for pollution prevention or cleaner production solutions. The North Carolina Division of the Pollution Prevention and Environmental Assistance (DPPEA, 1977) states that there are four basic types of contaminants that occur in plating/cleaning solutions:

- Particulates: any solid material suspended in the solution.
- Organics
- Inorganics, and
- Micro-organisms

These contaminants can lead to coating defects such as pitting, peeling and blistering.

2.2. Improved Operating procedures (including operator training)

The following references all refer to the principle of improved employee training and the formalisation of operating procedures for each plating line, and specifically the impact of these on a number of critical operations. This section summarises the areas identified in the literature where the most important improvements were made.

2.2.1. Employee Training

Training should include safety, rinsing techniques and chemical hazards. Training in the correct handling of chemical and required work practices and procedures should result in:

- A better understanding of how to optimise bath operation,
- Minimise spill generation, and
- Improve the consistency of bath formulation

Initial increases in costs experienced are soon made up with improved spill prevention, operational, OHS and Environmental performance (APPU 1995).

The Australian Institute of Metal Finishing (AIMF) have an important educative role through basic technician training courses in metal finishing and specific courses such as The Cleaner Production for Metal Finishing (Advanced Course) conducted in Melbourne and through their National conferences and State meetings (Reeve, 2007).

2.2.2. Housekeeping and preventative maintenance

The UNEC and others have specified a number of critical aspects of housekeeping and preventative maintenance, as it relates to pollution prevention in metal finishing. The following points summarise these critical aspects (Telukdarie, (2006), UNEC (1995), and APPU (1995)):

- optimising equipment efficiency, prevent foreign material entry prolonging bath life (keep area clean, filter incoming air),
- maintaining racks clean and free of defects to minimise contamination and decrease dragout,
- protecting anode bars from corrosion through the use of corrosion resistant tanks and equipment,
- minimising product losses, equipment failures

- minimising rejects (through bath quality maintenance, wash efficiency) and

- maintaining clean work environment to increases worker safety,

- preventing leaks and spills,

- managing inventory (maintaining minimum stocks necessary for production and control usage),

- chemical testing, (trial chemistries used at bench scale rather than full scale testing. Samples returned to manufacturer where possible), and

- managing water quality. Hardness in water decreases the ability of water to rinse effectively. I.e. The use of deionised water improves plating quality, extends bath life, increases rinse efficiency, and reduces water usage and sludge generation (MDEQ, 1996)

2.2.3. Monitoring Bath Composition/Chemistry.

In addition to housekeeping, (Telukdarie, 2006) and others looked at the monitoring of bath composition and chemistry (IAMS,1995), and the impacts of this on pollution prevention. The article stated that more consistent work piece quality and longer bath life, electrode life and improved efficiency is achieved with the maintenance of critical operating parameters within acceptable limits. The paper confirms that optimum bath chemistry is critical to ensure anode and cathode efficiency is maintained, and goes on to say that regular monitoring of bath chemistry with field test kits against supplier recommended concentration levels is critical, although there is a note stating that higher bath concentrations result in increased dragout and waste generation (EPA,1992). Additionally, Telukdarie focused on the importance of assessment tools and promoting cleaner production in order to promote change within the metal finishing sector in this area.

2.2.4. Determining and optimise the aqueous cleaning process

An assessment should be made as to the effectiveness of the existing cleaning operation. Aqueous cleaning uses a solution of water, detergents, and acid or alkaline chemicals for parts cleaning (FLDEP, 1995). These materials contribute greatly to facilities TDS load in their effluent. Cleaning by immersion with mechanical or ultrasonic agitation, and/or spray washing are most common configurations.

Factors affecting cleaning operations include:

- Substrate (what is being cleaned and its chemical compatibilities) (Innes, 1993)

- Degree of cleanliness required (EPA, 1990)

- Nature of the contaminant (Organic and/or Inorganic) (EPA, 1990), and
- Water Quality. Hard water can decrease the effectiveness of a cleaning system (Innes, 1993)

Aqueous cleaners consist of a base ingredient (Builders – such as NaOH, KOH, NaSilicates etc) and surfactants and emulsifiers. These systems can result in emusifed caustic waste waters requiring extensive treatment before disposal.

More flexible weak emulsifying systems with quick break properties or non-emulsifying systems using spray cleaning should be assessed. Additives and options are discussed in detail in an investigation by the Florida Department of Environment Protection (FL DEPO, 1995).

2.2.5. Equipment modification to prevent pollution

In a separate paper, the Department of Environment, Heritage and Natural Resources (DEHNR) states that various modifications to equipment used in metal finishers can play a distinct role in pollution prevention. For example the purity, bagging and placement of anodes used within the industry can assist in preventing pollution, as can the use of purified water in bath solution make-up and rinse water (DEHNR, (1997) and EPA (1992)).

2.3. General Waste Reduction

The two most commonly identified areas of waste minimisation were reducing dragout losses and reducing rinse water discharges.

2.3.1. Reduced Dragout Losses

Much of the literature on the topic of waste minimisation in metal finishing indicated that there was a direct link between reducing dragout losses and reducing the pollution loading to wastewater (ISTC (2008), MDEQ (1996), IAMS (1995) and Cushine (1994)). In the DPPEA's fact sheet in 1997, it was highlighted that dragout loss results in the need for additional raw material, the removal of that material from the waste water before discharge to sewer, disposal of the solid residues produced and processing of the treated waste water by the local sewage authority along with the introduction of additional clean water makeup.

Additionally, the fact sheet and other sources went on to state that most methods of dragout reduction are inexpensive to implement and have short payback periods. Methods such as pH/conductivity, measurement of surface tension etc should be used to monitor existing dragout rates in order to quantify the effectiveness of process and procedural changes (EPA (1992), DPPEA, (1997, 1999)).

2.3.1.1 Physical methods of process optimisation

Other articles have looked at physical methods of process optimisation, reducing build-up of impurities and increasing bath life including:

- Decreasing the work piece withdrawal rate and drainage time. Allowing bath liquid to drain directly back into the plating bath. Increasing drainage time form an industry standard of 3 seconds to 10 seconds reduces the dragout rate by 40%. IAMS, (1995)

- Improved racking, racking design and maintenance/cleanliness. Optimise drainage, prevent pooling of plating liquid on work, rack or irregular surfaces EPA (1992)

- Use of Drain boards and drainage tanks. Should cover the entire distance between tanks, be kept clean and properly maintained to prevent contamination (IAMS, 1995).

- Rinsing over the plating tank

- Dragout Tanks. Dead or static rinsing tanks used primarily on hot processes. Air agitation is often used to enhance rinsing. As concentration increases the bath solution can be added back to make up solution losses in the plating tank. EPA (1992), APPU (1995)

- Using air knives APPU (1995) and

- Improved design and drainage from barrel plating. (up to 10 times more dragout is commonly carried over for barrel plating) (IAMS, 1995), NOTE: Barrel plating in particular shows significant reductions with modifications (Sullivan, 2000)

- Installing In-tank Filtration. For the continuous removal of particulates >1µm (DPPEA, 1997).

2.3.1.2 Monitoring Bath Composition/Chemistry.

The chemistry and/or composition of the baths used in the metal finishing industry can have a significant affect on the drag-out losses associated with the business. Regular monitoring of bath chemistry should occur with the view of minimising concentrations necessary for effective operation to produce the required product quality (suppliers tend to set concentration specifications higher than absolutely required for effective operation). This will minimise the waste generation from this source (IAMS, 1995).

2.3.1.3 Optimising Bath Operating Temperature.

Similarly, the operating temperature of the metal finishing baths can have a significant affect on the drag-out losses. As bath temperature increases, the viscosity decreases, reducing the amount of plating material dragged out. Excessive temperatures should be avoided due to the detrimental effect on some bath additives, excessive energy usage, effect on water usage and increase handling due to the solution drying on the work pieces during removal (APPU, 1995).

- Advantages - High temperatures reduce the volume of dragout and allow for the use of lower solution concentrations.

- Disadvantages - Increased energy costs, evaporation rate, water usage and possible worker exposure to bath emissions.

2.3.1.4 Optimising Plating Solution Concentration.

The greater the concentration of plating chemical, the greater the viscosity and dragout potential. Optimising the plating solution concentration to the minimum required for maintenance of product quality should be investigated (APPU (1995), EPA (1992)).

- Advantages - Reduces dragout loss, chemical usage and cost, sludge generation.

- Disadvantages – Decreased tolerance to impurities, may be outside of contractual specifications from client (APPU, 1995).

2.3.1.5 Additives for Plating Baths.

Additives are used to aid the plating process and stabilise the plating system. Consequently these additives can have an impact on the drag-out losses experienced by the bath in question.

Mild chelators such as phosphates and silicates are generally used for most cleaning and etching processes. Once chelators enter the waste stream they can inhibit the precipitation of metals, requiring more extreme treatment regimes, producing greater quantities of solid PIW requiring disposal (EPA, 1992).

Common additives and their advantages/ disadvantages with respect to drag-out losses include:

- Wetting Agents (Non-ionic only).

    - Advantages – Reduce dragout by up to 50% and can improve finish quality.

- Disadvantages – Possible foaming or incompatibilities with some bath chemistries (APPU, 1995)

- Non – chelated process chemistries (e.g. Alkaline cleaning & etching).

    - Advantages – easier metal removal from wastewater and lower sludge handling and disposal costs.

    - Disadvantages – not applicable to electroless plating as chelating chemicals necessary in bath function (PRC, 1989). Non-chelated process cleaning baths usually require continuous filtering to remove solids (1-5 µm pore size).

2.3.2. Reduced Rinse Water Discharges

Adequate rinsing is critical in maintaining product quality. All parts must be efficiently rinsed to minimise staining, spotting, blistering or peeling of work pieces leading to increased rejection rates.

The rinsing process is the primary source of water usage and prescribed waste generation in metal finishing operations. Water and Waste minimisation can be achieved by minimising the input of contaminants into the wash water and by recovering and recycling materials from the rinsing process or by a combination of the two (EPA (1992), Pinkerton (1984)).

Examples of proven waste reduction initiatives listed in the literature include:

- Implementation of water and wastewater audits (i.e. you can not control what you can not measure)

- Use of conductivity meters to determine appropriate rinsing regimes

- Implementation of counter flow rinsing

- Implementation of multiple rinse cycles

- Replacement of process rinse tanks with spray rinsing

2.3.2.1 Alternative Rinsing Practices

Alternative rinsing practices can be used to minimise rinse water discharges. As Sullivan describes in the paper of 2000, there are specific techniques used in barrel plating that can achieve reduced rinse water discharges. Sullivan states that, due to the greater solution holding capacity of the barrel plating technique it is critical that the following elements are optimised:

i. Drainage time,

ii. Hole size relative to part size (largest possible)

iii. Maintain barrel (no hole blockages, clean system)

iv. Improve drainage. Angled withdrawal form plating solution Sullivan (2000)

Improved rinsing efficiency can be achieved through a number of methods. As IAMS (1995) describes, this includes maximising contact time whilst still achieving production requirements can be done through onsite assessment through experimentation.

Another method that could be used to achieve improved rinsing efficiencies is described in the EPA's 'Guidelines to Pollution Prevention in the Metal Finishing Industry' (1992) as being increased agitation. This practice will achieve higher rinsing efficiency with reduced contact time, and can involve the following aspects:

- A recirculated side stream of water for rinse tank or in-tank pump;
- Air agitation to create better turbulence than water;
- A filtered air pump (air sparging trough distribution pipe);
- A low pressure blower (which has less contamination issues than compressors);
- Mechanical agitation (although this takes up tank space); and
- Ultrasonic agitation

As the EPA (1992) describe, there are both advantages (including a decrease in dragout, reduced water and waste generation) and disadvantages (including the potential to require additional tankage, the compressed air needs to be contaminant free or may effect work quality and the manual system requires operator commitment) to this option.

2.3.2.2 Water Flow options for Rinses

There are a number of options for altering water flows in the rinsing process, and therefore reducing waste water from the rinse process. These have been detailed in a number of references including Ford (1994) and IAMS (1995) have been summarised in the following list:

- Counter current rinsing: this is an order of magnitude more efficient than additions in the direction of manufacturing flow.

- Static Rinsing (Dead rinsing / Recovery Rinsing): this is used as makeup water for process bath in hot systems. For low temperature processes where counter current rinsing not possible can be a dragging tank allowed to build up in concentration for reuse in the plating bath after concentration.

- Multistage rinsing: this involves using multiple ‘dead’ tanks.

- Warm rinsing: this technique is particularly effective for alkaline solutions where viscosity at room temperature limits rinsing efficiency (Ford, 1994)

- Reactive rinsing: this is the feeding of acidic pickle to alkaline rinse and visa versa. Where flows match reactive rinsing reduces water usage by 50%

- Spray or Fog Rinsing: this is fixed or variable low volume nozzles spraying over process tank returning potential dragout to plating tank. Varying nozzle sizes are available to suit the application, and this is a technique that is applicable to rack or barrel plating (IAMS, 1995) and can be combined with immersion rinsing. The advantages of this technique include reducing dragout by up to 75% for hot systems where water balance is possible, waste management costs and improved quality control while the disadvantages include potentially not reaching all parts of the work piece and it requires purified water to minimise bath contamination

2.3.2.3 Rinse Flow Control Systems

It is a critical concept in water conservation that you use only as much as you need. Optimising water usage reduces waste generation (liquid and solid) and makes recovery technologies more cost effective. There are a number of rinse flow control systems available on the market, and outlined in the literature that will assist in minimising water use and waste production. As outlined by the DPPEA and others, the first step in improved flow systems is determining the appropriate flow rate. Current flow must be measured and reduced as much as practicable based on the increase contaminant loading on product quality. The installation and use of flow meters allows for the careful monitoring of usage (DPPEA, 1999).

The DPPEA in the 1999 paper outlines a number of methods that can be used to restrict water flow and subsequently minimise wastewater discharge. These include:

  - Use of flow restrictors to maintain a constant flow of fresh water to process. These can be equipped with activation switching to ensure water flow is not occurring after completion of rinsing operation. Works best in consistent production applications. The advantages of this method include reduced water use and maintain flow at predetermined level while the disadvantages include difficulties in adjusting flow, increased operator responsibilities, more suited to consistent processing requirements rather than small scale job lots with varying geometries and plating conditions. Flow restrictors can be used with or without flow Cut-off Valves.

- Conductivity/pH meters and/or controllers can be used for highly variable drag-ins. Can reduce water consumption by up to 40% without additional labour or extensive process modification Joseph (2004). Allows for control through max and min set points or alarm system alerting staff of build up of contaminants. WMRC (2000). The advantages of this system include reduced amount of overflow water, extended bath life, and particularly useful on discontinuous/variable plating operations. Disadvantages include potentially expensive maintenance and cleaning requirements (ameliorated by the use of electrodeless conductivity sensors. WMRC (2000).

Table 1 below outlines the recommended start-points for the use of conductivity meters in rinses from various plating and cleaning processes.

Table 1 – "Acceptable Rinse Water Contaminant Limits" (DPPEA, 1999)

RINSE BATH FOR	CONDUCTIVITY in micromhos (umho)
Alkaline cleaner	1700
Hydrochloric acid	5000
Sulfuric acid	4000
Tin acid	500
Tin alkaline	70-1300
Gold cyanide	260-1300
Nickel acid	640
Zinc acid	630
Zinc cyanide	280-1390
Chromic acid	450-2250

2.3.2.4 Rinsewater Recycling and Recovery Techniques

As the literature illustrates, there are many techniques are available to recover water, metals or acids that have contaminated rinse water streams. The material is either returned to the process or sent off site for recovery/disposal. Volumes need to be minimised by the introduction of drag out and rinse water efficiency techniques.

One particularly popular method for recovering water is via rinse water recycling. This involves the reuse of the reactive rinsing solution (e.g. acid influent to alkali cleaning bath) (EPA, 1992).

Another method is Conventional physico-treatment. Care should be taken in using the treated wastewater from conventional hydroxide precipitation treatment processes (DPPEA, 1995). Treated wastewater quality may be improved through the use of proprietary water treatment materials (for example the VIROTEC system or proprietary reagents such as PRO-pHx, a silicate based material for removal of heavy metal contaminants from acid solutions) and/or additional technology for better control of contaminants (for example TDS) can lead to reuse in no critical washes and ultimately to achieving a closed loop wash water system as outlined by Heller (1999).

A third method is Chemical Recovery to produce a water stream of sufficient quality for reuse. (Chemical Recovery as outlined in See Sec 4). Here the chemicals are recovered in 3 ways:

i. Recycling back into the process,

ii. On-site recovery for resale, and

iii. Shipment off site for recovery / disposal.

Metal recovery can also be achieved via technologies such as evaporation, ion exchange, reverse osmosis, electrolysis and electrodialysis (Hunt, 1988).

Metals can be reused by:

i. Returning to the bath as makeup

ii. Sold or returned to suppliers

iii. Sold to a reclaimer, or used on site as plating metal anode material

Savings associated with the various methods of recovering water, metals or acids are site and process specific and depend on factors such as:

i. Volume of the waste containing the metals

ii. Concentration

iii. Potential to reuse some of the metal salts, and Treatment and disposal costs.

2.3.2.5 Recovery Technologies – Water re-use

There are various types of equipment which can assist in the recovery of process water in the plating process. Heller (1999) Many of these processes are more focussed on the metal recovery aspect of the technology and a more detailed discussion of some of these processes can be found in Section 2.5 – Chemical Recovery Technology

Types of equipment that have successfully been used in the metal finishing industry include:

- Evaporators. Atmospheric and Vacuum. Most applicable to concentration of dragout for return to a process bath. More economical when the amount of water is small (MDEQ (1996) ,Freedman (1995), Veit (1989), and Cushnie (1994))

    - Advantages. - Reuses recovered chemicals, no chemicals required, reduces liquid waste for treatment and disposal, requires no maintenance, widely applicable, low cost and can reuse rinse water

    - Disadvantages. – Energy intensive (better when bath already heated (Cushnie, 1994), needs multi stage counter current rinsing (minimising volumes) to be economical, high cost, chemicals can be corrosive to the evaporator,

    - Vacuum Evaporators – Operate by lowering the vapour pressure, reduce the boiling point required to evaporate water, so some heat sensitive ingredients are protected from degrading. Energy requirements reduce (capital cost increases) as we go from single effect, to multiple effect and Vapour recompression units (Freedman, 1995). Cold vaporisation units use ambient energy to provide vaporisation (Cushnie, 1994).

- Membrane Technologies. Size Separation Systems. Initial Removal of large particulates with a cartridge filter system recommended.

  St Lawrence Technologies in Canada in 2000 have written a data sheet that summarises the potential applications of membrane technologies to water and waste waters (St Lawrence Tech, 2002).

  Membrane technologies can be used for the removal of suspended solids, oils (Ferguson, 2001) and other impurities including dissolved ions (Srisuwan, 2006). Separation is achieved through a pressure differential across a membrane. Cross flow systems provide a continuous self cleaning effect allowing for high filtration rates to be maintained, though membrane fowling is always of concern in higher concentration wastes. Systems require periodic flushing and cleaning to maintain operability. This is a technology being looked at for platers looking towards zero discharge or total recycling.

The choice of membrane depends on the pH, temperature and specific application. Membranes are either organic polymers or inorganic (carbon fibre or ceramics). Ceramics are becoming more popular for their high temperature and chemical resistance (Freedman, 1995)

Microfiltration and Ultrafiltration are most commonly used in plating applications (Ferguson (2001) and Ieronimo (1995)). Listed below are the options in overview. IAMS (1995)

- Microfiltration. (0.05 – 3 µm) Oily waste streams. Oils and Greases separated from water, solvent and cleaning bath constituents (Ferguson, 2001). Can be used to remove cleaning solution dragout from rinse water lines (Cushnie, 1994). Recovery of Caustic cleaners. Does not remove dissolved ions. Final water polishing of treated waste waters (EPA,(1995) and Freedman (1995))

- Ultrafiltration. (3-130 nm) Facilities with mixed wastes containing emulsified oils from aqueous cleaners. Recirculates and concentrates process solutions. RI DEM (1994) does not remove dissolved ions.

2.4. Process Solution Maintenance – Methods and Technologies

A number of general principles are expounded in the literature and discussed previously are summarised below:

- Conventional Maintenance,/housekeeping. Extend bath life by keeping the plating area as clean as possible and preventing foreign matter and corrosion product from entering the bath. Keep equipment well maintained, clean and use corrosion resistant Tanks. Filter incoming air or water to reduce airborne and water born suspended matter.

- Monitoring bath Composition/Chemistry, Determine critical operating parameters and maintain the bath within acceptable limits. Monitor regularly and maintain bath at minimum concentrations necessary to maintain quality as increasing concentration increases dragout.

- Process bath operating temperature, Increase in temperature will reduce solution viscosity. The effect of temperature on solution stability needs to be taken into account as additives may breakdown reducing the active life of the bath.

- Plating Solution Concentration, Higher concentrations mean higher viscosity and therefore greater dragout. Reducing concentration improves drainage efficiency (EPA, 1992).
    - Advantages. Reduced Dragout losses, chemical usage rates/costs and sludge generation
    - Disadvantages. Decreased tolerance to impurities.
- Use of Additive. Generally materials added to reduce surface tension or maintain active ingredients in the bath in the soluble form
    - Wetting agents. Surfactants or wetting agents
        - Advantages. Reduce dragout losses and can improve finish quality
        - Disadvantages. Can cause foaming (particularly with air agitated baths). Incompatible with some bath chemistries
    - Non-chelated process chemicals. Inhibit the precipitation of metals and additives to maintain bath effective life. e.g. phosphates and silicates in etching operations
- Equipment Modification
    - Anode maintenance. Anodes with higher purity do not contribute as quickly to bath contamination.
    - Purified water. Minimises the addition of dissolved ions that will eventually impact on the effectiveness of the plating bath or cleaning operation
    - Improved vapour/mist control. Reducing or returning captured liquid otherwise vented to atmosphere
- Chemical Substitution. Simplify chemistries to allow for easier maintenance and reduced waste issues. E.g. replace cyanide with non-cyanide based processes.
- Acid solution regeneration. Processes such as distillation, acid sorption, membrane electrolysis, crystallisation and diffusion dialysis may be appropriate
- Spent Acid Bath Reuse. Reactive rinsing (see Section 2.3.2.4)
- Waste Segregation. Remove contaminants solids by filtration, carbonates by temperature reduction and precipitation processes. Removal of metal contaminants by precipitation.

- Low Current Electrolysis (Dummy Plating). Reducing the build-up of soluble contaminant metal (e.g. copper in Nickel and Zinc plating baths) using low current density electrolysis.

- Carbon treatment to remove Organics. Removal of introduced oil (Air agitation from compressor) or from bath breakdown products on either a batch or continuous basis.

2.4.1. Solution Maintenance Methods and Technologies

- Filtration is the most commonly applied method of corrective bath maintenance. Various equipment is used for filtration (Heller, (1999) and DPPEA (1997b)), with the most common being cartridge filters. Sand or multimedia filters are also commonly employed. Cartridge filters are available with in tank (DPPEA, 1997c) or external configurations, with the former used mostly for small tanks and the latter for large tanks (Williams, 2007).

- Carbon treatment of plating baths is a common method of removing organic contaminants. The carbon adsorbs organic impurities that are present as a result of oil introduction or the breakdown of bath constituents.

- Electrolysis is an electrolytic process in which metallic contaminants in a metal finishing solution are either plated out (low current density electrolysis) or oxidised (high current density electrolysis). The NMFRC report that electrolysis is employed most frequently with nickel electroplating (48%), chromium electroplating (13%), zinc electroplating (11%), copper electroplating (10%) and cadmium electroplating (7%).

- Sodium cyanide baths can be treated for excessive carbonate build up by “carbonate freezing” or crystallisation. Cyanide baths are adversely affected by carbonates build up which are formed as the result of breakdown of cyanide (especially at higher temperatures), excessive anode current temperatures and the adsorption of carbon dioxide from the air. Excessive carbonates can cause increased resistance in the bath, yielding low plating current densities, which normally accentuate the poor appearance that metallic impurities cause.

- Various chemical treatments of plating baths are performed to remove bath contaminants via precipitation. Chemicals used for this process include: barium cyanide, barium hydroxide, calcium hydroxide, calcium sulphate or calcium cyanide or proprietary reagents such as Virotech, or PRO-pHx, a silicate based material for removal of heavy metal contaminants from acid solutions.

2.5. Chemical Recovery and Substitution Technologies

As discussed in Section 2.3.2.5 there are a number of processes that will allow the recovery of metals and contaminants from the process water. The processes that are targeted on metal and chemical recovery are discussed in this section.

2.5.1. Chemical Recovery Technologies

The technologies described below are most effective on more concentrated solution, but are applicable, either separately or in combination (e.g. ion exchange followed by electrolytic recovery of metallic species from wash waters) to achieve the required waste minimisation outcome. The technologies either produce a concentrate able to be used directly back into the process, or recover constituents for re- use on or off site.

One such piece of equipment is the Electrolytic Metal Recovery (EMR) unit (MFASC, 1997). As outlined in the EPA paper of 1995, material is deposited on the cathode in the EMR process. Essentially two types of cathode used for this purpose: a conventional cathode (electrowinning or a high surface area cathode (HSAC). MDEQ (1996) Operation is capable of recovering 90 to 95% of metals such as Au, Ag, Cu, Zn and Cadmium (Bennati, 1983). Not applicable to chromium recovery. EMR is most effective when metal concentrations are high and can be used in conjunction with other techniques such as ion exchange. EPA (1995) EMR can also be used on spent plating baths to recover valuable residual metals. The Joint Services Pollution Prevention Opportunity Handbook (JSPPOH, 2003) indicates that recent innovations in design of electrowinning equipment extend the operating range of processes to include more dilute wastewaters (< 500 mg/l) in terms of metal and cyanide concentrations.

The advantages of EMR include the recovery of recyclable metals at 90 to 95% efficiency, no chemicals, low maintenance and similar to existing plating process. The disadvantages include the energy efficiency is very low for dilute solutions, requires good segregation of rinse waters to maintain recovered metal purity. High surface of some metals may have class 4 properties (spontaneous combustion). Not applicable to oxidising bath chemistries. High chloride levels may generate chlorine gas (EPA, 1995).

- Nanofiltration (0.9 – 6nm) Capable of removing dissolved Heavy Metals. Fane (1992)

- Reverse Osmosis. (0.1-1.5 nm) Uses semi-permeable membrane that blocks metal salts and additives. Recycling wastewater. Recovery of dragout from acid nickel process bath rinses (Freedman, 1995). This works best on dilute solutions for the recovery of water and concentrated plating residuals (MDEQ, (1996) and Benito, (2002)). Although not widely used, Reverse Osmosis has successfully been applied to a range of processes, including brass, chromium, copper, nickel, tin and zinc plating solutions, with nickel recovery being the most successful and frequent. Capable of removing 98% of dissolved solids and 99% of organics. Not suitable to oxidative process liquors such as chromic acid, nitric acid etc. (Cushnie, 1994).

- Ion Exchange. Batch system applicable to most plating baths and wash waters (Panayotova (2006) and MDEQ (1996)). Versatile technology that can be a major component in low or zero discharge plating shop configurations. Common applications include - treatment of water to produce high quality rinse water, recovery of chemicals from rinse water (return to plating bath) and treatment of plating baths to remove contaminants (EPA (1995) and Cushnie (1994). Best applied to relatively dilute streams in combination with other conventional dragout reduction practices. EMR on metal concentrates from Regenerant stream EPA (1995).

- Electro Dialysis. Electromotive forces selectively drive metal ions through an ion selective membrane. Alternating anion/cation stacks. Can be combined with electrowinning. Bolger (2002). Compatible with most plating baths (MDEQ, 1996). Reclaiming of nickel and gold from plating rinse waters or cyanide bath systems (Cd, Au, Ag and Zn) (Cushnie, 1994).

- Diffusion Dialysis. Ion exchange/Membrane technique used in Acid recycling. Movement by differential acid concentrations across the membrane. Popular for chemical solution recovery. Can remove metals and recycle water in plating or anodizing shop. EPA (1995). Can separate mineral acids from metals such as Cu, Cr, Ni, Fe and Al so that acid can be reused. Recovery rates as high as 95% for acids and 60 -90 % for metal contaminants (WMRC (2000b) and Cushnie (1994)). Popular with anodizers using large amounts of sulphuric acid (EPA ,1995)

- Acid sorption. Used on acid solutions including pickling or sulphuric acid anodizing baths. Metal rich slightly acidic solution passes up through the bed of alkaline anion exchange resin. Purified acidic solution desorbed from the resin with water. This technology is rarely used in the plating industry (Cushnie (1994) and EPA (1995)).

- Ion Transfer. Selectively removal of metallic cations from chromic acid process fluids. Generally restricted to chromic acid plating baths, etches and anodizing baths. Best used in maintaining relatively clean baths due to the low cation removal rates (Cushnie (1994) and EPA (1995)).

- Membrane Electrolysis. Anode and cathode compartments separated by an ion selective membrane. Used as a bath maintenance technology to maintain acceptable levels of contaminants in chromic based metal finishing solutions, (Cushnie, 1994).

2.5.2. Chemical Substitution Technologies

The Guide to Metal Finishing (USAID, 2007) lists key questions to consider in assessing chemical usage and mitigation strategies in the area of chemical substitution to less hazardous alternatives, optimisation of materials handling to reduce process contamination and releases to the environment through solid, water and air discharges.

The four major areas of waste minimisation of most interest have been identified as:

1. Chlorinated solvent use reduction/ elimination – chlorinated solvents have been used extensively in the metal working and metal finishing industry for degreasing and cleaning. The most commonly used degreasing solvents include: 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, chlorofluorocarbons and methylene chloride.

2. Cyanide use reduction/elimination – cyanide in either the sodium or potassium form has been a key component of plating solutions for many years. Some of the metals commonly plated from cyanide baths include: cadmium, zinc, copper, brass and precious metals. Cyanide forms a moderately stable complex with metal ions that permits the deposition of the metal under the influence of a suitable electrical potential.

3. Cadmium use reduction/elimination – compliance with environmental standards for companies that undertake cadmium plating has been identified as an issue of significant concern. Cadmium substitutes have had limited success primarily due to poor customer acceptance, poor quality of finish and higher cost.

4. Chromium use reduction/elimination – chromium is heavily used in electroplating and aluminium finishing. Environmental compliance issues have forced many companies to switch from Cr VI to Cr III operations.

Organisations and groups such as the National Metal Finishing Resource Centre (USA). Iowa Pollution Prevention Initiative (USA), Metal Finishing Industry Pollution Prevention Project task force (USA/Canada), US EPA and United Nations Environment Program – Cleaner production have all produced manuals, handbooks or guidelines to help metal finishing industries reduce water consumption and minimise waste production. Many of these publications provide details of successful case studies. Refer to the appendices for selected case studies.

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AISF. Australasian Institute of Surface Finishing. www.aisf.org.au

CERL. Construction Engineering Research Laboratory. US Army Corps of Engineers www.cecer.army.mil

CPPIC. Canadian Pollution Prevention Information Clearinghouse. www.ec.gc.ca/cppic/en/index.cfm

Ecoefficiency http://www.ecoefficiency.com.au/Metals/Metals.htm

Metal finishing Internet sites Collation at www.svti.sk/CleanVOC.htm

NCDENR. North Carolina Department of Environment and Natural Resources. www.enr.state.nc.us

NFESC. Naval Facilities Engineering Services Centre . Technical Library. Electroplating and metal finishing technologies.
http://205.153.241.230/topics/electro.html

OCAPP. Office of Compliance Assistance & Pollution Prevention
www.epa.state.oh.us/ocapp/ocapp.html

P2Rx Pollution Prevention Resource Exchange. www.p2rx.org

The Centre of Excellence in Cleaner Production Website, August 2008 available at http://cleanerproduction.curtin.edu.au/cecp/industry/metal.htm

WRRC. Waste Reduction Resource Centre. http://wrrc.p2pays.org/

Appendix 1 – Selected Case Studies

The following section lists numerous waste minimisation techniques that have been implemented in the USA that may be useful to any company specialising in metal fabrication and finishing.

Drag-out and Rinse Water Reduction Options

Option 1 - Modify rinsing methods to control drag-out by:

• Increasing bath temperature

• Decreasing withdrawal rate of parts from plating bath

• Increasing drip time over solution tanks; racking parts to avoid cupping solution within part cavities

• Shaking, vibrating, or passing the parts through an air knife, angling drain boards between tanks

• Using wetting agents to decrease surface tension in tank.

• slowing and smoothing removal of parts, rotating them if necessary;

• using surfactants and other wetting agents;

• using drainage boards to direct dripping solutions back to process tanks;

• installing drag-out recovery tanks to capture dripping solutions;

• using a fog spray rinsing technique above process tanks;

• using techniques such as air knives or squeegees to wipe bath solutions off of the part;

Option 2 - Utilize water conservation methods including:

• Flow restrictors on flowing rinses

• Counter current rinsing systems

• Fog or spray rinsing

• Reactive rinsing

• Purified or softened water

• Dead rinses

• Conductivity controllers

• Agitation to assure adequate rinsing and homogeneity in rinse tank

• Flow control valves.

Option 3 - Implement counter flow rinsing and cascade rinsing systems to conserve consumption of water. **Costs and Savings:** Costs: $75,000 to upgrade existing equipment and purchasing new and used equipment. Waste Savings/Reduction: reduce water use and wastewater treatment costs.

Option 4 - Use drip bars to reduce drag-out. **Costs and Savings:** Capital Investment: $100 per tank. Savings: $600.

Option 5 - Use drain boards between tanks to reduce generations of drag-out. **Costs and Savings:** Capital Investment: $25 per tank. Savings: $450.

Option 6 - Install racking to reduce generations of drag-out. **Costs and Savings:** Capital Investment: zero dollars. Operating Costs: minimal. Savings: $600.

Option 7 - Employ drag out recovery tanks to reduce generations of drag-out. **Costs and Savings:** Capital Investment: $500 per tank. Savings: $4,700.

Option 8 - Install counter-current rinsing operation to reduce water consumption. **Costs and Savings:** Capital Investment: $1,800-2,300. Savings: $1,350 per year. Waste Savings/Reductions: reduce water use by 90-99 percent.

Option 9 - Redesign rinse tank to reduce water conservation. **Costs and Savings:** Capital Investment: $100. Savings: $750 per year.

Option 10 - Increase parts drainage time to reduce drag-out.

Option 11 - Regenerate plating bath by activated carbon filtration to remove built up organic contaminants. **Costs and Savings:** Capital Investment: $9,192. Costs: $7,973. Savings: $122,420. Waste Savings/Reduction: 10,800 gallons. Reduce volume of plating baths disposed and requirements for virgin chemicals.

Option 12 - Use reactive rinsing and multiple drag-out baths. **Costs and Savings:** Savings: Reduce cost of treating spent process baths and rinse waters. Waste Savings/Reduction: increase lifetime of process baths and reduce the quantity or rinse water requiring treatment.

Option 13 - Improve control of water level in rinse tanks, improve sludge separation, and enhance recycling of supernatant to the process by aerating the sludge. **Costs and Savings:** Savings: $2,000. Waste Savings/Reduction: reduce sludge generation by 32 percent.

Option 14 - Install system (e.g. Low Solids Fluxer) that applies flux to printed wiring boards, leaving little residue and eliminates the need for cleaning CFCs. **Costs and Savings:** Waste Savings/Reduction: reduce CFC emissions over 50 percent.

Option 15 - Use mechanical scraping instead of acid solution to remove oxides of titanium. **Costs and Savings:** Annual Savings: $0; cost of mechanical stripping equals cost of chemical disposal. Waste Savings/Reduction: 100 percent. Waste Throughput Information: previously disposed 15 tons/year of acid with metals.

Option 16 - For cleaning nickel and titanium alloy, replace alkaline etching bath with a mechanical abrasive system that uses a silk and carbide pad and pressure to clean or “brighten” the metal. **Costs and Savings:** Capital Investment: $3,250. Annual Savings: $7,500. Waste Savings/Reduction: 100 percent. Waste Throughput Information: previous etching bath waste total was 12,000 gallons/year.

Option 17 - Clean copper sheeting mechanically with a rotating brush machine that scrubs with pumice, instead of cleaning with ammonium persulfate, phosphoric acid, or sulfuric acid; may generate nonhazardous waste sludge. **Costs and Savings:** Capital Investment: $59,000. Annual Savings: more than $15,000. Payback Period: 3 years. Waste Savings/Reduction: 40,000 pounds of copper etching waste reduced to zero.

Option 18- Reuse drag-out waste back into process tank.

Option 19- Recover process chemicals with fog rinsing parts over plating bath.

Chemical Recovery Technologies Options

Option 1 - Employ reverse osmosis system to reduce generation of drag-out. **Costs and Savings:** Savings: $40,000 per year. Capital Investment: $62,000.

Option 2- Reduce molybdenum concentration in wastewaters by using a reverse osmosis/precipitation system. **Costs and Savings:** Capital Investment: $320,000. Waste Throughput Information: permeate capacity of 18,000 gallons per day. Savings Relative to an Evaporative System: installed capital cost savings: $150,000; annual operating cost savings: $90,000.

Option 3 - Use activated carbon to recover solvent vapors, and then recover the solvent from the carbon by steam stripping, and distill the resulting water/solvent mixture. **Costs and Savings:** Capital Investment: $817,000 (1978). Waste Savings/Reduction: releases of solvent to the atmosphere were reduced from 700 kg/ton of solvent used to 20 kg/ton.

Option 4 - Regenerate caustic soda etch solution for aluminum by using hydrolysis of sodium aluminate to liberate free sodium hydroxide and produce a dry, crystalline hydrate alumina byproduct. **Costs and Savings:** Capital Investment: $260,000. Savings: $169,282 per year; from reduced caustic soda use, income from the sale of the byproduct, and a reduction in the cost of solid waste disposal. Payback Period: 1.54 years. Product/Waste Throughput Information: anodizing operation for which the surface area is processed at a rate of 200 M 2 /hour.

Option 5 - Use simple batch distillation to extend the life of 1,1,1-trichloroethane. **Costs and Savings:** Capital Investment: $3,500 (1978). Annual Savings: $50,400. Product/Waste Throughput Information: facility handles 40,450 gallons 1,1,1-trichloroethane per year.

Solution Maintenance Methods and Technologies Options

Option 1 - Install ion exchange system to reduce generation of drag-out. **Costs and Savings:** Capital Investment: $78,000. Operating Costs: $3,200 per year.

Option 2 - Use electrolytic metal recovery to reduce generation of drag-out. **Costs and Savings:** Capital Investment: $1,000.

Option 3 - Utilize electrodialysis to reduce generation of drag-out. **Costs and Savings:** Capital Investment: $50,000.

Option 4 - Use ion exchange and electrowinning, reverse osmosis, and thermal bonding when possible.

Option 5 - Use sludge slagging techniques to extract and recycle metals. **Costs and Savings:** Capital Investment: $80,000 for 80 tons/year and $400,000 for 1,000 tons/year. Operating Costs: $18,000 per year for an 80 ton facility. Waste Savings/Reduction: reduces volume of waste by 94 percent.

Option 6 - Use hydrometallurgical processes to extract metals from sludge.

Option 7- Convert sludge to smelter feed.

Option 8- Remove and recover lead and tin from boards by electrolysis or chemical precipitation.

Option 9 - Install an electrolytic cell which recovers 92 percent of dissolved copper in drag-out rinses and atmospheric evaporator to recover 95 percent of chromatic acid drag-out, and recycle it into chromic acid etch line.

Option 10 - Implement the electrodialysis reversal process for metal salts in wastewater. **Costs and Savings**: Savings: $40,100 per year in operating costs.

Option 11 - Implement the electrodialysis reversal process for metal salts in wastewater. **Costs and Savings**: Savings: $40,100 per year in operating costs.

Option 12 - Oxidize cyanide and remove metallic copper to reduce metal concentrations.

Option 13- Regenerate plating bath by activated carbon filtration to remove built up organic contaminants. **Costs and Savings:** Capital Investment: $9,192. Costs: $7,973. Savings: $122,420. Waste Savings/Reduction: 10,800 gallons. Reduce volume of plating baths disposed and requirements for virgin chemicals.

Option 14- Install pH controller to reduce the alkaline and acid concentrations in tanks.

Option 15 - Install atmospheric evaporator to reduce metal concentrations.

Chemical Substitution Technologies Options

Option 1 - Substitute cyanide plating solutions with alkaline zinc, acid zinc, acid sulfate copper, pyrophosphate copper, alkaline copper, copper fluoborate, electroless nickel, ammonium silver, halide silver, methanesulfonate-potassium iodide silver, amino or thio complex silver, no free cyanide silver, cadmium chloride, cadmium sulfate, cadmium fluoborate, cadmium perchlorate, gold sulfite, and cobalt harden gold.

Option 2 - Substitute sodium bisulfite and sulfuric acid for ferrous sulfate in order to oxidize chromic acid wastes, and substitute gaseous chlorine for liquid chlorine in order to reduce cyanide reduction. **Costs and Savings:** Savings: $300,000 per year. Waste Savings/Reduction: reduces feedstock by 50 percent.

Option 3 - Replace hexavalent chromium with trivalent chromium plating systems.

Option 4 - Replace cyanide with non-cyanide baths.

Option 5 - Replace conventional chelating agents such as tartarates, phosphates, EDTA, and ammonia with sodium sulfides and iron sulfates in removing metal from rinse water which reduces the amount of waste generated from precipitation of metals from aqueous waste streams. **Costs and Savings:** Costs: $178,830 per year. Savings: $382,995 per year. Waste Savings/Reduction: 496 tons of sludge per year.

Option 6 - Replace methylene chloride, 1,1,1-trichloroethane, and perchloroethylene (solvent-based photochemical coatings) with aqueous base coating of 1 percent sodium carbonate. **Costs and Savings:** Waste Savings/Reduction: reduce solvent use by 60 tons per year.

Option 7 - Replace methanol with nonflammable alkaline cleaners. **Costs and Savings:** Waste Savings/Reduction: eliminate 32 tons per year of flammable methyl alcohol.

Option 8 - Substitute non-cyanide for a sodium cyanide solution used in copper plating baths. **Costs and Savings:** Waste Savings/Reduction: reduce 7,630 pounds per year.

Option 9 - Use alternative coatings for solvent based paints to reduce volatile organic materials use and emissions, such as:

• high solids coatings (this may require modifying the painting process; including high speed/high pressure equipment, a paint distributing system, and paint heaters); **Costs and Savings:** Waste Savings/Reduction: 30 percent net savings in applied costs per square foot.

• water based coatings - **Costs and Savings:** Waste Savings/Reduction: 87 percent drop in solvent emissions and decreased hazardous waste production;

• powder coatings - **Costs and Savings:** Capital Investment: $1.5 million. Payback Period: 2 years. Example is for a large, wrought iron patio furniture company.

Option 10 - Change copper bright-dipping process from a cyanide dip and chromic acid dip to a sulfuric acid/hydrogen peroxide dip. The new bath is less toxic and copper can be recovered.

Option 11 - Use alcohol instead of sulfuric acid to clean copper wire. One ton of wire requires 4 liters of alcohol solution, versus 2 kilograms of sulfuric acid. **Costs and Savings:** Capital Investment: $0.

Option 12 - Replace caustic wire cleaner with a biodegradable detergent.

Option 13- Replace chromated desmutting solutions with non-chromated solutions for alkaline etch cleaning of wrought aluminum. **Costs and Savings:** Annual Savings: $44,541. Waste Savings/Reduction: sludge disposal costs reduced by 50 percent.

Option 14 - Replace barium and cyanide salt heat treating with a carbonate/chloride carbon mixture, or with furnace heat treating.

Option 15 - Replace thermal treatment of metals with condensation of saturated chlorite vapors on the surface to be heated. **Costs and Savings:** Waste Savings/Reduction: this process is fast, non-oxidizing, and uniform; pickling is no longer necessary.

Option 16 - Use less hazardous degreasing agents such as petroleum solvents or alkali washes. For example, replace halogenated solvents (e.g., trichloroethylene) with liquid alkali cleaning compounds. (Note that compatibility of aqueous cleaners with wastewater treatment systems should be ensured.) **Costs and Savings:** Capital Investment: $0. Annual Savings: $12,000. Payback Period: immediate. Waste Savings/Reduction: 30 percent of 1,1,1-trichloroethane replaced with an aqueous cleaner.

Option 17 - Substitute chromic acid cleaner with non-fuming cleaners such as sulfuric acid and hydrogen peroxide. **Costs and Savings:** Annual Savings: $10,000 in treatment equipment costs and $2.50/lb. of chromium in treatment chemical costs. Product/Waste Throughput Information: rinse water flow rate of 2 gallons per minute.

Option 18 - Substitute less polluting cleaners such as trisodium phosphate or ammonia for cyanide cleaners. **Costs and Savings:** Annual Savings: $12,000 in equipment costs and $3.00/lb. of cyanide in treatment chemical costs. Product/Waste Throughput Information: rinse water flow rate of 2 gallons per minute.