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Pollution Prevention Program

# Electroplating Tip Sheet

Recovery and Recycling of Bath Chemicals



## Introduction

In the electroplating industry, valuable chemicals can be recovered or recycled from processes that require the immersion of parts in metallic solutions for coating. After the metallic coating step, the parts are water rinsed to remove excess drag-out. The resulting solution (a combination of rinse water and drag-out) contains components of the previous metallic coating process. This is solution from which recovery and metal recycling is most beneficial.

## Chemical Recovery and Recycling

A number of commercially available systems are available to remove metallic chemicals from rinse water and to return those chemicals to the process bath. These processes provide an economic benefit through maximum utilization of purchased supplies, minimization of waste disposal expense, and reduction of rinse water. In some cases it may be possible to recover chemicals to the extent that, the water requirement may be reduced to equal the amount required to compensate for evaporative loss. The use of any one of the below suggestions can help to recover chemicals and prevent pollution, but the implementation of a combination of suggestions along with drag-out and rinse water minimization programs can significantly increase waste reduction and reduce costs. It is up to each facility to determine what combination of suggestions will work best for them, being sure to weigh all advantages against disadvantages. Appendix A is a schematic for chemical recovery and recycling and Appendix B is a summary table of the recovery techniques with their advantages and disadvantages. The applicable technologies are briefly discussed below:

1. Electrowinning: Electrowinning is a process used to recover metals, such as cadmium, tin, copper, solder alloy, silver, nickel, and gold, from concentrated solutions using the electroplating process. In an electrowinning process cathodes, made of thin starter sheets of the metal being recovered or stainless steel blanks from which the recovered metal can be retrieved, are mounted in an open tank. As the current passes from the anode to the cathode, the metal deposits on the cathode. This system generates a solid metallic slab that can be reclaimed or used, depending on quality restrictions, as an anode in an electroplating tank. Metals can be recovered continuously by electrowinning in a drag-out tank, or as a batch process from spent rinse solutions.

2. Ion Exchange: Ion exchange can be used to recover metals from a dilute rinse solution. The chemical solution is passed through a series of resin beds that selectively remove cations or anions, or both. As the rinse water passes through the beds, the resin exchanges ions with the metallic ions in the rinse water. The metals are then recovered from the resin by regenerating the resin with an acid or alkaline solution, or by using electrowinning recovery techniques. The metals are then removed from the regenerant solution and the spent resin (a resin that can no longer be regenerated) is disposed of as hazardous waste. The treated rinse water is of high purity and can be returned to the process for reuse.

3. Evaporation: Evaporation has been successfully used to recover plating bath chemicals. In one technique water is evaporated from a static rinse tank to reduce its volume and increase the chemical concentration so that it can be returned to the process bath. In another technique, water from the process bath is evaporated to make room in the process bath for spent rinse water to be added as makeup. Evaporated water can be condensed in some systems for reuse in the rinse system.

   There are two typical evaporator designs used: atmospheric evaporation and vacuum evaporation. Atmospheric evaporation can occur in a heated open tank, an enclosed packed or tray towers, or a small fully enclosed specialized units. Atmospheric evaporators on chrome plating lines have been used simultaneously as evaporators and as plating bath fume scrubbers. Evaporation does not remove contaminants from the concentrate. Controlling buildup of metallic and organic impurities in the evaporator concentrate is necessary; ion exchange can be used for this purpose (See Section 3). Vacuum evaporators operate similarly to atmospheric evaporators, but the solution is placed in a boiling chamber under a vacuum. The vacuum will lower the solution's boiling point. During operation, the resultant vapor is removed from the chamber and can be either discharged or returned to the process for reuse. Vacuum evaporators should be used when dealing with heat sensitive solutions.

   There are limitations to the use of evaporation. Equipment cost are generally high. Energy requirements are usually significant. Generally evaporation is economically feasible only when applied in combination with multi-stage counter current rinse systems.

4. Ultrafiltration: Ultrafiltration is a separation technology that uses a semipermeable membrane to concentrate material from dilute solutions. The membrane can be made from natural materials such as cellulose or from synthetic polymers and can be tailored to specific tasks. The membranes use the principal of cross filtration where the bulk of the fluid flows parallel to the membrane surface and only the filtrate that passes through the membrane flows perpendicular to it. The flowing liquid scours its surface and keeps material from building up on the surface. The material being concentrated can be recirculated through the

system until the desired concentration level is reached. The clean filtrate can be disposed or reused.

A. Electrodialysis: Electrodialysis employs selective membranes and an electric potential to separate positive from negative ions in the solution into two streams. To accomplish this, the rinse solution is passed through cation and anion-permeable membranes. Cation exchange membranes allow cations such as copper or nickel to pass, while anion exchange membranes permit anions such as sulfate, chloride, or cyanide to pass. The concentrated solutions can be recycled through the plating baths, while the ion-depleted water can be recycled through the rinse system. Electrodialysis is effective in removing metals from dilute solutions such as wastewater rinses.

B. Reverse Osmosis: Reverse osmosis is a pressure driven membrane separation process. The process uses a semipermeable membrane that allows purified water but not dissolved salts to pass through it (See Figure 1). The salts, thus recovered, are returned to the process bath. The permeate rinse water can then be returned to the rinse system for reuse. The most common application of reverse osmosis in metal finishing operations is the recovery of drag-out from acid nickel process bath rinses. Reverse osmosis membranes are not suitable for solutions having high oxidation potential such as chromic acid. Also, the membranes will not work well to separate many nonionized organic compounds. So other methods, such as activated carbon treatment, must be used in conjunction with it.

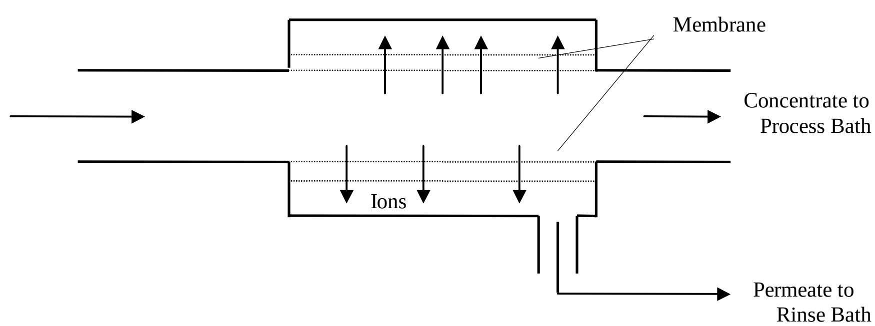


**Figure 1**
**Schematic for Reverse Osmosis Process**

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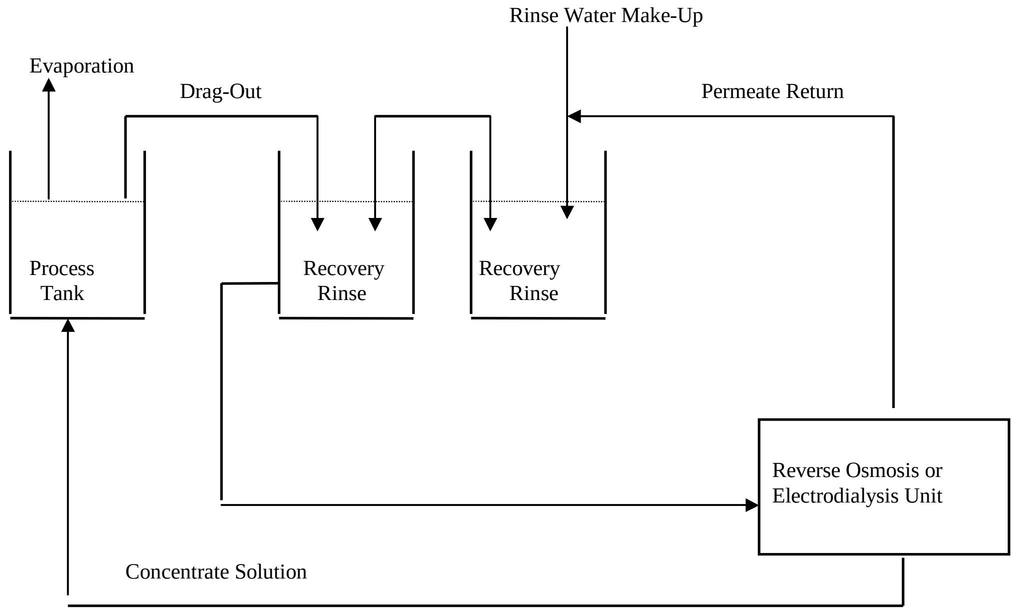
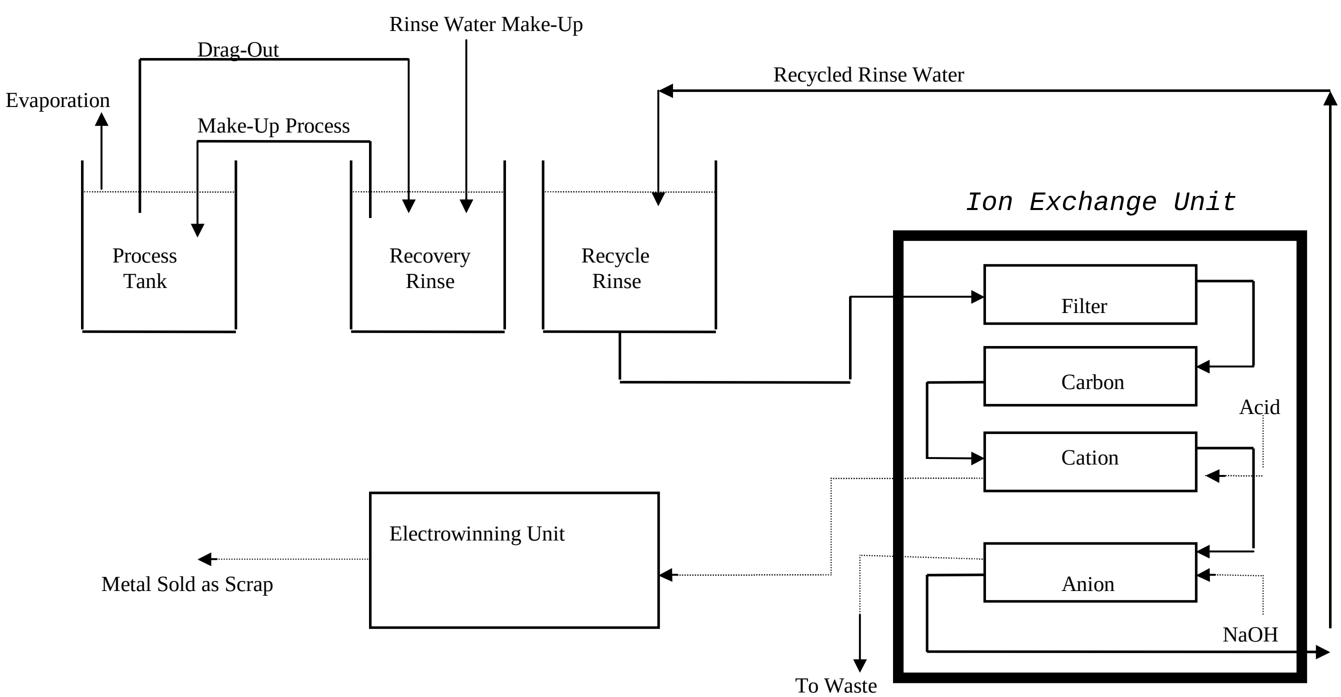
# Appendix A
# General Schematic for Chemical Recovery/Recycle

**A.** Reverse Osmosis or Electrodialysis Schematic:




**B.** Ion Exchange or Electrowinning Schematic:



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# Appendix B
# A Summary of Recovery Techniques

| Technique/ Application | Advantages | Disadvantages |
|---|---|---|
| Electrodialysis<br><br>Au, Fe, Ag, Zn, Sn, Pb, Watts Ni, NiSB, NiB, CuCN | ■ Achieves higher concentration than reverse osmosis or ion exchange<br>■ Energy efficient<br>■ Organics not concentrated<br>■ Inorganic salt transport at different rates minimizes return of unwanted organics | ■ Must filter the feed<br>■ Membrane sensitive to flow distribution, pH and suspended solids<br>■ Use of multicell stacks, incurs leakage<br>■ Chemical adjustment of recovered material<br>■ New technology - membrane life uncertain |
| Electrowinning<br><br>CuCN, Au, Pb, Ag, Zn, Cu pre-etch, Cu final etch, acid Cu, Sn-Pb, SnAlk, $SnSO_4$, Watts Ni, CdCN, Electroless Ni | ■ Recovers only metals<br>■ Results in salable non-hazardous product<br>■ Energy efficient, less than 10¢/lb-Cu<br>■ Low maintenance<br>■ Eliminates metal ion and impurity build-up | ■ Must constantly monitor solution concentration<br>■ Fumes may form and require hood scrubbing system<br>■ Solution heating encouraged to maximize efficiency |
| Evaporators<br><br>Acid Cu, Sn-Pb, Au, Fe, Pb, Watts Ni, NiSB, NiB, Zn, CuCN, Ag, CdCN, Cr etch, Cr | ■ Established and proven technology, very reliable<br>■ Simple to operate<br>■ Widely applicable<br>■ Can exceed bath concentration | ■ Energy intensive<br>■ Most evaporators designed for steam heating<br>■ Multi-stage countercurrent rinsing essential<br>■ Returns bath and impurities<br>■ Additional treatment may be needed to control impurities<br>■ May require pH control |

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## Appendix B (Continued)

| Technique/ Application | Advantages | Disadvantages |
|---|---|---|
| Ion Exchange<br><br>Au, Cr etch, AgCN, Cr, Sn, Zn, Cu pre-etch, Cu final etch, acid Cu, Watts Ni, NiSB, NiB | ■ Low energy demands<br>■ Handles dilute feed<br>■ Returns metal as metal salt solution | ■ Requires tight operation and maintenance - equipment complex<br>■ Limited concentration ability<br>■ May require evaporation to increase concentration<br>■ Excess regenerate required: 3-5X stoichiometric quantity, thus waste<br>■ Requires close monitoring of feed concentration |
| Reverse Osmosis<br><br>Watts Ni, NiSB, NiB, Zn | ■ Achieves modest concentration<br>■ Small floor space requirements<br>■ Less energy intensive than evaporation<br>■ Can return valuable additives | ■ Limited concentration range of operation<br>■ Fouling of membranes due to feeds high in suspended solids - feed filtration essential<br>■ Membrane sensitive to pH<br>■ Some materials fractionally rejected |
| Ultrafiltration<br><br>Cd, Cr, Cu, Au, Fe, Pb, Ni, Ag, Sn, Zn | ■ Low operating costs<br>■ Very compact | ■ Limited temperature range of operation<br>■ Fouling of membranes |