# ‘Saving And Minimization Of Contaminants By Recovering Cations And Anions And Water Recycling’

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The European Community have directives such as RoHS (Rectriction of Hazardous Substances); WEEE (Waste, Electrical And Electronic Equipment); and ELV (End of Life Vehicle).Minimization for contaminants for applying in chemical and electrolytic treatments and oil and grease separation in degreasing processes**:** Interchange columns for retarded retention of ionic cations and metallic anions. Hydrofugues miscivility separation of water no contaminated by volatile organic compounds (VOC’s). Membrane-filtering by permeate or nanofiltering device to retain cations and anions from a tertiary process to obtain better quality water and refused water to be reused for washing or secondary tasks. Recover of rinsing water from nickel, hard chrome and decorative chrome processes.

Key Words

Lower energy and water consume
Maintenance costs reduction
Lower ambient emissions

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*Introduction*

The purification of hard chromium plating solution is an important contributor to good results. Chromium bath purification enhances the performance of the bath by eliminating inconsistencies that can arise as a result of the contamination of dissolved metallic cations. In the European Community and especially in the Scandinavian countries metal behaviour, such as nickel, zinc, copper, lead and particularly chromium, is minimized and regulated. This is what this paper is about and a continuance of the work already initiated in 2003.

When cations build up in the bath, different problems associated with the conductive nature of the bath become apparent. Voltages are gradually turned up, plating times get longer, and the quality of parts decreases. Eventually the problems become so severe that the bath must be dumped and replaced by a fresh, clean solution. An innovation in ion exchange technology is available to effect chromium bath purification.

Known as the reciprocating flow ion exchange technique, it has been developed and implemented to improve product quality, eliminate bath dump, and aid in the reduction of power costs by maintaining a clean, conductive bath solution at all times. Other important fact is the technologies and new technologies, as an alternative to chromium, are marking its trajectory on the army and the automation field. Because of this, working with chromium III coating or other alternatives such as cobalt coatings is usual nowadays.

Purification of hard chromium plating solutions using this technique has been utilized for years to achieve these better bath performance characteristics. But it is concierge and produces contaminant emissions and, therefore, its environment impact has to be minimized both as gas and for its metal impurities. These metal impurities are mixed with nickel, iron, copper and so on. They have to be purified and recycled.

Therefore, chromium substitution and optimization is determined with different alternatives. The aeronautical, automation and general industry are the determinant leading trades, in respect to both production and research, together with legislation, for protecting the environment from contaminants. As an example, the Defence Ministry CHAT changed the use of electrolytic by projection of thermal spray coating.

The U.S. Hard Chromium Alternatives Team (HCAT) is currently executing projects to quality HVOF thermal sprays coatings (principally WV/Co) as a technologically superior, cost-effective alternative to electrolytic hard (EHC) plating, which is extensively used in manufacturing and repair of military aircraft components. Two projects on landing gear and propeller hubs have been completed and the technology is being inserted into repair depots. Projects are in progress on hydraulic actuators and gas turbine engine components. Results of rod/seal testing on deformer and materials and component rig testing on the latter will be presented. Standards and specifications for deposition, grinding, and stripping of the thermal spray coatings have been developed and issued by SAE. In general, thermal spray coatings have demonstrated superior fatigue, corrosion and wear properties to the EHC coatings.

Other alternative is the nanocrystalline electrodeposition coating plating. Both the Defence Ministries and Universities are working simultaneously on that field.

Wear resistance and hydrogen embrittlement are issues of great concern for steel plating operations. Steels that are susceptible to hydrogen embrittlement should be heat-treated to remove hydrogen. The temperature used is on the order of 205 °C (400 ºF), and exact temperature may be alloy dependent. Why not use this temperature to make thee coating harder and more wear resistance? In this paper, friction, wear and hydrogen embrittlement tests were conducted before and after heat-treatment, and where compared to coatings. The microstructures of nanocrystalline coating, before and after heating-treatment, where analysed by SEM, TEM and X-ray. The mechanism of the excellent wear resistance of the nanostructure material is described.

*Evaluation Of Nanocomposite Coatings As Environmentally Acceptable Alternative To Hard Plating*

The US Air Force Research Laboratory has been working with Current Technologies Cooperation (CTC) to evaluate alternatives to electroplated hard (EHC) for a variety of applications. One effort focused on performing screening tests on numerous nanoestructured coatings or amorphous coatings containing nanoparticles or micro-particles. Electrodeposited nanocrystalline cobalt, with and without tungsten carbide particles, electroless nickel (mid-phosphorous, ENP) coatings with various sizes of diamond particles (150, 1,000, 2,000 and 150 nm + 1,000 nm), and electroless nickel-.cobalt phosphorous (Eni-CoP), cobalt phosphorous (Eco-P), and cobalt boron (Eco-B) –all with and without co-deposited diamond particles, were tested and compared to EHC, polycrystalline cobalt, and electroless nickel coatings without occluded particles. The intent was to elucidate the improvements in performance that can be obtained with decreasing grain or particles size. Preliminary results, which were reported in the earlier paper, suggested that all of the ENP, Eni-CoP, and Eco-P process with occluded diamond particles have the potential to impart the required tribological properties, while reducing the environmental impact to plating process. To conclude this phase of work, additional studies where performed to obtain thicker ( e.g., 5-10 mils or thicker) ENP coatings with 150 nm diamond particles occluded and 2-mil thick Eco-B and electrodeposited nanostructure nickel-cobalt coatings, both with 150 nm diamond particles occluded. This paper discusses the adhesion, thickness analysis, hardness, and abrasive wear resistance results that were obtained during screening test, and plans for follow-on work in nanostructured coatings and nanoparticulated occlusion plating.

Hexavalent plating has been used for many years to provide hard, durable coatings with excellent wear and corrosion resistance properties. However, hexavalent baths have come under increasing scrutiny because of the toxic nature of the bath, effects on the environment, and workers' health. This project is investigating the various parameters affecting plating from a trivalent bath. This is an update on our accomplishments to date involving the plating of pump rotors in regard to the hydrodynamics and electrical field effects on the varying geometry of the pump rotor. Continuing work on the bath chemistry, diffusion layer, hydrodynamics, and electrically mediated process parameters will be discussed. The project is being founded by CTMA and a commercial partner.

Some companies are developing a new way to protect metals from corrosion using only silicates-common sand-like minerals found in the earth's crust. No . No phosphate. Just better performance without environmental or regulatory worries. A pilot line was installed to validate chromate replacement over zinc plating. This paper details the capabilities of the pilot line and documents the better adhesion, better heat tolerance, better flexibility, and better stress performance of the environmentally friendly proprietary coating.

After reviewed the alternative, new chromium technologies of electrodeposited nanocrystalline coating plating, which are not yet defined in all trades, except passivating for acid zinc baths Zn/Fe, Zn/Ni, Zn/Co, etc and automation or aeronautical business.

After reviewed the nanocomposite coatings new technology as an alternative to chromium, we see that there are not yet well defined in surface treatment areas - mechanical, automotive and aeronautic- with the exception of pasivation treatments for acid zinc baths, Zn/Fe, Zn/Ni, Zn/Co, etc.

*Purification and Recovery Techniques*

The biggest advantage of eliminating bath dumps or periodic bailouts in a high production facility is the ability to maintain consistent production quality and plating rates. Several techniques are utilized to control contaminant build-up to enable continuous operation of hexavalent plating solutions. The most efficient technology is dictated by the plating solution type (decorative or hard ) and the relative production loading.

*Metal Charged Effluents Treatment by Electrolysis*

The electro-oxidation and electro-reduction phenomena are ruled by electrolysis laws, which we are going to remind now.

*Principles of Electrolysis*

The dissolution of an electrolyte in a solvent induces formation of species positively charged (cations) and negatively charged (anions). The fact of applying a difference of potential between two electrodes immersed in an electrolyte solution creates an electric field, thus causing ions migration. There are three characteristic ways of transporting matter to the electrolyte: migration, convention and diffusion.

*The Migration*

It refers to the movement of the charges. Cations move in the field direction towards the cathode and the anions in the opposite direction.

*The Convention*

Under the effect of different factors like temperature, agitation, different density, the transportation of matter can be modified. Therefore, the convention's reaction is conditioned by the mentioned variables.

*The Diffusion*

This is a phenomenon due to the existence of a concentration gradient around the electrode. The gradient is generated by the electrochemical reaction developing in the interface of the electrode/solution. This variation in the concentration provokes the spices moving from the mores concentrated areas to less concentrated ones. Unlike the other two ways of transporting matter, the diffusion phenomenon takes only place in the area corresponding to the interface of the electrode/solution.

These are the basic principles of electrolysis where oxidation reaction, oxidation-reduction, and stronger reducers occur, according to the potential scale values of metal electro-negativity, that is, Nernst's law.

*Application and Implementation of An Electrodeposition Unit for Purifying Heavy Metal Effluents*

Electrodeposition is a technique particularly well adapted to effluent treatment charged with heavy metals (Cd, Cr, Pb, Zn, Ni, Cu, Hg) or precious metals (Au, Ag, Pd). The metal deposit in the cathode can be retrieve, purified and recycled. The system is suitable for different application, like recovery of metals in static rinsing. If a cellule is fitted in the "dead" rinsing circuit, it will increase considerable the circuit's life and it will avoid environment pollution or contamination. It also achieves a reduction of environment cost and energetic consume.

However, the non-electroactive components will be preserved. Consequently, it will not be possible to recycle the rinse indefinitely. Therefore, it should be purified.

This type of electrodeposition process, can be used for holding and recuperating metals in the three types of zinc baths: cyanide, acid, and exempt. It can also be applied for rinsing nickel, nickel wood, watts, chemical nickel, etc.

*Other Factors to Avoid Contamination*

There are enumerated below, other important parameters which are beginning to be taken into consideration and that are getting an environment grant for them by the EU:

- Decyanidation
- Chemical o mechanical destruction of cyanide
- Dichromate
- Specific traitment for water: to decarbonate
- Coagulation

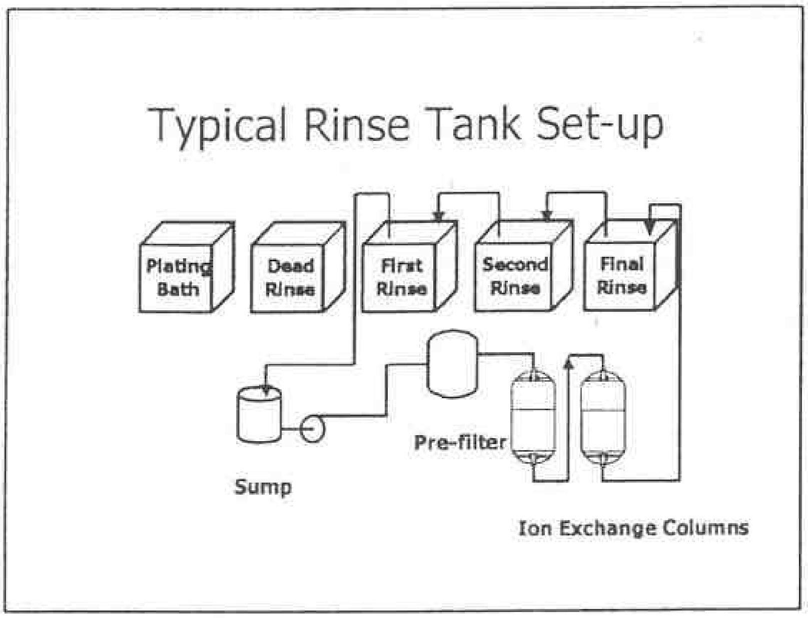
- Neutralization
- Microfiltering for electrolytic regeneration
- Flocculation and decantation
- Final filtering with sand
- Ionic plasma

The processes are intended to reach environmental self-controlled parameters of the following values:

| | | | | | |
|---|---|---|---|---|---|
| pH | 5.5 to 8.8 | Fe | 〈0.2 mL | Sn | 〈1 mL |
| MES | 〈6 mL | Al | 〈0.2 mL | Cd | 〈0.5 mL |
| $Cr^{+6}$ | 〈0.01 mL | Cu | 〈0.05 mL | $Cr^{3+}$ | 〈0.05 mL |
| $CN^{-}$ | 〈0.001 mL | Zn | 〈0.5 mL | P | 〈5 mL |
| Ni | 〈1 mL | Ob | 〈0.2 mL | F | 〈5 mL |

*Ion exchange resins*

Ion exchange resins are one of the best available and most durable technologies for removing relatively low concentrations of ionised contaminants from water industrial process.



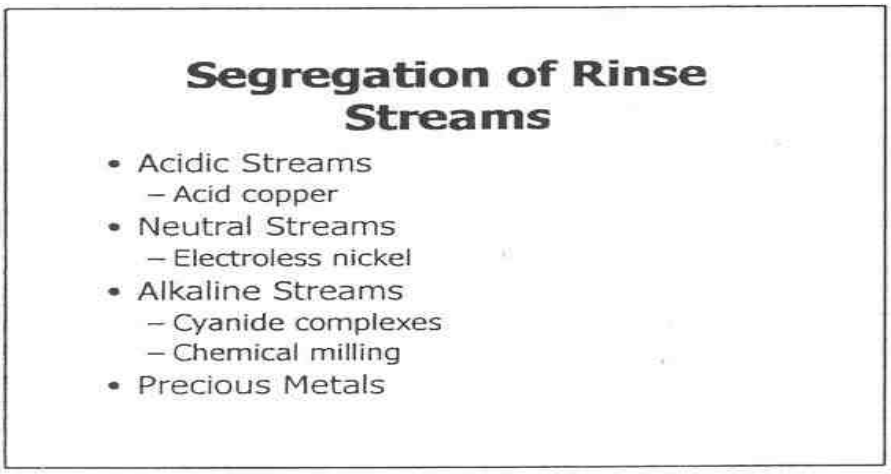
Elimination of potential discharge of metals to the environment by elimination and discharge of water waste.

*Recycle Systems*

Saving water
Saving contaminants
Saving chemical products
Saving process waste water

*Segregation Of Rinse Water Strems*

For years, most plating shops have combined rinse waters into a common stream for bath treatment.




*Reciprocating Flow Ion Exchange – System Operation*

As outlined in Figure 1, chrome bath solution is treated in a bath wise manner. A volume of contaminated solution required for purification is transferred to a feed tank. The solution is allowed to cool by radiant means (90°C) prior to being purified by the reciprocating flow ion exchange system.

The solution is subsequently processed through dyak cartridge filters and through the ion exchange bed of the system. As the chromic acid solution at 60 % of its normal bath strength passes through the ion exchange bed, the metal contaminants are stripped out of the solution (up to 80% in a single pass). The purified chromic acid flows to the product storage tank. The excess volume that results from dilution is easily matched by the natural evaporation loss from the hard chrome bath.

After a predetermined amount of feed solution hast been processed, the unit will automatically effect a regeneration of the resin using sulphuric acid and water. 93% w/w sulphuric acid is supplied, automatically diluted to the correct strength an pumped through the bed. Excess sulphuric acid is washed out of the bed with water. This step generates a diluted waste stream containing metal contaminants, some small traces of chromic acid, and sulphuric acid. The waste stream is to be treated prior to discharge. Upon completion of the regenerating sequence, the unit begins to process more feed solution. The cycle repeats itself continuously and automatically.

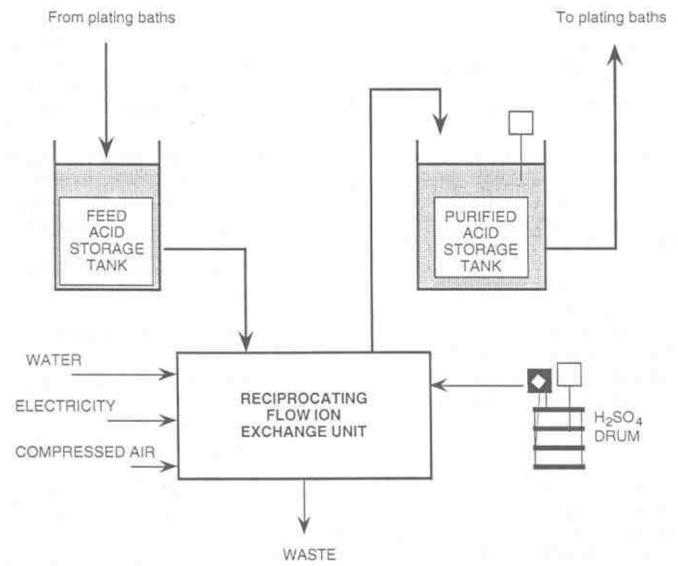



Figure 1 - Typical Process Schematic

*Economic consideration*

An economic comparison of three methods of processing 1000 gallons of contaminated chromic acid plating solution is outlined in Table 1. The three methods consider hauling the liquid waste, full in-house waste treatment of the bath solution, or the use of reciprocating flow ion exchange.

Liquid haulage is the most expensive option and is increasingly fallowing into disfavour since many of the recycling centres are no longer accepting liquid chrome waste due to the transport liabilities involved. The chemical cost for treatment and batch replacement combine to make on-site treatment an expensive alternative. The sludge generated when the reciprocating flow ion exchange is employed is only a fraction of the volume that would otherwise be produced.

In addition, chrome bath operating costs would be lower as savings dur to lower electrical requirements, higher productivity, and lower reject rates become significant.

Table 1

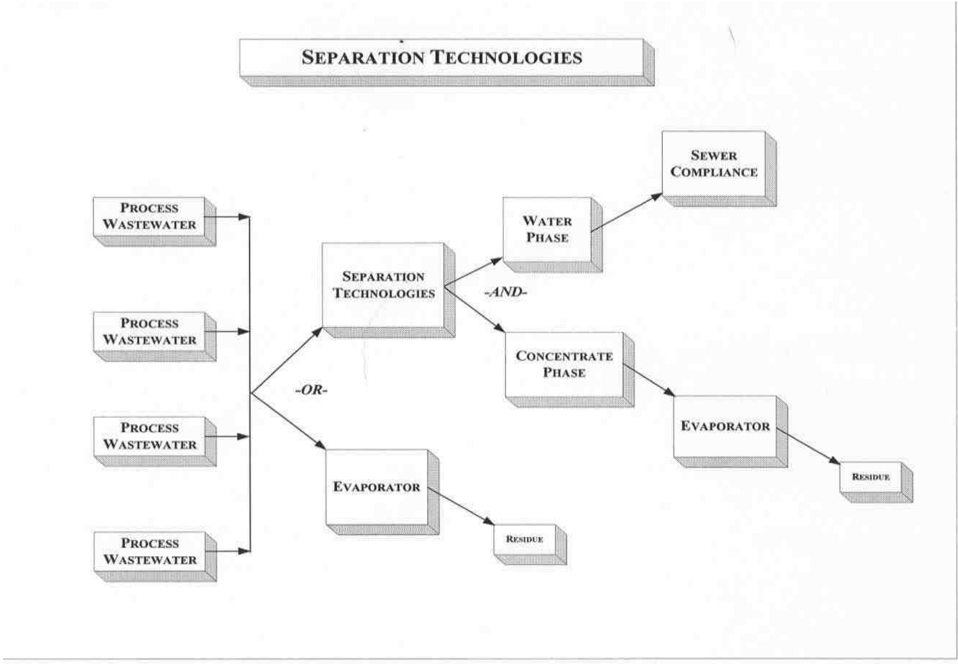
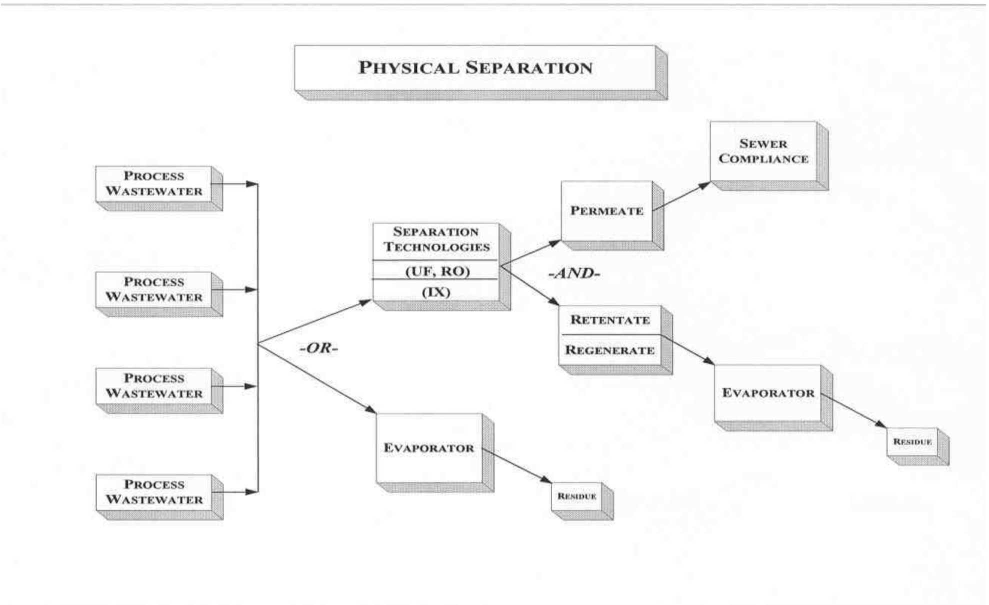



Table 2



*Hard Chrome Plating Applications*

Hard chrome plating operations often require another approach for controlling contamination build-up. Long plating cycles and high evaporative losses allow rinsing over the plating tank, and supplemental rinsing is minimal or not required. As a result, drag-out losses cannot be relied on to remove cation contamination from the plating solution. For this application, ion exchange can be applied directly on the plating solution. Specialty high purity resins, with a high percentage of cross linking, can perform for a limited time on concentrated chrome solutions, but will suffer a high attrition rate and more frequent replacements will be necessary. When evaporation losses are high, dilution of the plating solution prior to sending it to the ion exchanger helps extend the life of the resin.

Figure 2- Hard Chrome Plating Application

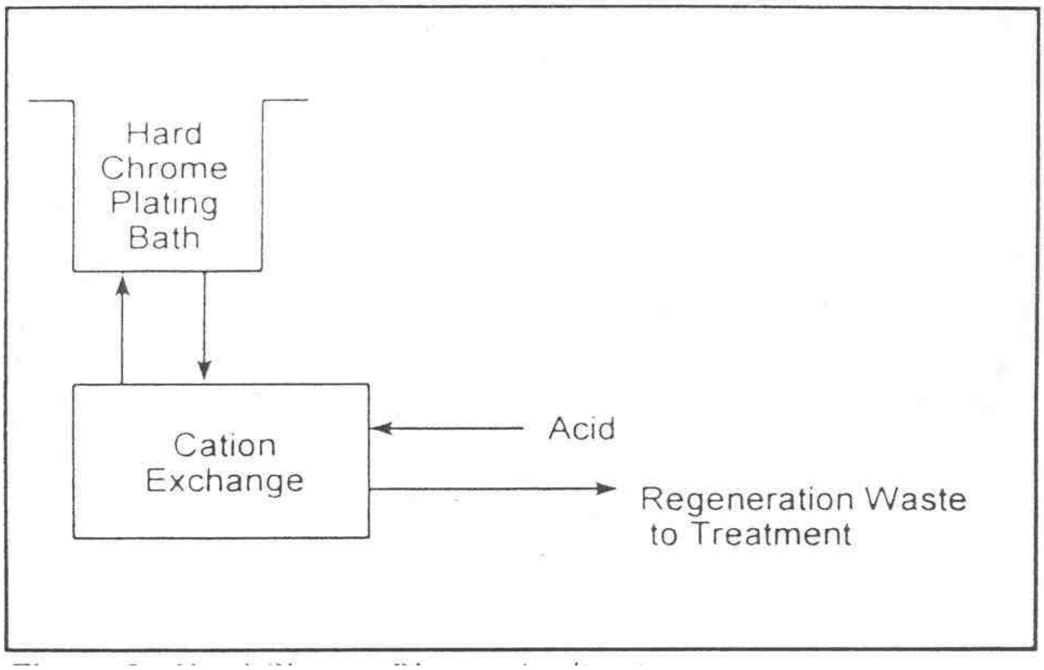


Figure 3 “Alternative Bath Purification Method

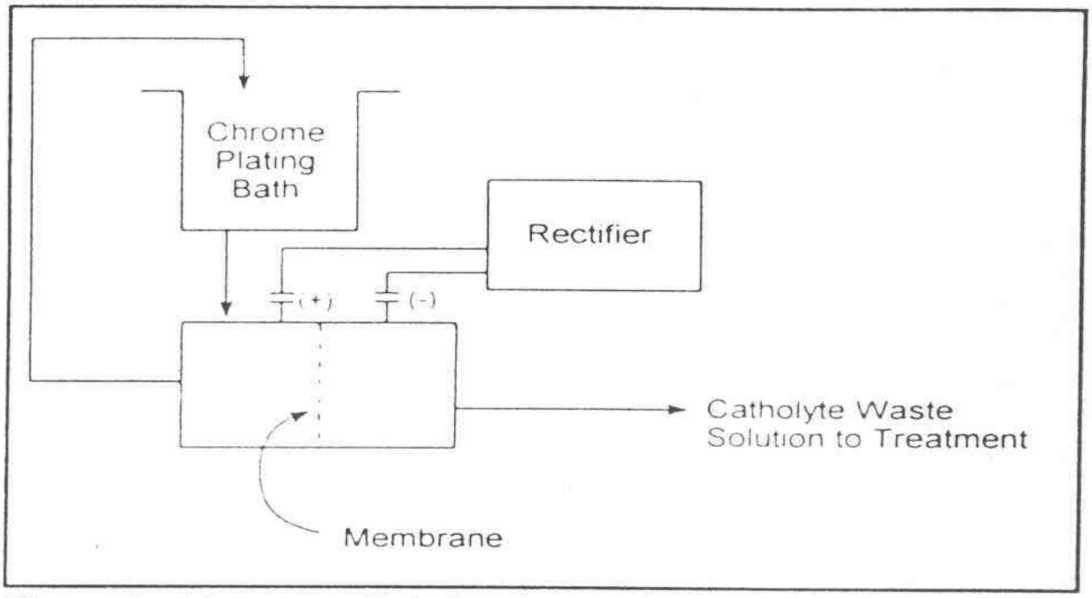



Figure 4

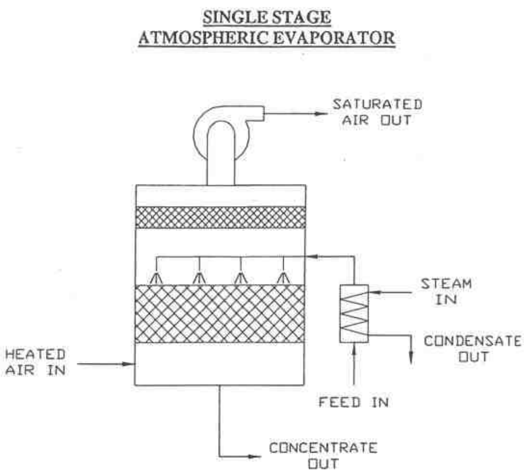



Figure 5

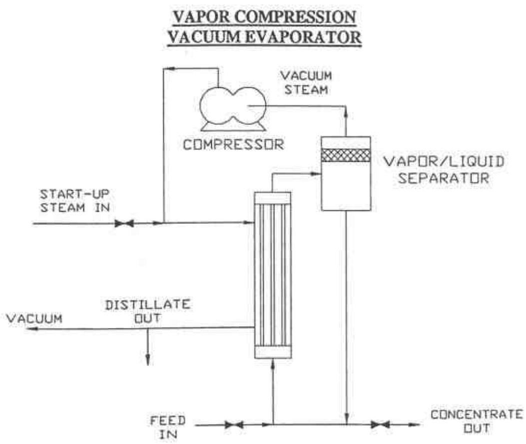


Figure 6

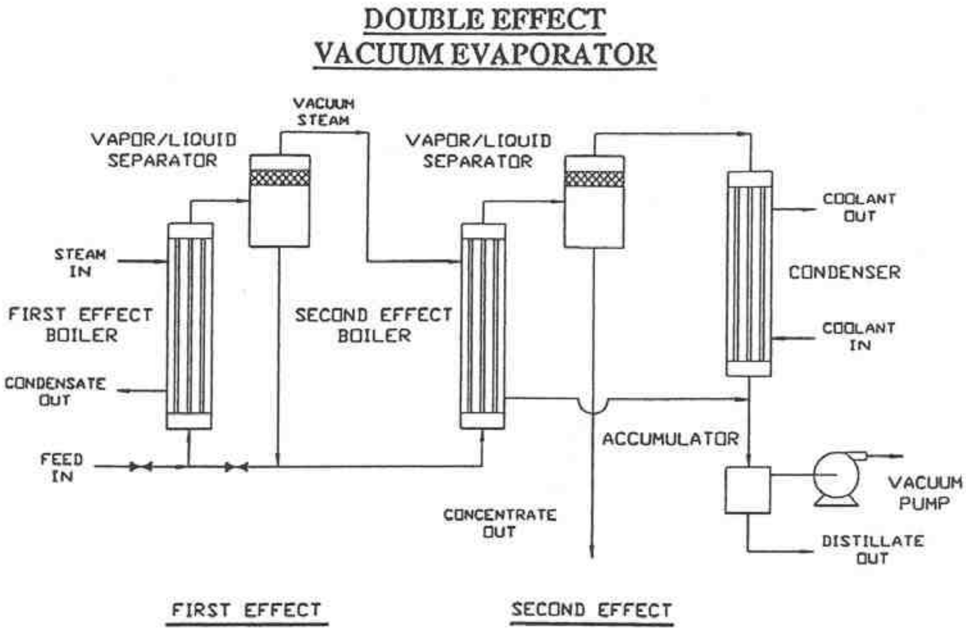



Table 3 - Chrome Plating Solution Recovery – Relative Cost comparison

| **Recovery Technique** | **Capital Equipment** | **Labour** | **Recovery Efficiency** | **Utilities** | **Chemical** | **Miscellaneous** |
|---|---|---|---|---|---|---|
| Porous Cup | Low | Low | Low | Low | Low | Bath Purification / Recovery |
| Evaporation | Low | Low | Moderate | High | N/A | Bath Recovery Only |
| IX Evaporation | Moderate | Moderate | High | High | Low | Bath Purification / Recovery |
| IX Evaporation with Rinse Water recycle | High | Moderate | High | High | Moderate | Bath Purification / Recovery & Rinse Water Recovery |
| Electro-dialysis | Moderate | Moderate High | Moderate | Moderate | Low | Bath Purification / Recovery |
| Conventional Treatment | Moderate | High | N/A | Low | High | No Recovery & High Disposal Cost |

Table 4 – Purification Economics

| ITEM | ON-SITE TREATMENT | RECOFLO ION EXCHANGE | OFF-SITE DISPOSAL |
|---|---|---|---|
| Bath replacement | 2,800 € | --- | 2,800 € |
| Chemicals | 1,388 € | 432 € | --- |
| Solid disposal | 1,073 € | 112 € | --- |
| Liquid Disposal | --- | --- | 6,400 € |
| Total Cost | 5,261 € | 544 € | 9,200 € |

## Summary

1. Maintenance of hexavalent chrome plating solution no longer requires wasting the solution to control contaminant build-up.
2. Continuous bath purification enhances productivity by maintaining contaminant concentrations within acceptable range and provide more predictable performance from the plating solution.
3. Careful evaluation of the production operation is essential to document actual loadings which determine the most efficient recovery and contaminant control method.
4. Total treatment cost at new and existing facilities can be reduced significantly because most of the hexavalent chromium is recovered and only the contaminant cations are sent to treatment. Purchasing recovery/purification equipment can reduce treatment equipment cost for the new facility.

## Conclusions

1. Reciprocating flow ion exchange process is the best solution for continuously purifying chromic acid solution.
2. It has become readily accepted in the industry as an economical solution to remove metals from hard chrome plating baths.

3. Nickel, chrome and other metals should be recycled.
4. Energetic saving in all processes should be adopted.
5. Cost reduction by eliminating and minimizing sludge with metal content.
6. Saving of chemical products such as additives in the physical-chemical depurator stations.

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