CHROME BATH PURIFICATION TECHNOLOGY: WATERVLIET ARSENAL

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The purpose of the present EP cell units is to remove dissolved metal impurities, in particular iron, from the arsenals baths and convert Cr^{+3}, trivalent chromium, to Cr^{+6}, hexavalent chromium.

The EP cell technology, which is also referred to as porous pot electrolysis, has been shown to be relatively ineffective in removing iron and other dissolved metal contaminates from chrome baths. Also, it generates large quantities of concentrated chromic acid waste.

The arsenals chrome baths have been relatively free of operating problems. However, the good operating conditions may be the result of a high turnover rate of chrome baths rather than the effect of the EP cell units. The hard chrome plating and surge tanks hold approximately 26,700 gallons of chromic acid solution or about 13,000 kg of chromium (as Cr). The mass balance shows a quantity of 4,270 kg of chrome lost yearly from the tanks (dragout, fume exhaust, miscellaneous losses), not including the chromium plate on the gun tubes. Therefore, approximately 33% (4,290 kg of 13,000 kg) of the baths are replaced annually.

IONSEP™

A technology with higher efficiency for chrome bath purification is electrodialysis or ED. Test of ED units versus EP cell (porous pot electrolysis) on identically contaminated chrome solutions showed that the ED technology removed approximately three times more dissolved metal than the EP cell units over a period of 16 days.

The ED units do not generate a chromium waste by-product, but rather a metal hydroxide sludge.

The slide presentation indicates how the ED units will be installed at WUT Arsenal.

The units consist of an ED cell unit that is placed into the plating tank, a catholyte tank located near and plumbed to the ED cell, and a power source (rectifier).

In operation, a direct current is passed through the ED cell and the catholyte solution is circulated through the cell. The cell is constructed with a selective membrane that has an inner cathode compartment and outer anode compartment. An alkaline catholyte solution is circulated through the cathode compartment and the anode compartment is exposed to the chromic acid bath.

The cations, like iron in the bath, are electrically driven through the selective membrane and into the cathode compartment. These cations precipitate as hydroxides. Trivalent chromium present near the anodes is converted to hexavalent chromium. The catholyte solution is periodically replaced (approximately every two weeks). This waste can be treated at the IWTP.

One ED unit is required for each chrome plating tank. The units are sized according to the volume of the baths and the introduction rate of contaminants. Some bench scale testing is needed for proper sizing of the units.

An economic analysis shows the capital cost for implementation at $139,680 including $48,000 equipment cost. The operating cost/savings shows a positive cash flow of $167,460 during the first year. The major savings are from reduced raw material purchases (chromic acid and electrodes for the EP cell units) and the disposal cost for 3,000 gallons of EP cell (chromic acid high strength solution) annually. The payback for this investment is 0.8 years.

IONSEP™

ELECTRODIALYTIC PROCESSES

FOR:

MORE EFFICIENT USE OF CHEMICALS

MORE RELIABLE PROCESSING

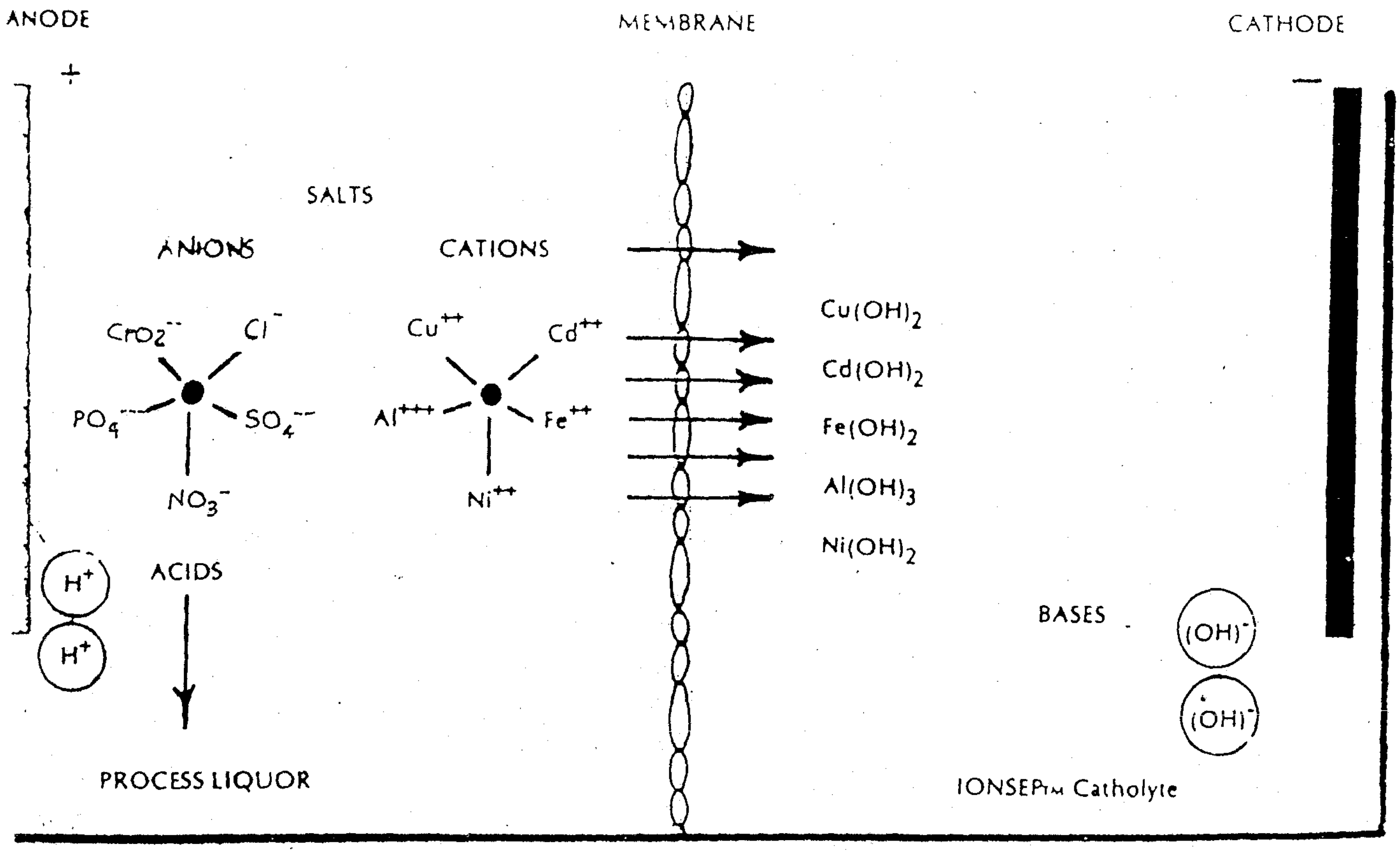
CLOSED LOOP PROCESSING

Each year thousands of tons of heavy metal waste are made in chemical processing that must be securely landfilled. This waste **(inefficient use of process chemicals)** increases cost of manufacture and results in a high and increasing cost of waste disposal. Ionsep's new technology provides for more efficient use of chemicals, more reliable processing and closed loop processing.

IONSEP PROVIDING NEW TECHNOLOGY

Acids are reacted with bases and metals everyday to make salts. If it was possible to convert salts in an aqueous solution back to separate acids and bases, acids and bases could be used again and again. Ionsep has developed and is now making available commercially a simple process for converting any salt in an aqueous solution into the separate acid and base of the salt using electricity in a membrane electrodialytic process. This simple capability of converting a salt to an acid and a base makes IONSEP Electrodialytic Processes broadly useful in chemical processing.

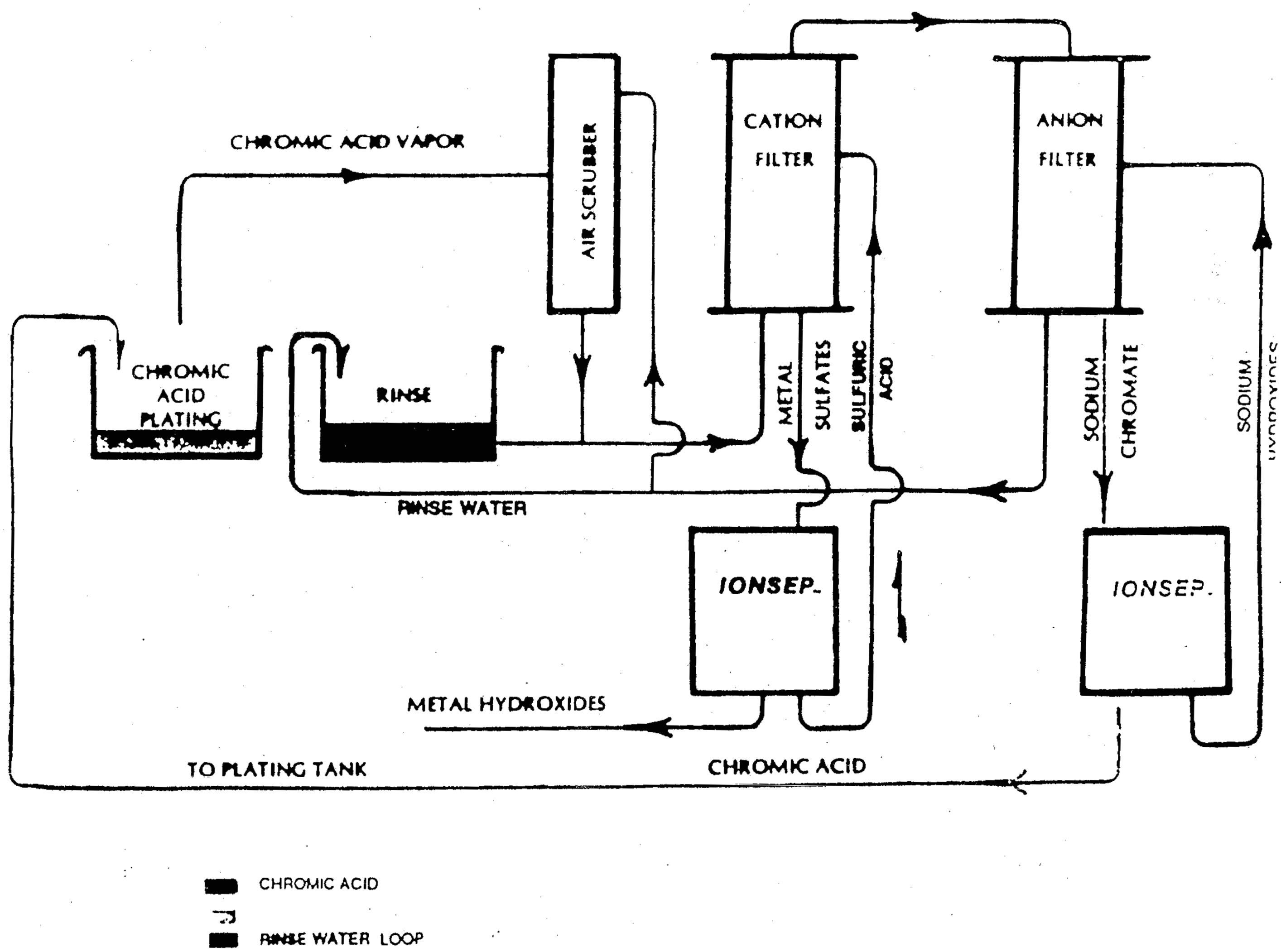
CONVERSION OF SALTS



CLOSED LOOP PROCESSING

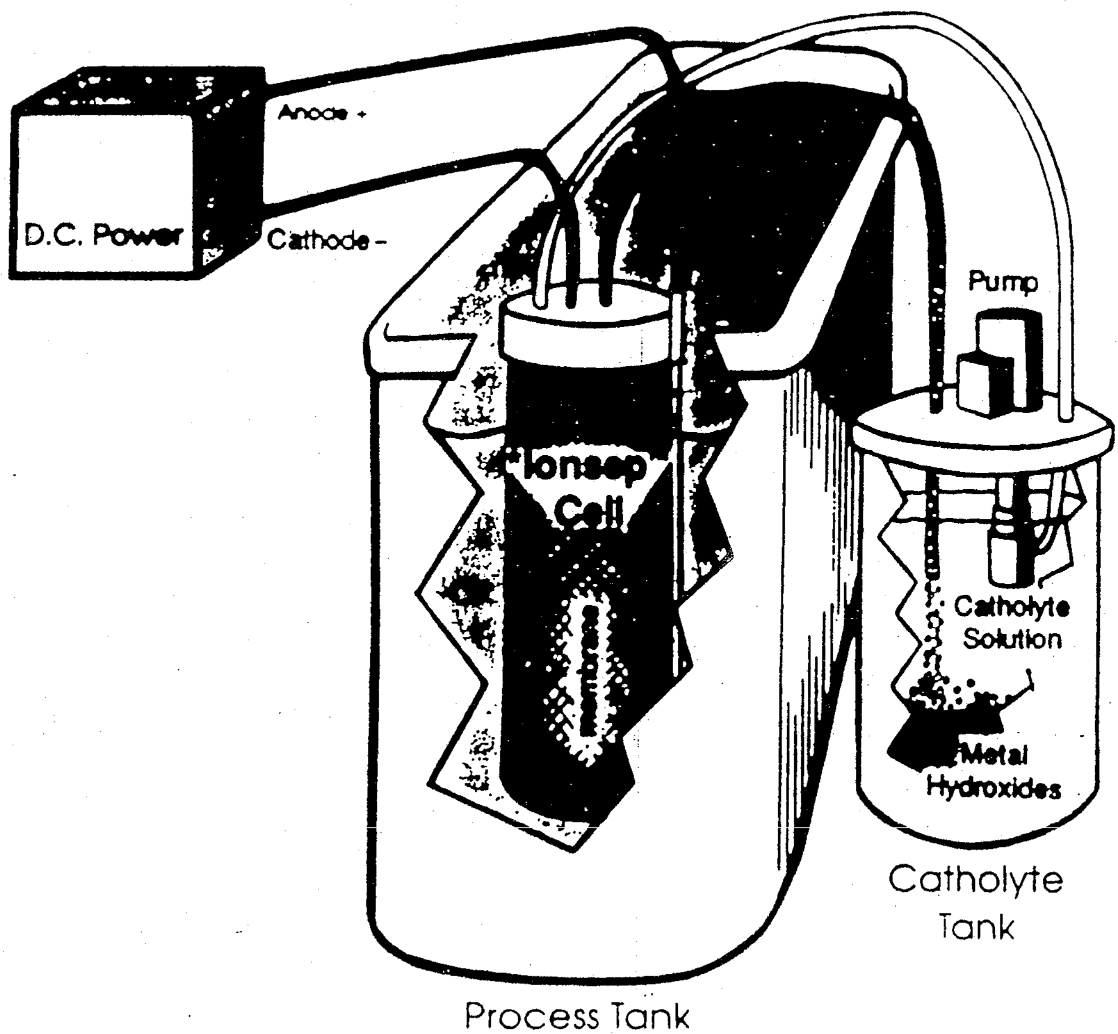
A process with no loss of chemicals to the environment (closed loop) may not be possible. But, it is desirable to lower cost of manufacture by operating more reliable and efficient processes while reducing waste. *IONSEP* electrodialytic processes provide two important steps towards closed loop processing: (1) purification and restoration of acidic and alkaline process liquors; and, (2) reforming and separating chemicals used to regenerate ion filters.

IONSEP'S CLOSED LOOP SYSTEM



A SIMPLE PROCESS

The *IONSEP* process comprises a membrane electrochemical cell, designed for immersion in a process liquor, a rectifier, a process liquor containing metal salts, an *IONSEP* catholyte solution and a pump to flow the catholyte solution through the cell. The membrane separates the process liquor from the catholyte solution and acts as an "Electrochemical Traffic Controller" that lets metal cations go from the process liquor through the membrane (electrofilters the metals) into the catholyte solution and keeps anions in the process liquor. The metal cations are continuously converted to hydroxides in the catholyte solution and the anions are continuously converted to acids in the process liquor. The hydroxides of multivalent metals (cadmium, zinc, iron, copper, aluminum, calcium, etc.) are substantially insoluble in the catholyte and can be removed for use. The *IONSEP* process is unique in that salts of multivalent metal cations can be converted. There is essentially no electrodeposition of metals. The *IONSEP* process can be operated at reproducible capacities for months. The capacity of the *IONSEP* process is varied by voltage.



A BROADLY USEFUL PROCESS

CHROMIC ACID PLATING LIQUORS

- All metal impurities removed and maintained at low level
- Permits recycle of rinse or rinse concentrate to plating
- Provides reliable plating with less power and higher rates
- Provides closed loop processing for chromic acid plating

CHROMATING LIQUORS

- Metals removed and acids reformed continuously
- Liquors maintained at composition for best chromating
- Disposal of chromating liquor essentially eliminated
- Provides for more reliable chromating, lower use of chemicals and potentially closed loop processing.

ACIDS—ETCHING, ANODIZING, PICKLING ETC.

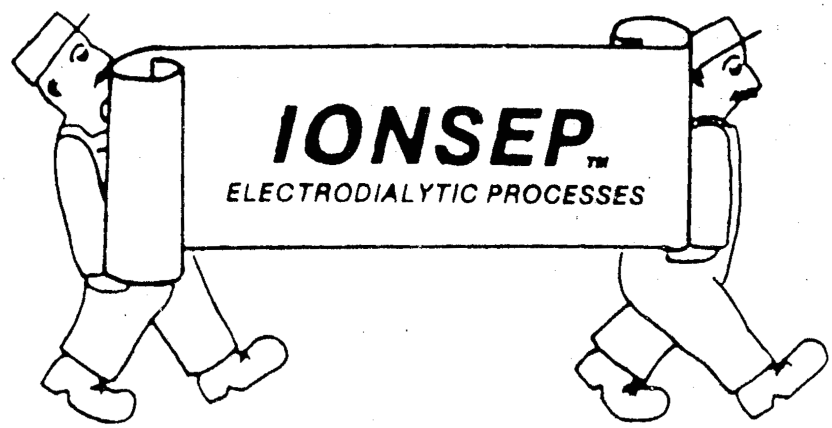
- Acids reformed continuously and metals removed
- Composition of liquors maintained essentially constant
- Provides more reliable processing and more efficient use of chemicals
- Potential for closed loop processing

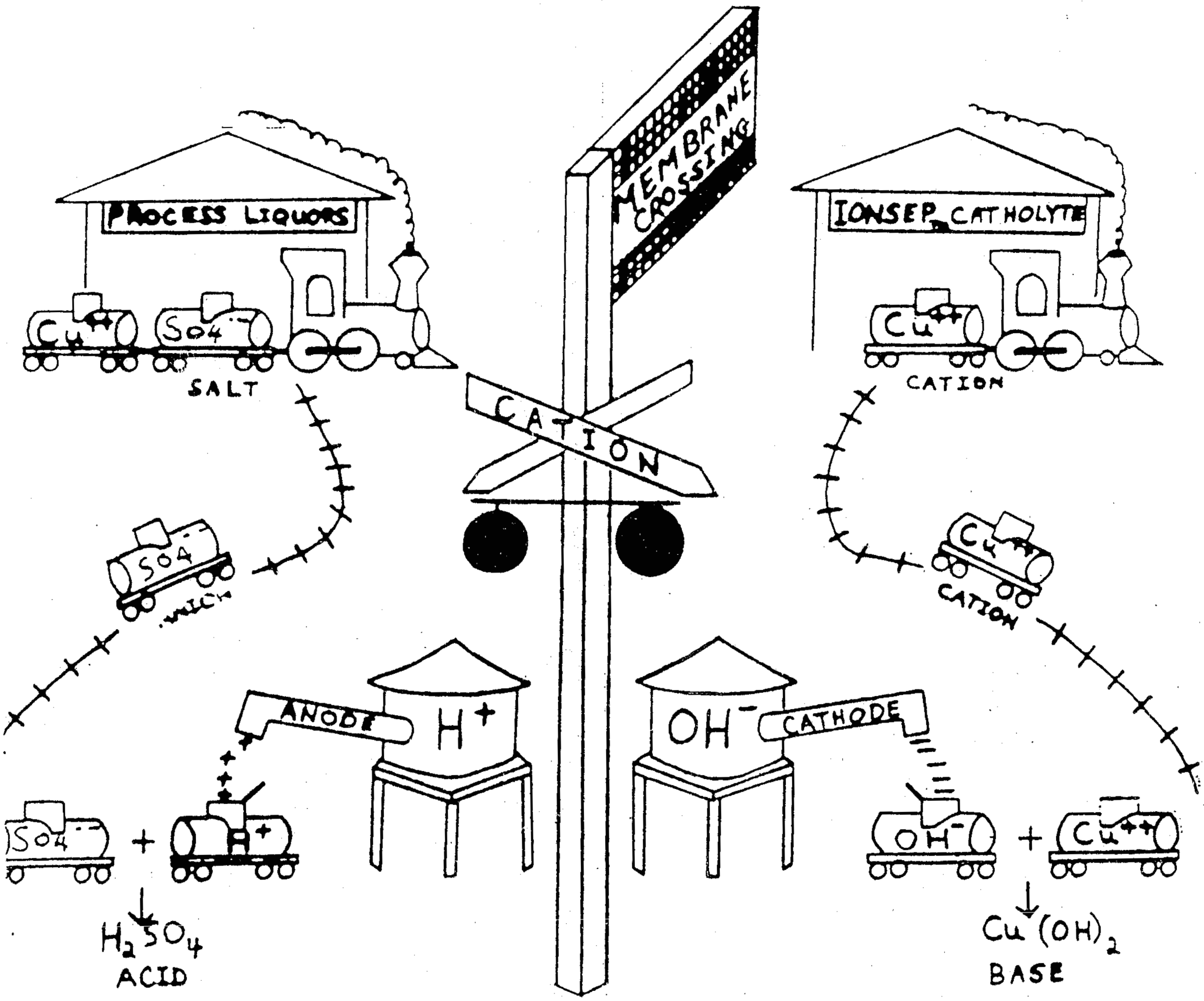
CAUSTIC ELECTROSTRIP—SODIUM CHROMATE SOLUTIONS

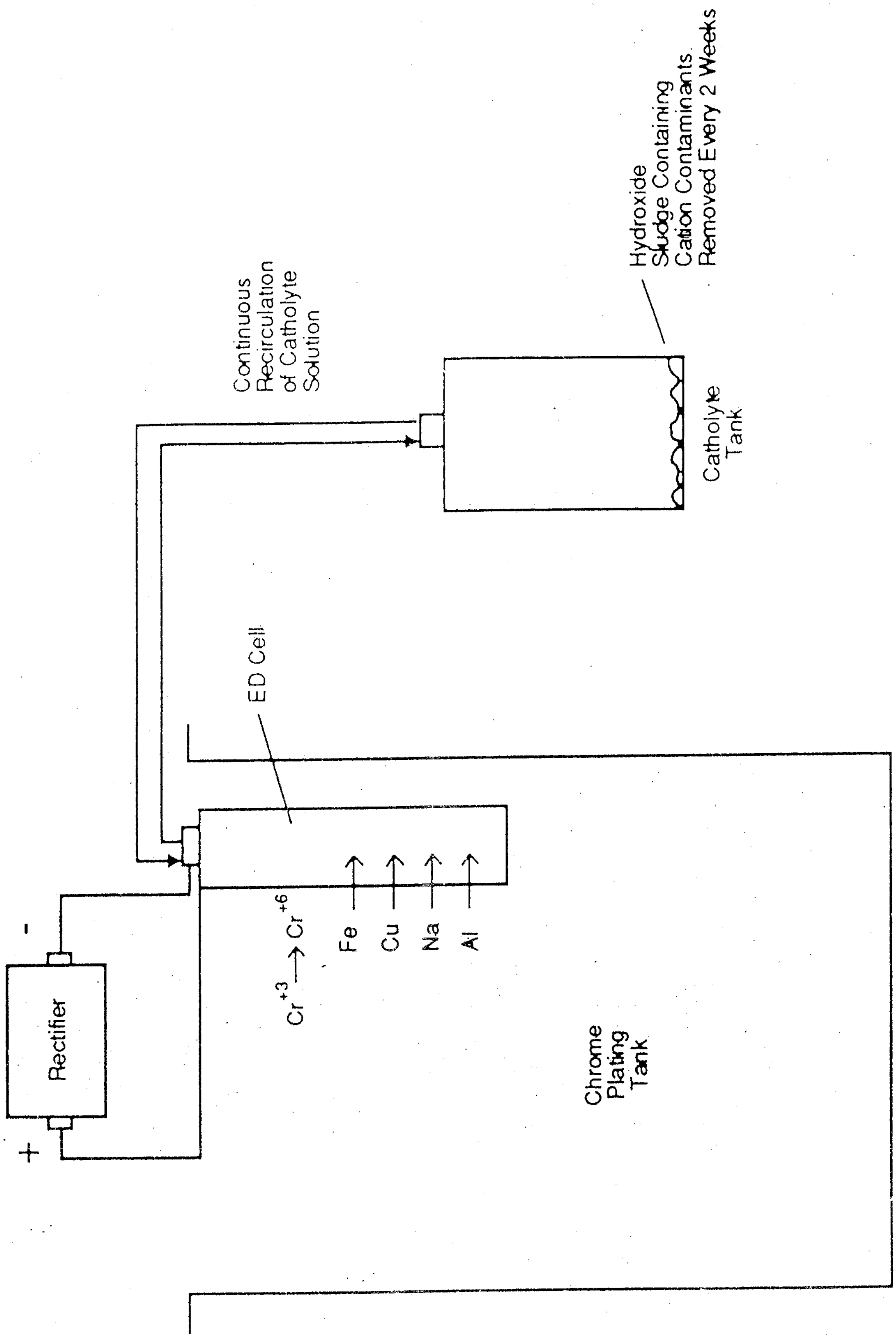
- Converts sodium chromate to sodium hydroxide for reuse and chromic acid for another use with removal of multivalent metal impurities.

ORGANIC DYES FOR METALS

- Dyes restored-metal impurities removed from dyebath
- Provides more reliable dyeing and lower dye usage
- Potential for closed loop processing.


IONSEP™
ELECTRODIALYTIC PROCESSES


MEMBRANE CROSSING
PROCESS LIQUORS
IONSEP™ CATHOLYTE
Cu^{++}
SO_4^{--}
SALT
CATION
CATION
SO_4
Cu^{++}
CATION
ANODE
H^+
OH^-
CATHODE
SO_4^{--} + H^+
H_2SO_4
ACID
OH^- + Cu^{++}
$Cu(OH)_2$
BASE


Continuous
Recirculation
of Catholyte
Solution
Hydroxide
Sludge Containing
Cation Contaminants
Removed Every 2 Weeks
Catholyte
Tank
ED Cell
Rectifier
-
+
$Cr^{+3} \longrightarrow Cr^{+6}$
Fe
Cu
Na
Al
Chrome
Plating
Tank

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IVADIZER

ADVANTAGES

✓ IMPROVED CORROSION RESISTANCE

✓ EMPLOYEE SAFETY

✓ POLLUTION FREE PROCESS

✓ NO HYDROGEN EMBRITTLEMENT

✓ 925 DEGREE SERVICE TEMPERATURE

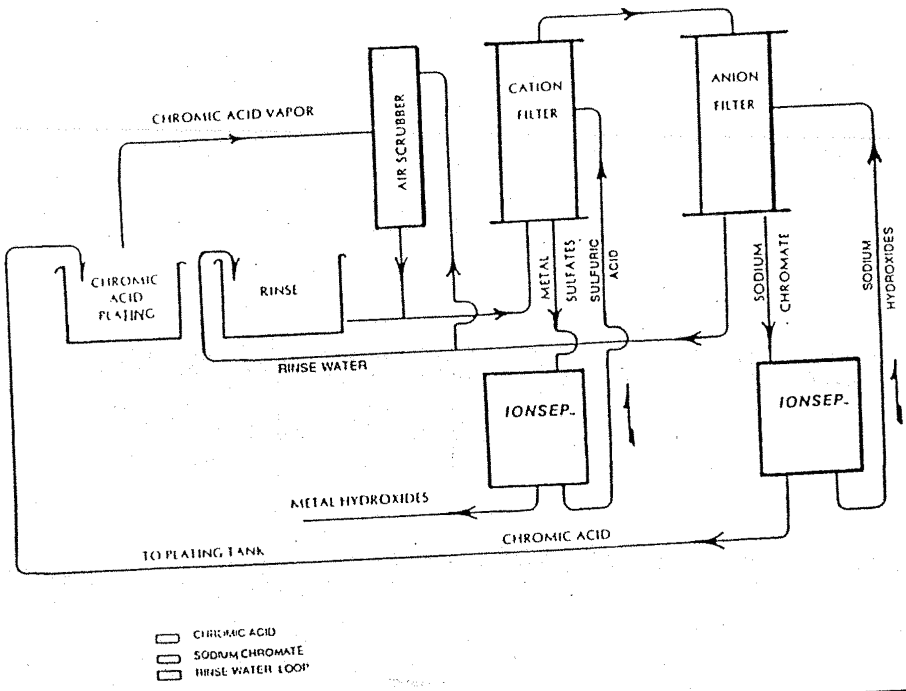
✓ NO EFFECT ON FATIGUE LIFE

IVADIZER

DISADVANTAGES

- DRY TORQUE PROBLEMS
- COATING INTERNAL DIAMETERS
- HIGH CAPITAL COST
- PROCESS ACCEPTANCE PROBLEMS AT THE COMMODITY COMMANDS

CHROME RECOVERY - RINSEWATER



CHROME RECOVERY - RINSEWATER
ECONOMIC DATA

EQUIPMENT COST: $95,000 (installed)

OPERATING COST: $9,000 per year

ANNUAL COST SAVINGS: $35,700 per year

PAYBACK: 3.1 years

CHROME RECOVERY - RINSEWATER
HAZMIN DATA

WASTE STREAM REDUCED: chrome sludge and water

QUANTITY REDUCED: 19,200 lbs Cr sludge
1,728,000 gal water

COST SAVINGS OF WASTE DISPOSAL: $42,000

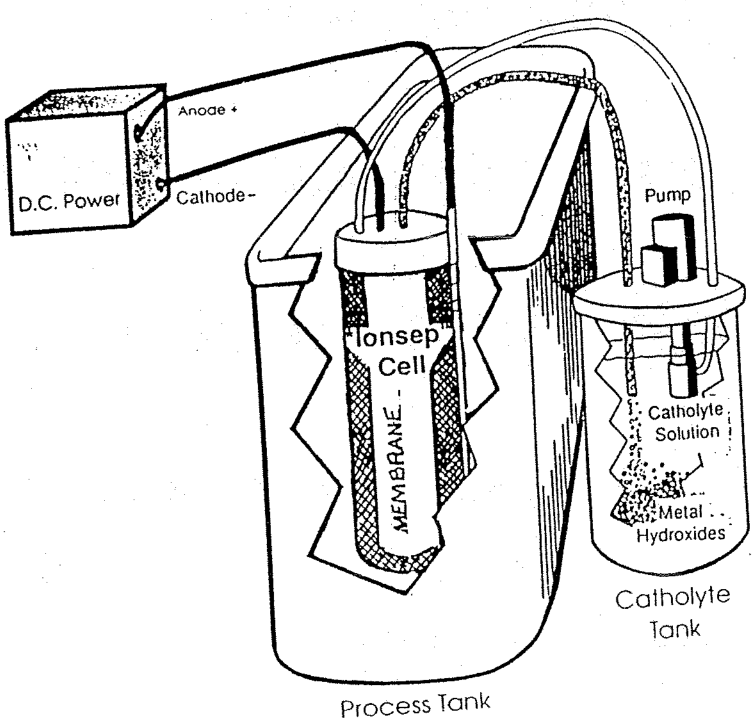
CHROME RECOVERY - RINSEWATER
ADVANTAGES

- ✓ RECLAMATION OF RINSEWATER
- ✓ RECLAMATION OF CHROME
- ✓ BETTER RINSING - DI WATER
- ✓ APPROACHES "ZERO WASTE" GENERATION

CHROME RECOVERY - RINSEWATER
DISADVANTAGES

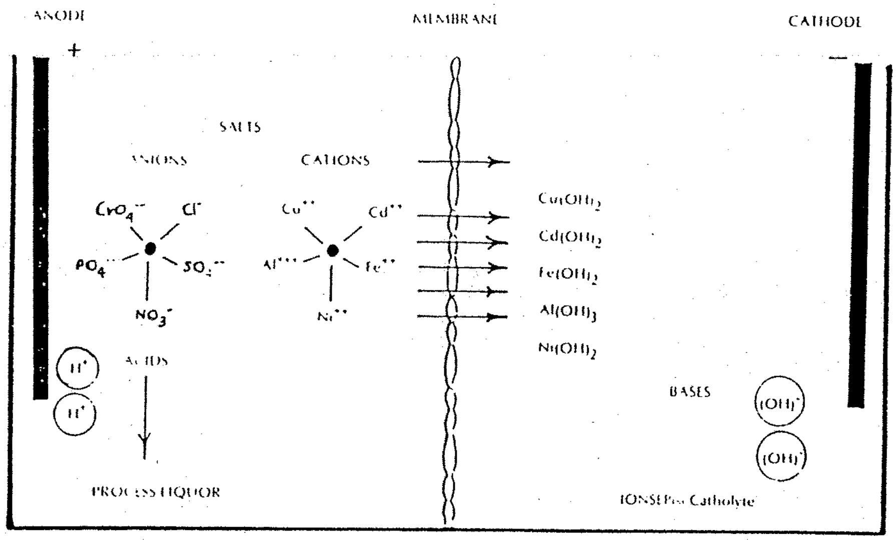
- CONSUMES VALUABLE SPACE IN THE SHOP
- GENERATES A METAL HYDROXIDE SLUDGE WHICH CONTAINS CHROME
- HIGH CAPITAL COST

CHROMIC ACID PURIFICATION



THE IONSEP PROCESS

CONVERSION OF SALTS



CHROMIC ACID PURIFICATION
ECONOMIC DATA

EQUIPMENT COST: < $30,000 (installed)

OPERATING COST: $6,000 per year

ANNUAL COST SAVINGS: To be determined

PAYBACK: To be determined

CHROMIC ACID PURIFICATION
HAZMIN DATA

WASTE STREAM REDUCED: chromic acid plating solution

QUANTITY REDUCED: 200 gal Chromic acid

COST SAVINGS OF WASTE DISPOSAL: $1,100

CHROMIC ACID PURIFICATION
ADVANTAGES

- ✓ CONVERTS TRIVALENT CHROME TO HEXAVALENT CHROME
- ✓ RECLAMATION OF CHROME
- ✓ BETTER PLATING QUALITY
- ✓ REDUCES REWORK
- ✓ REDUCES PITTING AND "TREES"
- ✓ REMOVES METAL IMPURITIES: Ni, Pb, Fe, Cu, etc.

CHROMIC ACID PURIFICATION
DISADVANTAGES

- OCCUPIES SPACE IN THE TANK (8 INCHES SQUARE)

- OCCUPIES SPACE IN THE SHOP

- GENERATES HEAT IN THE TANK

- REQUIRES EMPLOYEE MONITORING

IN-TANK FILTRATION
(Flowking Filtration System)

PURPOSE: Filter plating solutions to remove particulate contaminants and eliminate chemical spills due to equipment malfunction.

EQUIPMENT COST: $<$ 1,000 - AIF Funding

STATUS: Filter systems installed on 12+ process tanks
Purchasing additional filter systems

ADVANTAGES: No Chemical Spills
Reusable Filter Media
Increased Circulation
Ability to Treat Solution
Improved Solution Agitation

SOLUTION RECLAMATION

CADMIUM STRIP SOLUTION

PURPOSE: Develop a procedure to remove cadmium and other metals from the cadmium strip solution, eliminating the requirement for disposal.

STATUS: A Chemical Technician is testing a procedure obtained from the Boeing Aircraft Company which will precipitate the cadmium from the strip solution. Prototyping is complete. Preparing to implement.

BENEFITS: Minimize Hazardous Waste Generation
Cadmium sludge may be recycleable
Reduce Landfill Liability

REPLACEMENT PROCESS

CADMIUM PLATING

PURPOSE: Locate, perform R&D testing, and implement a substitute for cadmium plating which is less hazardous to the Environment.

STATUS: Two Chemists are working with Boeing Aircraft Company in Seattle, Washington to test a Zinc-Nickel coating. This process is being used on landing gear struts for the 767 aircraft. Hydrogen embrittlement relief for this coating is also being studied.

BENEFITS: Elimination of a toxic chemical (cadmium)
Employee Safety
Reduced Landfill Liability
Better Corrosion Protection

REPLACEMENT PROCESS

HARD CHROME PLATING

PURPOSE: Locate, perform R&D testing, and implement a substitute for hard chrome plating which is less hazardous to the Environment.

STATUS: Two Chemists are working with Boeing Aircraft Company in Seattle, Washington to test a Nickel-Tungsten-Silicon/Carbide coating. Plating parameters and QA test procedures are being developed.

BENEFITS: No Hazardous Waste Generation
Employee Safety
Heat Treatable

REPLACEMENT PROCESS

ALUMINUM CONVERSION COATING

PURPOSE: Locate an alternative process for aluminum conversion coatings or "Alodine".

STATUS: We have investigated four processes. To date, no substitute for "Alodine" has been located. Investigating "Alodine" purification equipment.

COATINGS INVESTIGATED:
- SANCHEM PROCESS
- BOEING AEROSPACE PROCESS
- MICHIGAN CHROME & CHEMICAL PROCESS
- NAVY PROCESS - onboard ships

DESCOM CTX ASSIGNMENT

PROBLEMS TO OVERCOME

EQUIPMENT

- Verification of Equipment Capabilities
- Manpower to Develop Purchase Packages
- Available Space Requirements
- Funding for Projects

PROBLEMS TO OVERCOME

PROCESSES

- Manpower to Investigate New Processes
- Approval of Substitute Processes by the Commodity Commands and Army R&D Community

CONCLUSIONS

EQUIPMENT

✓ The Ivadizer will decrease cadmium plating requirements.

✓ Chrome recovery equipment will be operational at CCAD by March 1992. It is economical, if it works.

✓ Chromic acid solutions can be reclaimed using the electrodialysis process.

✓ In-tank filtration WORKS!

CONCLUSIONS

PROCESSES

✓ The cadmium strip solution can be recycled.

✓ Hard chrome plating may be a dinosaur.

✓ Cadmium plating will be eliminated in the near future. Zinc-Nickel may be its replacement.

✓ Aluminum conversion coating solutions can be recycled.