

*Permit by Rule for  
Treatment of Aqueous  
Wastes Containing  
Cyanides*

Department of Toxic Substances Control  
January 14, 2009

# Agenda

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- Background
- Cyanide characteristics
- How the rulemaking fits into existing PBR regulations
- Cyanide Regulations
- Contact information



# What is Cyanide's Human Toxicity

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- Routes of Exposure
  - Inhalation of gas
  - Dermal absorption
  - Ingestion
- Acutely toxic
  - Inhalation, dermal, & oral can be lethal
- Long term
  - Not carcinogenic
  - Nervous system, and thyroid effects

# Cyanide Waste $[\text{C}\equiv\text{N}]^-$ Toxicity

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- All cyanide wastes do not pose the same level of toxicity.
  - type of cyanide compound used;
  - concentration of the cyanide compound;
  - concentration of other co-contaminants;
  - strength of the cyanide-metal complex bond;
  - pH; and
  - temperature of the aqueous solution.

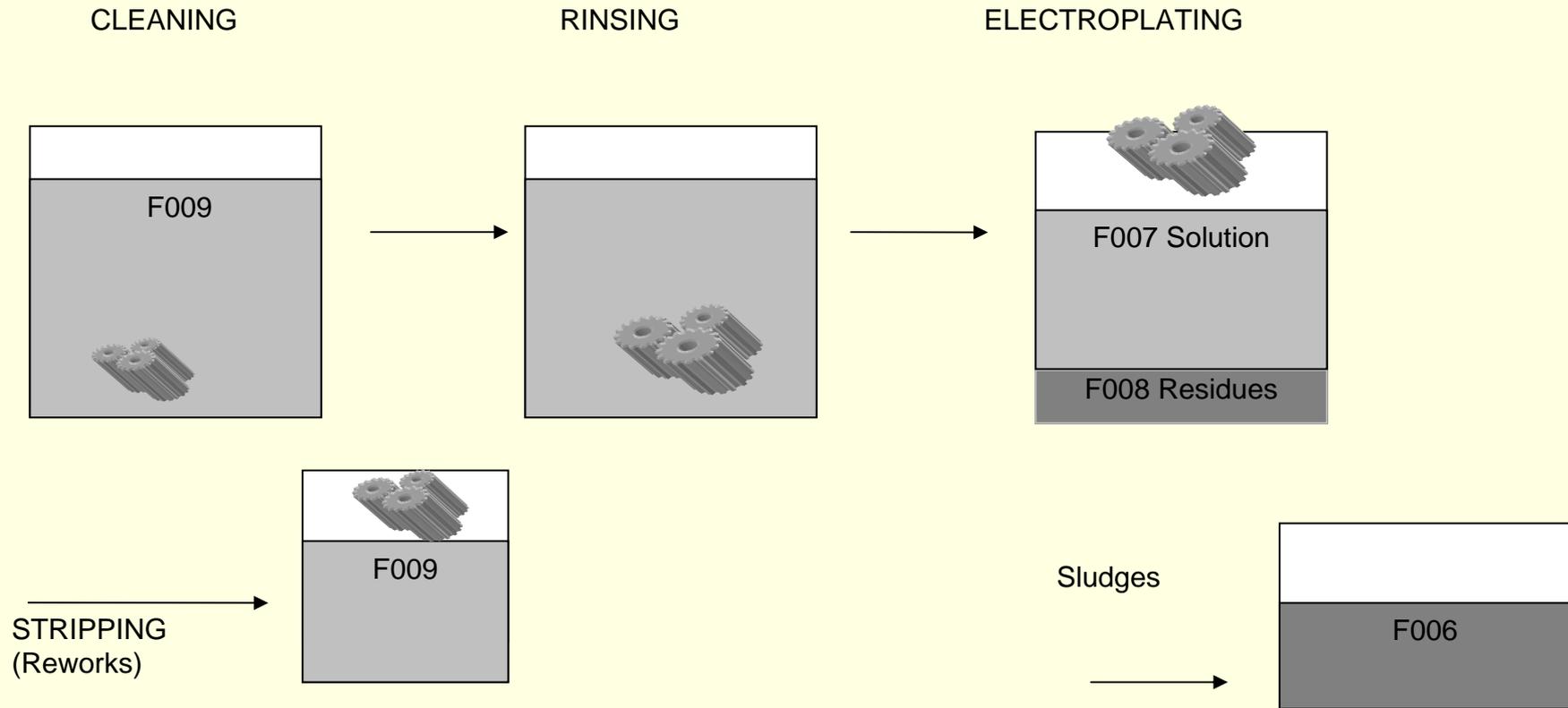
# Cyanide

## Hazardous Waste Characterization

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- Toxicity
- Reactivity
  - criteria is narrative in regulations & SW-846
- Extremely Hazardous Presumption
  - 22 CCR, Chapter 11, Appendix X
- Waste Codes
  - D003 & F006-F012
- Effects of Concentration
  - Low concentration ~ aquatic toxicity
  - As concentration increases ~ reactivity
  - High concentrations ~ extremely hazardous

# Waste From Electroplating (F006-F009) Example



Rinse waters are not F007, F008, or F009, unless mixed with a listed waste.

# Regulatory Background

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- Cyanide treatment was originally proposed as one of the original PBR eligible waste streams/ treatment processes
- PBR regulations adopted under DTSC authority
- Legislature passed statute to create both conditionally authorized and conditionally exempt (AB 1772, 1992)
- Certified Program Created (SB 1082, 1993)

# Regulatory Background

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- Consent Orders in lieu of Standardized Permits during this period to allow businesses to operate.
- Proposed regulations were revised in response to many issues
  - Potential hazards due to reactivity and toxicity
  - Cyanide did not appear to fit the intent of PBR
  - Development of risk based concentrations levels

# PBR Concept

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- Known and proven technology used to treat hazardous waste generated onsite.
  - waste stream/treatment processes were well characterized
  - processes could reliably be operated safely
  - processes did not have a track record of treatment upset or treatment failure
- Intended to cover the broadest category of waste streams
- Not intended for specific patented technologies

# PBR Statues

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- Innovative technologies can be certified and become eligible for PBR (HSC 25200.1.5).
- Concerns that need to be addressed to be eligible for PBR (HSC 25200.17(b)):
  - waste stream hazards
  - hazards of the treatment process
  - treatment complexity
  - levels of specialized training, or equipment
  - accidents that may occur

# What about CA and CE?

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- The Conditional Authorization has a specific prohibition for the treatment of any waste which is reactive or extremely hazardous (HSC 25200.3(d)(5))
- The Conditionally Exemption requires the waste not be extremely hazardous and the eligible PBR treatment must to be listed as of Jan 1, 1992

# Transition of Authority

## **DTSC Authority**

- Standardized permits
- Notifications
- Consent orders
- Technology Certifications
- Recycling letters

## **CUPA Authority**

- New Notifications for PBR cyanide treatment

## **DTSC Authority**

- Standardized Permit
- Technology Certifications
- Recycling Letters
- New Consent Orders

August 6, 2008

# How does this rulemaking fit into existing regulations?

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## Title 22 California Code of Regulations

Chapter 10 Definitions

Chapter 11 Waste Determination

Chapter 12 Generator Requirements

Chapter 13 Transportation Requirements

Chapter 15 Interim Status TSD Requirements (PBR facilities)



Chapter 45. Requirements for Units and Facilities Deemed to Have a Permit by Rule

**§67450.11. List of Influent Waste Streams and Treatment Process(es) for Influent Waste Streams Eligible for Treatment Pursuant to Permit by Rule.**

**§67450.11(d)**

# Existing PBR Requirements

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- Submittal of PBR notification and forms
- Submittal of fee form
- Effluent discharge requirements
- Maintain compliance and documentation:

Waste analysis plan

Inspections

Training

Contingency plan

Closure plan

Container standards

Tank standards

Secondary containment

Corrective action

Financial assurance

# Definitions

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- Wastewater § 66260.10
- Permit by Rule § 66260.10
- Onsite § 66260.10
- Container § 66260.10
- Tank § 66260.10
- Ancillary equipment § 66260.10
- Publicly owned treatment works § 66260.10
- Reactive § 66261.23(a)(5)
- Extremely hazardous waste § 66261.110
- Aqueous waste § 67450.11(b)

# Cyanide Regulations §67450.11(d)

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- (1) Applicability
- (2) Eligible waste streams
- (3) Eligible treatment processes
- (4) Best Management Practices
- (5) Non-aqueous not allowed under PBR
- (6) Electrowinning of process solutions
- (7) Dilution (bleeding) of process solutions

# (1) Applicability

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- Treatment is not regulated under the federal Resource Conservation and Recovery Act (RCRA);
- Waste is a hazardous waste because it contains a cyanide with or without metals;
- Treatment is conducted with processes listed;
- Treatment is conducted in tanks or containers;
- Operator is in compliance with the BMP requirements; and
- Discharges to air comply with applicable air pollution control and worker safety regulations.

# Cyanide Regulations §67450.11(d)

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## (2) Eligible Waste Streams

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- Aqueous wastes generated by rinsing workpieces and fixtures;
- Aqueous wastes generated by reverse osmosis or ion exchange columns when facilities maintain zero discharge of wastewaters derived from cyanide treatment;
- Aqueous wastes generated by rinsing containers, pumps, hoses, and other equipment used to transfer cyanide solutions onsite;

## (2) Eligible Waste Streams

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- Aqueous wastes generated by the following onsite recycling activities:
  - rinsing spent anode bags prior to onsite reuse;
  - rinsing empty containers prior to onsite reuse.
- Aqueous wastes generated by onsite laboratories conducting analyses and testing;

## (2) Eligible Waste Streams

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- Spent process solutions if managed by electrowinning; and
- Spent process solutions after being diluted in accordance with the requirements in 22 CCR §67450.11(d)(7)

## (5) Non-aqueous not allowed

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- Non-aqueous cyanide containing wastes may not be treated under this authority
- Aqueous is defined as 1% of suspended solids, as measured by Method 209C in “Standard Methods for Examination of Water & Wastewater” (§ 67450.11(b))
  - Suspended solids are the solids that can be retained by a filter, but do not include dissolved solids, such as metal ions in process solutions.
- Solids are not allowed to be treated under this proposed regulation

# Cyanide Regulations §67450.11(d)

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# (3) Eligible Treatment Processes

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- **Chemical oxidation processes**
  - Requires a basic pH between 10 and 12.
  - Two step chemical process
    - Cyanide ( $\text{CN}^-$ ) is oxidized to cyanate ( $\text{OCN}^-$ )
    - Cyanate is converted
- **Separation technologies** do not destroy the cyanide, but form a more concentrated waste stream that requires further treatment.
- **Electrowinning & Dilution** for Process Solutions

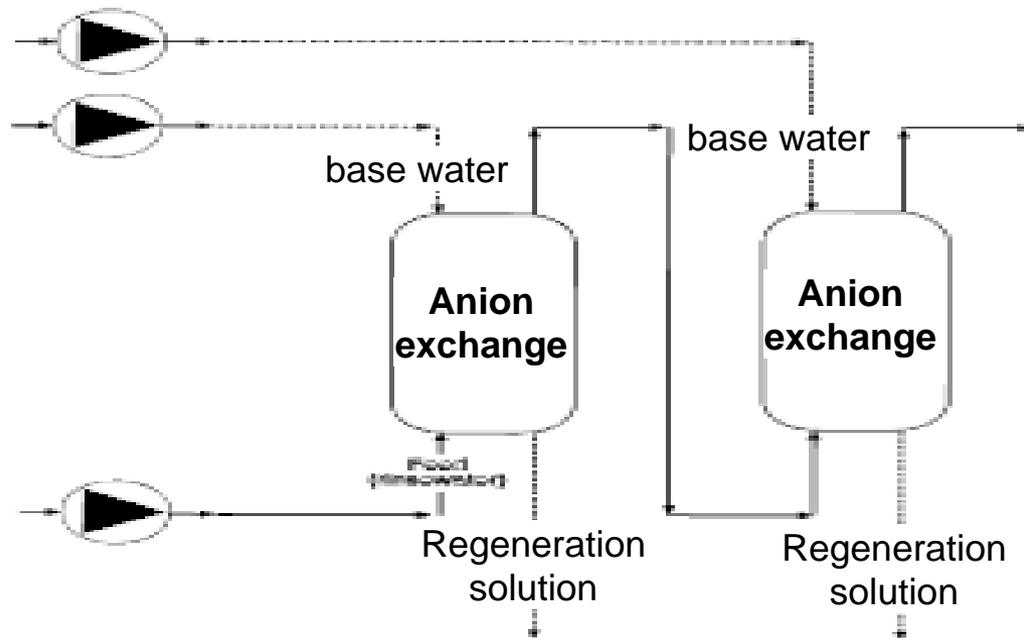
# (3) Eligible Treatment Processes

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- Oxidation by addition of hypochlorite (bleach);
- Alkaline chlorination (chlorine gas);
- Electrochemical oxidation;
  - electrolytic cell creates chlorine gas
- Oxidation by addition of peroxide or ozone, with/without ultraviolet light;

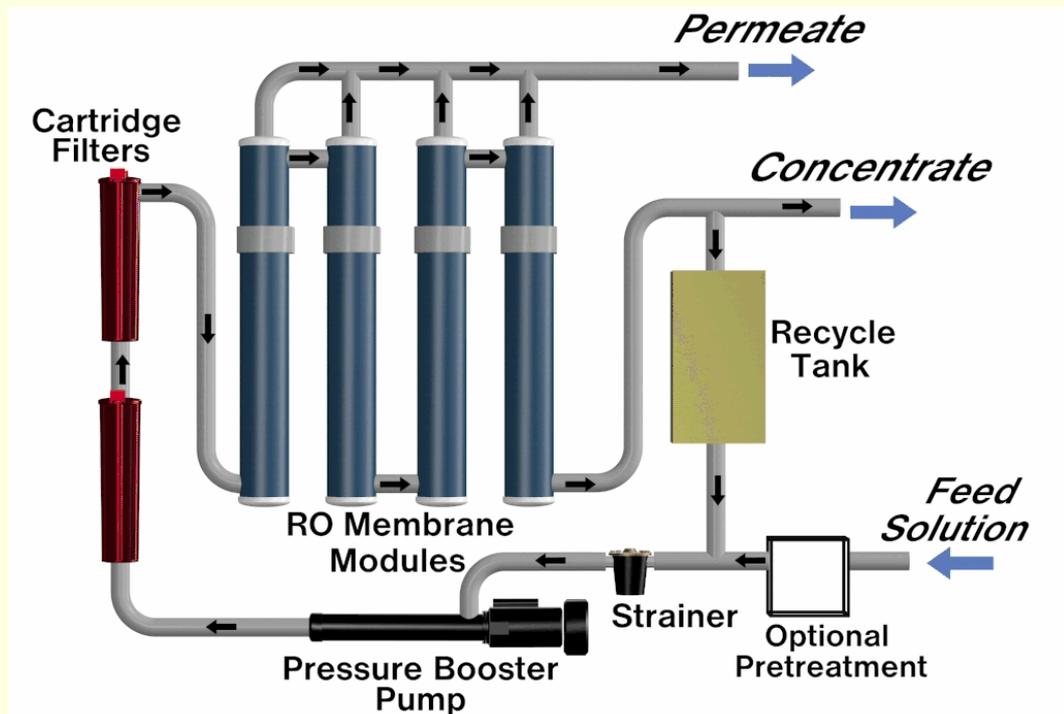
# (3) Eligible Treatment Processes

- Ion Exchange - anion resin bed contains negative ions which are exchanged with cyanide anions as wastewater passes through it.



# (3) Eligible Treatment Processes

- Reverse Osmosis - A semi-permeable membrane allows the passage of water. Pressure is exerted on the wastewater to force water across to the fresh water side against the concentration gradient.



## (6) Electrowinning of Process Solutions

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- Spent process solutions containing recoverable amounts of metal may be treated by electrowinning in order to recover metals
  - Incidental treatment of cyanide contained in the spent process solution by the electrowinning process is also authorized
  - Electrowinning means the electro-deposition of metals from spent process solution.

# (7) Dilution of Process Solutions

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- Spent cyanide-containing process solutions may be treated by slow addition to the rinsewaters for the purpose of reducing cyanide processing hazards provided:
  - Solutions resulting from the authorized mixing are further treated by processes listed
  - Owner/Operator managing this cyanide-containing spent process solutions comply with additional requirements
    - Dilution only into existing rinse waters
    - 5000 ppm total cyanide concentration
    - F006 Recycling/Justification Statement
    - Recordkeeping.

# Dilution Only into Existing Rinse Waters

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- Rinseates are limited to aqueous waste generated from rinsing:
  - workpieces & fixtures
  - containers, pumps, hoses, and other equipment used to transfer cyanide solutions onsite;

# Maximum Total Cyanide

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- Concentration of cyanide of the diluted receiving solutions must not exceed 5000 milligrams per liter of total cyanide
  - $5,000 \text{ mg/l} = 5,000 \text{ ppm} = 0.5\%$
- Written method must be documented in the waste analysis plan for ensuring that the concentration of total cyanide does not exceed 5000 mg/l in the aqueous waste resulting from the authorized

# F006 Residual Solids

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- The residual solids such as filtercakes and sludges from clarifiers removed by any treatment process allowed in § 67450.11 are:
  - Recycled by a facility that recovers metals from the residual solids, or
  - Partially reclaimed for further processing by another metal recovery facility; or
  - Determined not amenable for recycling due to technological or economic reasons and a justification statement is prepared

# Justification Statement

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- A justification statement is prepared by January 30 for any shipment of F006 not recycled in the previous calendar year.
- The justification statement shall include:
  - chemical composition of the residual solids
  - chemical composition of the spent process solutions diluted
  - current year cost estimates for treatment
  - basis of the decision

# Economic Decision not to Recycle

Offsite Treatment & Disposal		PBR Treatment & Recycling	
COST: Sludge disposal	\$	COST: Sludge recycling	\$
COST: process solution offsite treatment	\$	COST: process solution onsite treatment	\$
TOTAL		TOTAL	

# Basis for Decision not to Recycle F006

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- Conclude if the basis for the decision to not recycle
  - Technological: Specify the chemical, physical, hazardous characteristics, or other properties that affect recycling the residual solids; or
  - Economic: Provide a comparison of the hazardous waste management costs for the residual solids and the spent process solutions;
- Justification statement may include any other information

# Recordkeeping

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- Records are maintained for 3 years and are made available to the CUPA or DTSC:
  - Written POTW approval;
  - Revised waste analysis plan; and
  - Documentation the residual solids have been
    - sent offsite for metals recovery or reclamation; or
    - shown to be not amenable to recycling and a justification statement has been prepared

# Cyanide Regulations §67450.11(d)

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- (1) Applicability
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## (4) Best Management Practices

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- The owners or operators of facilities shall implement the following best management practices to reduce waste generation, and minimize or eliminate releases to work areas and the environment
- Anyone treating under this PBR authority must implement these BMPs

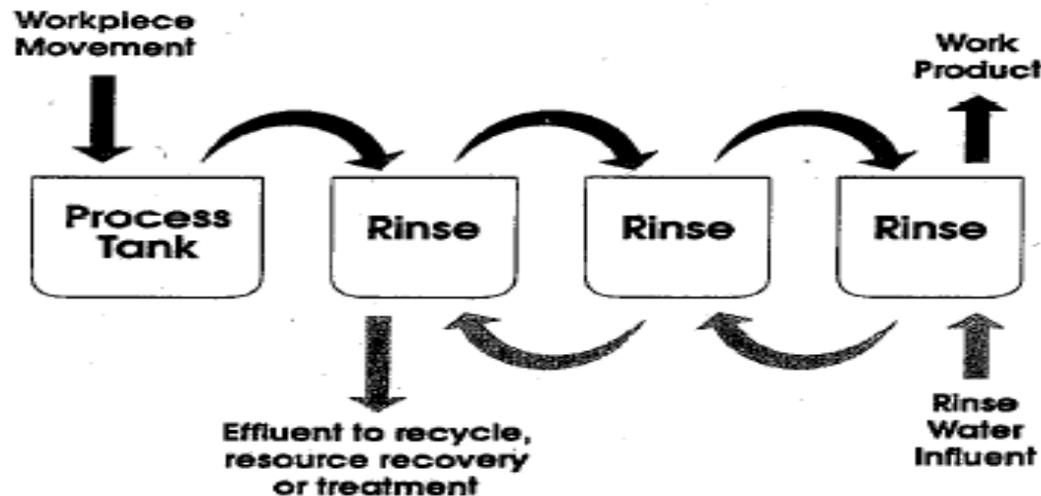
# Holding Racks & Drain Boards

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- Use holding racks and/or drain boards between all process and rinse tanks to contain plating drag-out, rinse solution drag-out, and return drag-out solutions to process tanks.
  - Drain boards route dragout back to the bath
  - Holding racks make draining more efficient

# Countercurrent Rinsing

- Use countercurrent rinsing to reduce water use and wastewater generation; when multiple sequential rinse tanks are used.



**FIGURE 2: Countercurrent Rinse System**

# Cyanide Alternatives

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- Every 4 years, the use of cyanide process baths will need to be reviewed to determine if a non-cyanide alternative is available:
  - Source Reduction Evaluation Review and Plan (SB 14 Plans);
  - Environmental Management System; or
  - environmental performance evaluation plan.

# Training

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- Provide initial and annual training to employees, who handle cyanide process solutions, cyanide rinse waters, or manage cyanide waste.
- Training must include procedures to:
  - reduce drag-out of plating baths,
  - minimize contaminants in process baths,
  - extend process bath life,
  - minimize chemical spills and splashes from process and rinse solutions handling practices, and
  - respond to chemical spills to reduce waste and minimize releases from process and rinse solutions handling practices.

# Regulations Web Page

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- [http://www.dtsc.ca.gov/LawsRegsPolicies/Regs/Cyanide\\_Final.cfm](http://www.dtsc.ca.gov/LawsRegsPolicies/Regs/Cyanide_Final.cfm)
- Final Regulatory Documents
  - Text of Final Regulations • Final Statement of Reasons • Responses to Comments • Negative Declaration
- Regulatory Background
  - Initial Statement of Reasons • 45-Day Proposed Regulatory Text • First 15-Day Public Notice and Comment Period • Second 15-Day Public Notice and Comment Period • Draft Negative Declaration • Initial Study

# Cyanide PBR - Web Page

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- **<http://www.dtsc.ca.gov/HazardousWaste/cyanide/index.cfm>**
  - Generator Requirements
  - Permit By Rule Program
  - Permit by Rule: Treatment for Aqueous Waste Containing Cyanide
  - Other Regulatory Issues
  - Pollution Prevention
  - Additional Guidance

# Additional Guidance

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- Capsule Report: Managing Cyanide in Metal Finishing
- Capsule Report: Approaching Zero Discharge in Surface Finishing
- Project Summary - Technical Resource Document: Treatment Technologies for Metal/Cyanide-Containing Wastes, Volume III, US EPA, 1988
- Summary Report - Control and Treatment Technology for the Metal Finishing Industry In-Plant Changes
- Summary Report - Control and Treatment Technology for the Metal Finishing Industry Ion Exchange
- Technical Approaches to Characterizing and Cleaning Up Metal Finishing Sites Under the Brownfields Initiative

# DTSC Contact Information

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- Evelia Rodriguez
  - (916) 322-3810
  - [erodrigu@dtsc.ca.gov](mailto:erodrigu@dtsc.ca.gov)
  
- Regulatory Assistance Officers
  - 800-72TOXIC
  - [RAO@dtsc.ca.gov](mailto:RAO@dtsc.ca.gov)
  
- [\*\*www.dtsc.ca.gov/HazardousWaste/cyanide/index.cfm\*\*](http://www.dtsc.ca.gov/HazardousWaste/cyanide/index.cfm)

# Questions?

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