

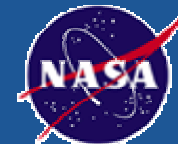
Integrating Common Needs for Shared Solutions Technical Workshop
September 19, 2003, Lisbon, Portugal

INTEGRATING COMMON PROBLEMS FOR SHARED
SOLUTIONS TECHNICAL WORKSHOP

REDUCTION/ELIMINATION OF
EMISSIONS FROM HEXAVALENT CHROME
(Cr⁶⁺) PLATING BATHS



Centro Para Prevenção da
Poluição (C3P)



INEGI

IDENTITY OF CHROMIUM

❖ Oxidation state of +2 to +6;

Chromium occurs in the environment predominantly in:

Trivalent state - occurs naturally

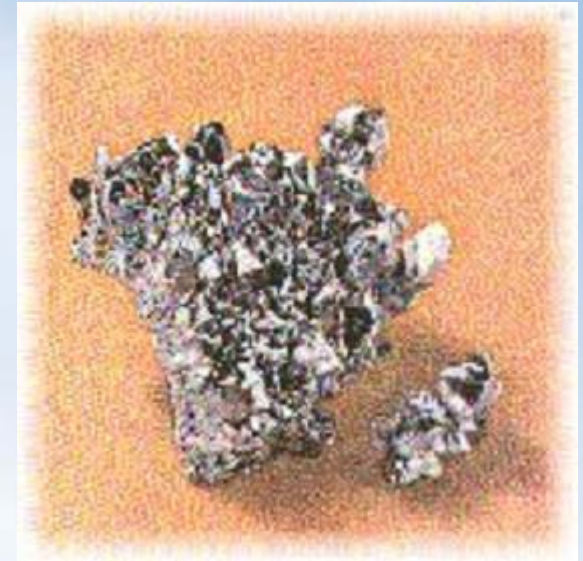
Hexavalent state, metallic chromium - industrial processes

❖ Soils and rocks contain small amounts of chromium in the trivalent state

❖ Physicochemical properties

Solubility - Cr^{6+} = Soluble
 Cr^{3+} = Insoluble

❖ Chromium III less toxic than chromium (VI)



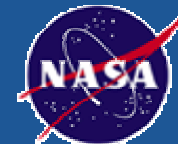
DISTRIBUTION OF CHROMIUM COMPOUNDS

SOIL - Cr^{3+} predominates

Cr^{6+} is easily reduced to Cr^{3+} and its occurrence is often the result of human activity

WATER - Hidroxides and complexes of chromium (III)
In surface waters, ratio of Cr(III) to Cr(VI) varies widely

AIR - Present in form of particles or aerosols
Both trivalent and hexavalent chromium are released into the air



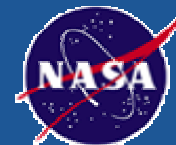
EFFECTS OF Cr⁶⁺ ON HUMAN HEALTH

- ❖ Respiratory problems
- ❖ Gastrointestinal effects
- ❖ Reproductive problems



MAJOR USES

- ❖ Leather tanning industry
- ❖ Manufacture of catalysts
- ❖ Pigments and paints
- ❖ Fungicides
- ❖ Ceramic and glass industry
- ❖ Photography
- ❖ Chromium alloys and chromium metal production
- ❖ Chromium plating
- ❖ Corrosion control



LEGISLATION

Air emissions

Ordinance n.º286/93, March 12

$Pb + Cr + Cu = 5 \text{ mg/m}^3\text{N}$

$CaCrO_4 = 1 \text{ mg/m}^3\text{N}$ (for $\geq 5 \text{ g/h}$)

$Cr_2(CrO_4)_3 = 1 \text{ mg/m}^3\text{N}$ (for $\geq 5 \text{ g/h}$)

$SrCrO_4 = 1 \text{ mg/m}^3\text{N}$ (for $\geq 5 \text{ g/h}$)

$PbCrO_4 = 5 \text{ mg/m}^3\text{N}$ (for $\geq 25 \text{ g/h}$)

$K_2CrO_4 + ZnCrO_4 = 0,1 \text{ mg/m}^3\text{N}$ (for $\geq 0,5 \text{ g/h}$)



LEGISLATION

Wastewater

- ❖ Industry discharge in surface water: DL n.º 236/98, August 1
Emission Limits: Cr (VI) = 0,1 mg/l
 Cr (VI) + Cr (III) = 2 mg/l
- ❖ Metal Finishing Industry: Ordinance n.º 1030/93, October 14
Emission Limits: Cr (VI) = 0,1 mg/l
 Cr (III) = 3 mg/l
- ❖ Leather Tanning Industry: Ordinance n.º 512/92, June 22
Emission Limit: Cr (VI) + Cr (III) = 2 mg/l

LEGISLATION

Occupational Environment

Portuguese Standard - NP 1796, 1998

Personal Exposure Limit

chromium (metal and its compounds), as Cr = 0,5 mg/m³

zinc chromate, as Cr = 0,01 mg/m³

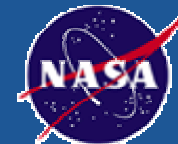
lead chromate, as Cr = 0,05 mg/m³

tert- Butyl chromate, as CrO₃ = 0,1 mg/m³

chromium (soluble salts and chromic), as Cr = 0,5 mg/m³

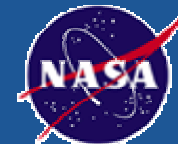
Cr (VI), soluble in water, as Cr = 0,05 mg/m³

Cr (VI), insoluble in water, as Cr = 0,05 mg/m³



Alternatives to Hex-Chrome

- ❖ Alternative coatings, and processes exist
- ❖ Critical processes and customer preference limit these.
- ❖ As environmental pressures continue, more alternatives are made available, however customer expectations make some alternatives less possible to implement.
- ❖ While implementation of an alternative may not be possible, process changes or treatment of emissions is possible to keep process within present and forecasted regulations.



Emissions from Hard Chrome Plating

Existing Technology to Reduce Emissions

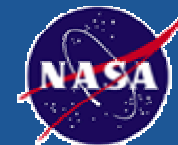
Problem

- ❖ Hydrogen gas is released in the hard chrome plating process.
- ❖ This gas entrains chromic acid and a mist is formed at surface of bath.
- ❖ Treatment of emissions or controls are necessary to prevent chromic acid mist from entering plating room environment and the environment.

Some options available for reducing emissions

- ❖ Addition of chemical suppressants to plating bath that reduce misting
- ❖ Chromium extraction from collected air stream prior to discharge at stack
- ❖ Encapsulation of plating bath with hood to contain chromium mist.

(zero or near to zero discharge of chromium)



Fume Suppressants

Chemical Fume Suppressants

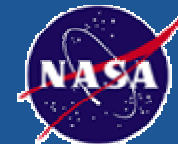
❖ Chemical fume suppressants are added directly to chromic acid bath in order to reduce or suppress fumes or mists at the surface of an electroplating bath or solution.

Fume Suppressants

- ❖ Temporary fume suppressants are dissipated by the decomposition of the active chemical components
- ❖ Permanent fume suppressants are dissipated by drag-out of the solution.

Fume Suppressants: Foam Blankets & Wetting Agents

- ❖ Foam Blankets physically suppress mists
- ❖ Wetting agents lower the surface chemistry of bath to reduce misting.



Mist Suppressants

Plastic Floating Spheres

- ❖ 75% reduction with 3 inch layer thickness of 1.5" spheres

Moisture Extractors

- ❖ Vertical Moisture Extractor
 - ❖ Centrifugal force to remove chromic acid mist from a vertical exhaust stream
 - ❖ Smaller particles can pass through causing emission limits to be exceeded
- ❖ Blade mist eliminators (Horizontal air stream)
 - ❖ Vary in design and efficiency influenced by gas velocity, blade spacing and shape, seal integrity and cleaning frequency.
 - ❖ 30% of plating shops use this technology in US as primary emission reduction, second only to packed bed scrubbers. (1994 est.)



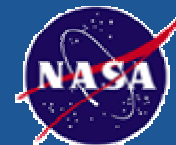
Mist Supressants

Scrubbers (Packed Bed Scrubbers or “Wet Packed Scrubbers”)

- ❖ Entrained chromic acid in air stream is transferred to wetted packed media, and then to a volume of recirculated fluid
- ❖ Scrubbers absorb gaseous component of chromic acid into liquid phase of recirculated fluid
- ❖ Excess liquid is removed from final air stream
- ❖ Multiple beds can increase efficiency

Disadvantage

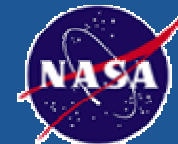
- ❖ Increase in liquid hazardous waste while solving air pollution problems if the system is not designed as closed loop



Mist Suppressants

Mesh Pad Mist Eliminators (Vertical or Horizontal Airflow)

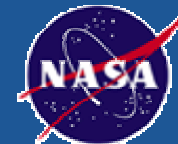
- ❖ Fluids not used during typical air-cleaning operations
- ❖ Emissions reduced by directing air through multiple layers of plastic filament
- ❖ Efficiency is dependent upon: particle or droplet size, air velocity through pad, filament diameter, filament orientation and pad depth
- ❖ Works through intertial impaction of droplets and interception of droplets by downstream fibers in mesh pad
- ❖ Multiple layers and different types of filaments increase efficiency
- ❖ High efficiency without extreme pressure drops or clogging of mesh pads within system can be achieved with proper setup and design
- ❖ Many variations and setups exist with this type of system



Mist Supressants

Fiber Bed Mist Eliminators

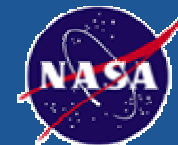
- ❖ Use of very fine filaments in a fiber bed mist eliminator targets very small particles of chromic acid mist
- ❖ Similar to mesh pad systems, intertal forces eliminate larger particles
- ❖ Very small particles eliminated through Brownian motion
- ❖ Horizontal airflow is directed through vertical cylinder that contains filter material.
- ❖ Extracted particles coalesce into droplest on fiber surface and drain via gravity through drain on bottom of the unit.
- ❖ Can suffer from cloging like mesh pads, but can be alleviated by prefiltering or positioning fiber bed after a mesh pad mist eliminator.



Plating Bath Containment

Encapsulating Tank Covers (Emission Elimination Device or EED)

- ❖ Technology developed more recently
- ❖ Cover placed over tank and the mist beneath the cover is contained
- ❖ The gases evolved during the plating process pass through a selective membrane system
- ❖ Typically only oxygen and hydrogen are emitted
- ❖ Prevents nearly all emission of chromic acid to the air
- ❖ Worker exposure and environmental emission are eliminated as risk areas



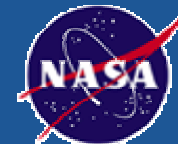
Plating Bath Containment

EED Advantages

- ❖ Emission does not contain any hazardous properties
- ❖ System typically does not require an exhaust system or stack to vent process air outside of facility because all emissions are contained under the hood
- ❖ No exhaust system and no fan motors allow for increased energy efficiency within a facility
- ❖ No chromium bearing solutions or wastes are generated (as with wash down cycles for mesh pads or wet packed scrubbers)

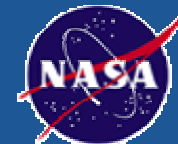
Possible Drawbacks

- ❖ Plating in tank must be stopped before parts can be added or removed
- ❖ Requires either identical start/stop or ability for parts to undergo several plating cycles because of design



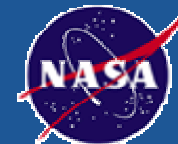
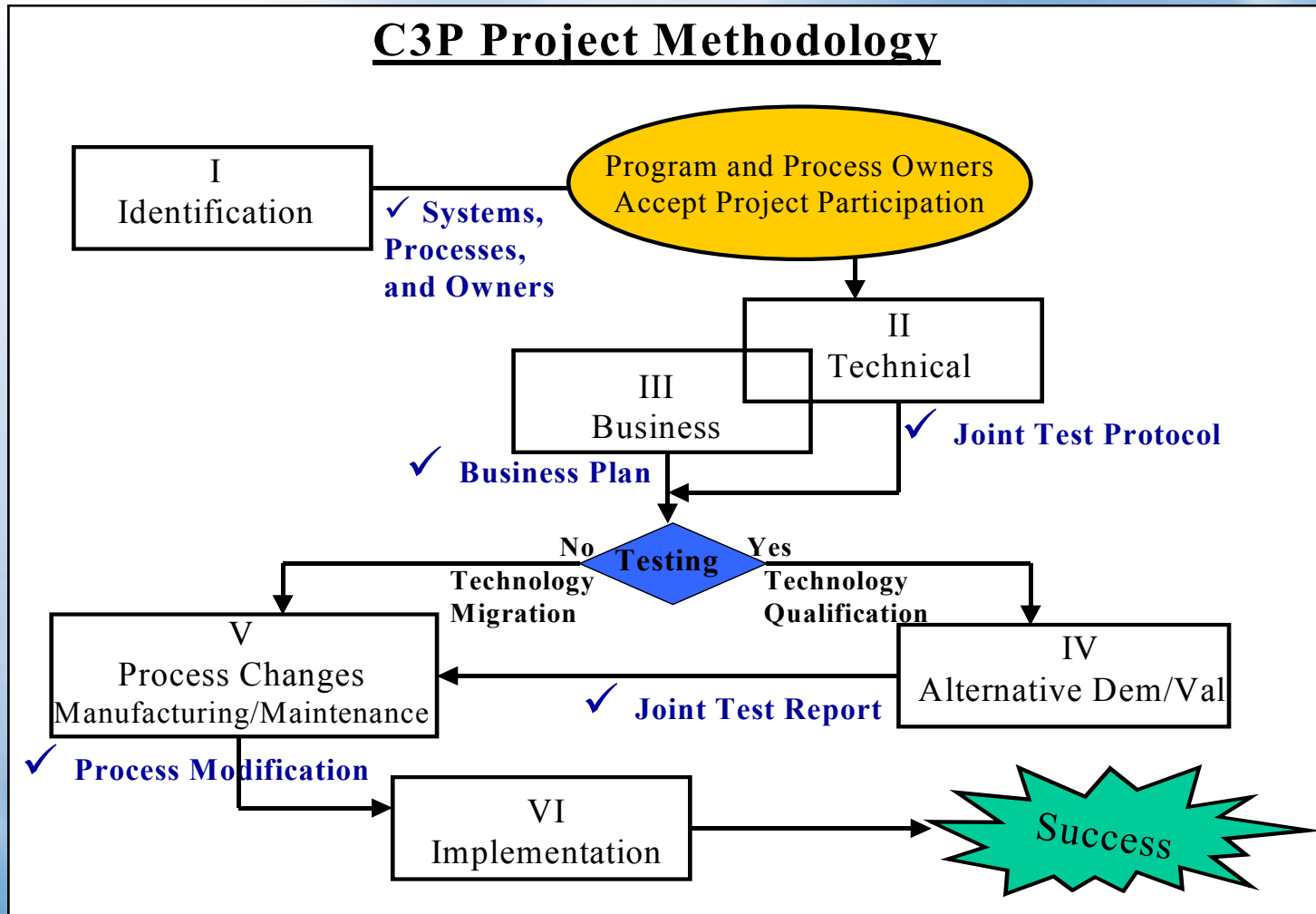
Combination Systems

- ❖ All these and other types of chrome plating systems can be combined in various ways to best accommodate a facility.
- ❖ Advantages of using multiple devices in one system:
 - ❖ Chemicals can be segregated
 - ❖ Duct work can be kept clean
 - ❖ Inlet loading can be reduced on end-of-line unit.



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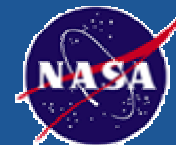
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Next Steps

Stakeholders Already Identified

- ❖ Assist in identifying other stakeholders within the plating industry who may have the need to reduce Chrome emissions.
- ❖ Information from stakeholders necessary to build PAR and JTP
 - ❖ Design and purpose of current plating shop
 - ❖ Identify current chrome emissions levels and desired levels



Next Steps

C3P

- ❖ Continue to identify stakeholders within plating industry
- ❖ Build PAR and JTP
- ❖ Build Test Plan, demonstrate and validate alternative technologies
- ❖ Work with stakeholders to implement validated technologies

