Zero Air Emissions for Hard Chrome Plating and Chromic Acid Anodizing Applications An Alternative Emission Control Technology

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The incorporation of "covers" used to encapsulate hard chrome plating and chromic acid anodizing tanks in lieu of exhaust fans, wet scrubbers, or mesh pad mist eliminators is an environmentally sound technology and a proven cost effective alternative approach to containing chrome mists generated during the chrome electroplating and chromic anodizing processes. The cover incorporates strategically sized and positioned membranes that allow free passage of hydrogen and oxygen gasses generated during electrolysis, while at the same time preventing the escape of water vapor or chrome mist. The use of covers, in Beta site testing, meets or exceeds OSHA PEL guidelines for concentration of hexavalent chromium in the area of the chrome plating tank, ensuring minimum operator exposure. Not only is this technology state-of-the-art, it historically pays for itself in 12-18 months based upon reduced operating costs, equipment replacements, and ongoing routine maintenance.

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BACKGROUND:

Section 112 of the Clean Air Act as amended in 1990 requires promulgation of final standards that limit the discharge of chromium compound air emissions from existing and new hard chromium electroplating, decorative chromium electroplating, and chromium anodizing tanks.

DEFINITIONS:

ACT – Clean Air Act
EPA – Environmental Protection Agency
HAP – Hazardous Air Pollutants
MACT – Maximum Achievable Control Technology
NESHAP – National Emission Standards for Hazardous Air Pollutants
MG – Milligrams
DSCM – Dry Standard Cubic Meter
EED – Emission Elimination Device

FINAL RULE:

40 CFR Parts 9 and 63

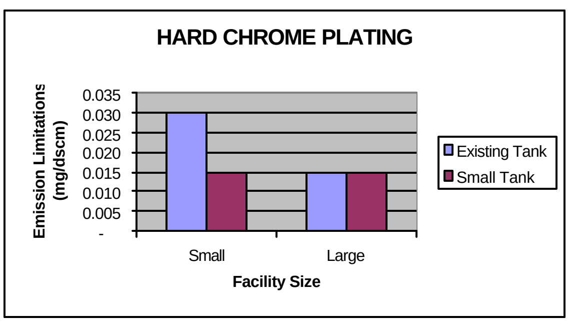
National Emission Standards for Chromium Emissions from Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks

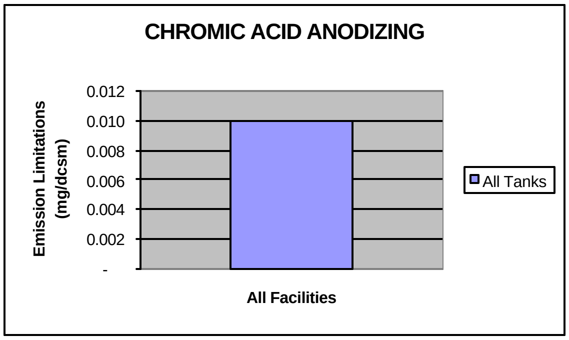
SUMMARY:

The EPA has identified 189 compounds that are considered hazardous air pollutants (HAP) to be regulated under Section 112 of the Act. $Chromium^{+6}$ compounds are included among these compounds. Chrome platers and anodizers comprise a significant number of emitters of these compounds into the atmosphere. The Final Rule ensures that emitters of emissions from these compounds apply technologies that will provide significant reductions. All identified sources are required to limit emissions to the level of the maximum achievable control technology (MACT). The most common names for this rule are either the MACT Standard or the Chrome NESHAP.

MACT STANDARDS:

The following charts represent emission requirements of the MACT Standards.





CONTROL DEVICES:

The following control devices are recognized as technologies meeting the emission levels as mandated by the MACT Standards.

- Mesh Pad Mist Eliminator Systems
- Fume Suppressants
- Packed Bed Scrubber Systems
- Encapsulating Tank Covers

ENCAPSULATING TANK COVERS:

This paper addresses the implementation of encapsulating tank covers, hereafter referred to as the Chrome Plating Emission Elimination Device (EED), on hard chrome plating and chromic acid anodizing process tanks, as an alternate control devise used to eliminate Cr^{+6} emissions to the outside environment.

This paper specifically addresses hard chromium plating processes but the conclusions apply equally to chromic acid anodizing processes.

CHROME PLATING REACTIONS:

The following equations represent, though somewhat simplistically, the chemical reactions that take place during chrome plating.

$CrO_3 + H_2O \rightarrow H_2CrO_4 + CrO_4 + 2H^+$

Chromium Trioxide | Water | Chromic Acid

$2H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_20 \rightarrow$

$Cr_2O_7^{-2} + 2H + H_20$

<u>Deposition Reaction</u>

$Cr_2O_7^{-2} + 14H^+ + 12(e)\,[CAT\ SO_4^{2-}] \rightarrow 2Cr^0 + 7H_20$

<u>Side Reaction</u>

$2H^+ + 2(e) \rightarrow H_2(gas) + Mist\,(H_2SO_4 + Cr^{+6} + H_20)$

As the cell voltage increases, the following reactions occur, in order:

Reaction at the cathode:
1) Reduction of Hex Chromium to Trivalent Chromium
$Cr^{+6} \longrightarrow Cr^{+3}$
2) Reduction of Hydrogen Ions to Hydrogen Gas
$2H^{+} \longrightarrow H_2$
3) Deposition of Chromium Metal
$Cr^{+6} \longrightarrow Cr^{0}$

Reaction at the Anode:
1) Oxidation of Lead to Lead Dioxide
$Pb^{0} \longrightarrow PbO_2$
2) Generation of Oxygen
$2H_2O \longrightarrow O_2 + 4H^{+}$
3) Oxidation of Trivalent Chromium to Hex Chromium
$Cr^{+3} \longrightarrow Cr^{+6}$

EED DEFINITION:

As a stand-alone, self-contained system requiring no exhaust fans, scrubbers or mesh pad mist eliminators, fume suppressants, or exhaust ducts and vents to the outside environment, the EED System has by definition, zero emissions to the outside environment.

APPLICATION FOR PERMITTING THE EED SYSTEM:

The Emission Elimination Device (EED) falls under the control technique of air pollution control devices (APCD) not listed in 40 CFR parts 9 and 63. Since the device has been recognized by the USEPA as a control device, the level of permitting needs only to go through the regional level of the Federal EPA system. The permitting required by each individual user must show the work practices to be used and the compliance maintenance that is to be followed.

Outline of steps to be followed:

Application for permit to install (PTI).

- Local Authority
- State Authority
- Regional Authority

This application must follow guidelines as outlined in 40 CFR Section 63.345 provisions for new and reconditioned sources.

This permit is to be applied for as soon as practicable, but no later than 30 days after initial work has begun.

Once on line the EED is required to have a performance test as part of the permit to operate (PTO). The notification of startup of the device shall be submitted no later than 30 days after such date.

Once operational a performance test must be conducted in the presence of the administrator. The administrator requires a 60-day notice of the test so they may be present.

All testing must be part of the record keeping process and must be submitted no later than 90 days following the test to the administrator.

DESIGN CONSIDERATIONS:

An adapter plate is affixed to top of the plating tank lips with appropriately placed and properly sealed openings for buss bar, plumbing, electrical conduits, etc. A hinged EED cover, with counter weights (or other mechanical opening devices), is then placed on top of the adapter. A deformable sealing gasket material (compatible with process chemicals) is placed between tank lip and adapter plate. A water seal trough, integral to the adapter plate, serves as the seal between the EED cover and the adapter plate.

The EED system is comprised of the following components as shown in Figure 1:

- Chrome Plating Tank
- EED Adapter Plate
- Adapter Plate-Tank Lip Seal
- Adapter Plate-EED Cover Water Seal
- EED Membrane & Frame
- EED Membrane Cover
- Evacuation System

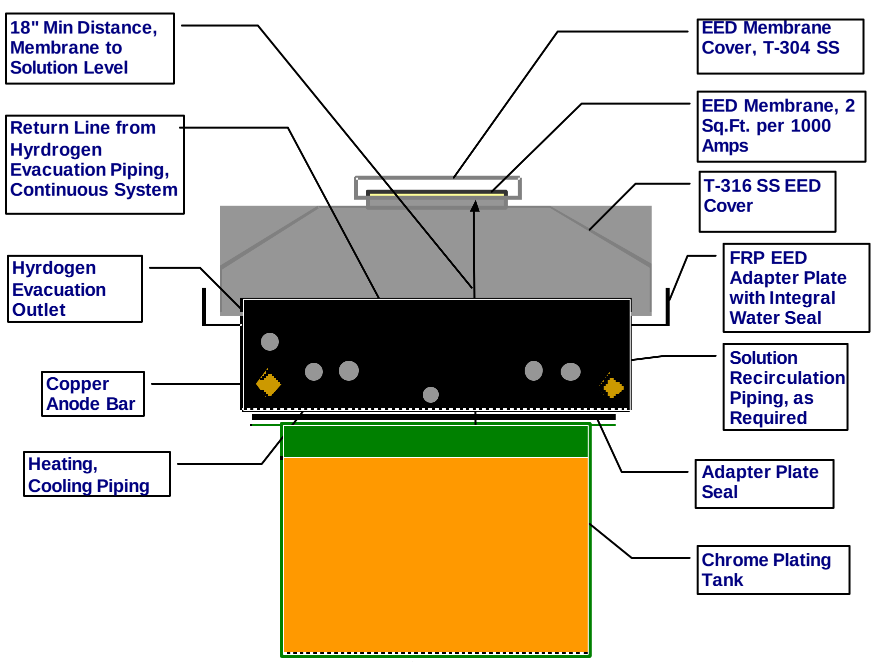


Figure 1

The aforementioned bussing, heating and cooling feed and discharge lines, water fill lines, solution recirculation piping, and other feeds, as required, are installed and sealed through the EED Adapter Plate. The adapter plate with the integral EED “water seal” along with the EED Cover completes the 100% sealing of the EED system.

The EED Adapter Plate is fabricated as follows:

- Material: CoRezyn 8441 Fire Retardant FRP Vinylester
- Thickness: 3/8"
- Color: Black

A typical EED Adapter Plate is shown in Figure 2 below.

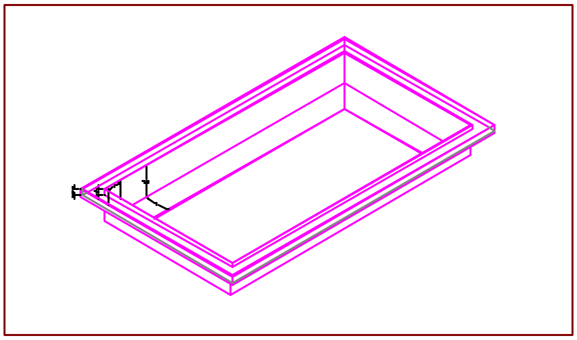


Figure 2

The EED Cover is fabricated form 10-gauge T-316 stainless steel material as represented in Figure 3.

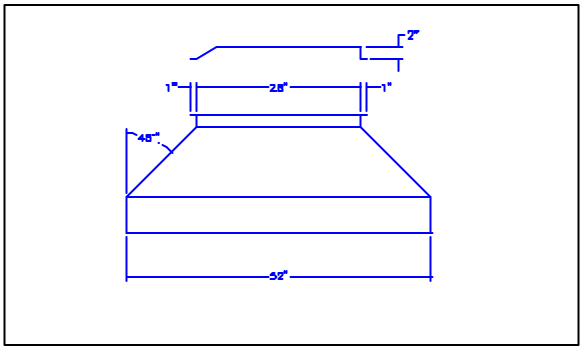


Figure 3

THEORY OF OPERATION:

As chrome plating takes place, several things occur simultaneously beneath the cover. Water vapor is created due to the operating temperature of the hard chrome bath. Chrome mist is generated due to electrolysis. Additionally, hydrogen and oxygen gasses are created at the cathode and anode due to the inefficiency of the hard chrome plating bath. As the water vapor rises beneath the cover, a cloud forms that blankets the plating solution. Chrome mist that comes in contact with the vapor cloud is “washed” by the water vapor, creating heavy chrome droplets that fall by gravity back into the plating tank. As the water vapor continues to rise, it comes in contact with the cover, condenses, form water droplets, which in turn fall back into the plating tank. The hydrogen and oxygen gases will rise too the highest point beneath the cover where the patented membrane allows free passage of these gases into the room atmosphere. Refer to Figure 4 below.

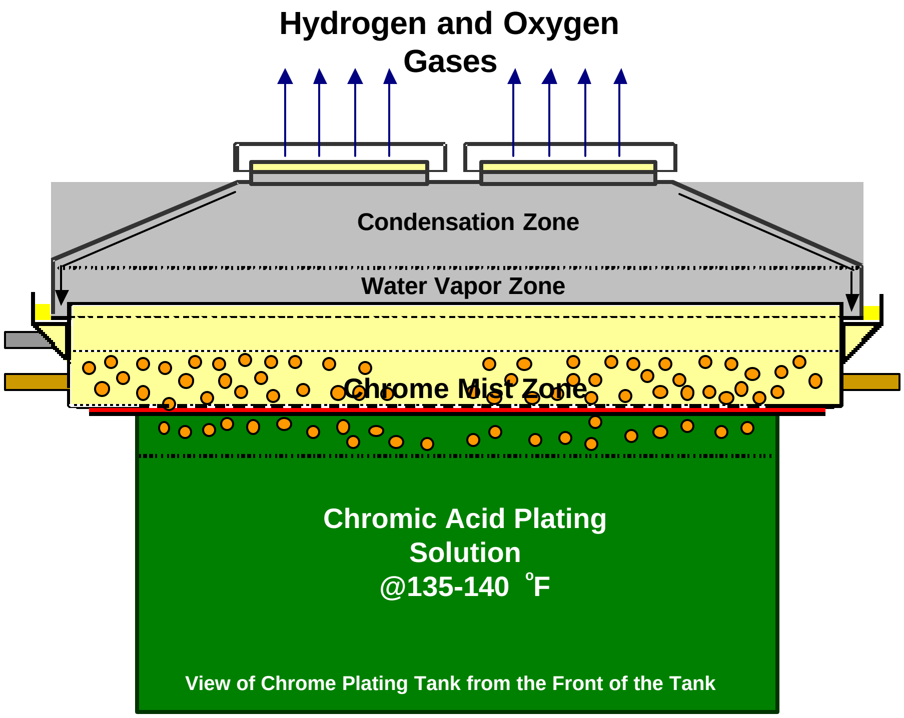


Figure 4

THE EED PLATING PROCESS:

- Place parts to be plated onto the bus bars. Verify that the contacts are cleaned and secured to avoid any sparking during plating.
- Close the cover.
- Turn on the rectifier. Plate for the specified time.
- On completion of plating, turn off the rectifier and initiate the evacuation unit for the evacuation per the specified time.
- After the evacuation process is completed, open the cover and remove parts from the tank.

THE EVACUATION PROCESS:

On completion of the plating cycle, residual hydrogen and oxygen gasses and water vapor must be evacuated from the EED prior to opening the cover. Once the rectifier has been turned off, the residuals remaining beneath the cover will naturally dissipate within 8-10 minutes. To expedite the evacuation process, which will require approximately 30-90 seconds, a manual system is included as a component of the EED system. The evacuation system consists of a regenerative blower, vapor extractor, and filter cartridges. The operation is as follows: The blower is activated, the air flow passes through the vapor extractor where residuals are filtered, through the blower, and into the room atmosphere through a set of 0.1 micron filter cartridges. See Figure 5 below.

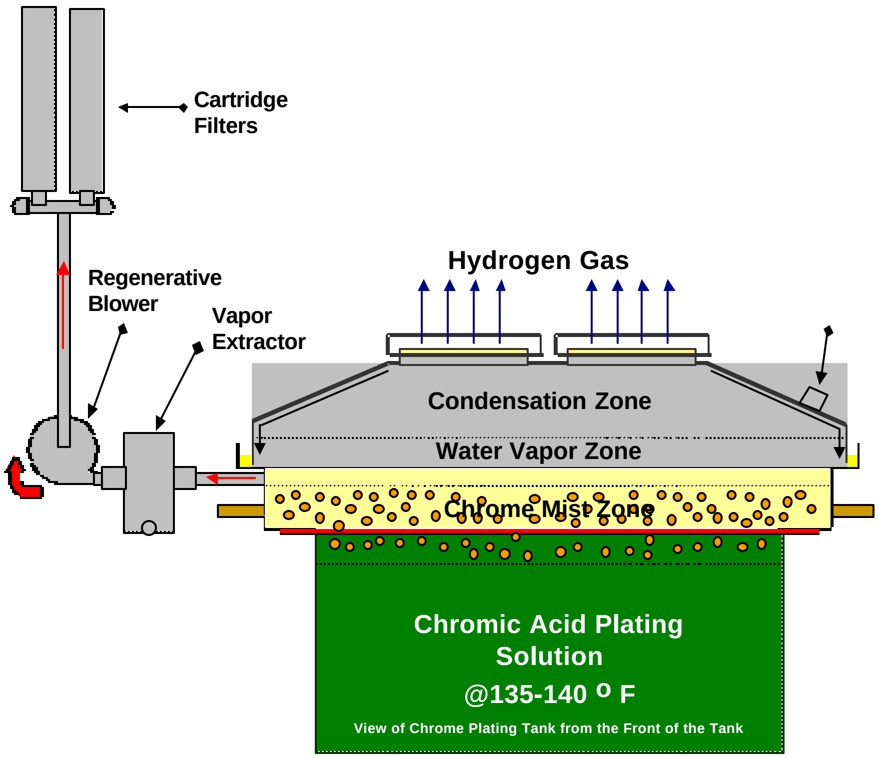


Figure 5

Chart 1 represents typical measured results at the evacuation system final filter prior to air discharge into the room environment.

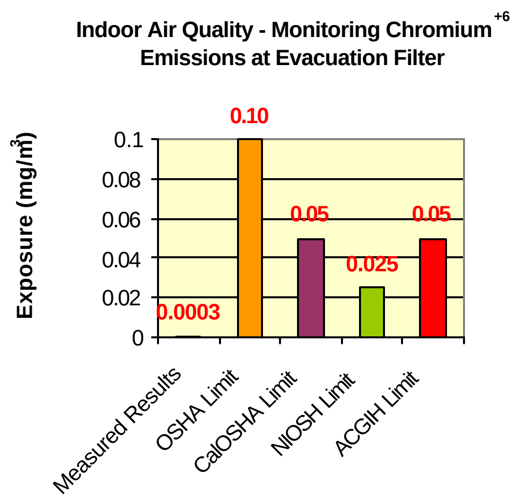


Chart 1

ADVANTAGES OF THE EED:

Operational Cost Savings:

- When compared to a conventional exhaust system on a tank with a surface area of 30 square feet, the total savings with an EED system over 15 years is conservatively \$330,000 (or \$22,000 per year).
- Scrubber maintenance costs are eliminated.
- The need for costly heated make-up air to replace evacuated air is eliminated, if applicable.
- The need for chrome plating fume suppressants is eliminated as well as other methods of fume suppression, i.e., polypropylene balls.
- Energy requirements are reduced by 60-70%.
- Floor space required for exhaust systems is eliminated making it available for more productive uses.
- The EED system has an extremely long life estimated to be 15 years or longer. Only chromic acid compatible materials of construction are used with the EED unit eliminating any need for replacement due to corrosion.

Safety:

- Reduced danger of hydrogen explosion; tanks are off during start-up – preventing arcing. The patented design allows hydrogen to freely leave the EED. In the unlikely event of an explosion, the EED shields the operator from any splashing solution.
- Potential hood or duct fires eliminated.
- Noise from fan and pump motors is eliminated.
- The potential for worker exposure is minimized when the EED is installed because no Cr^{+6} molecules are emitted to the atmosphere while plating is taking place. See Chart 2.

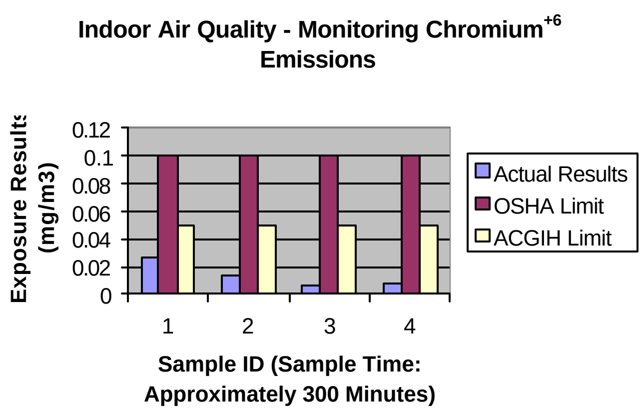


Chart 2

Environmental:

- **Air:** The need for exhaust hoods, ductwork and fume scrubbers/fans is eliminated. Because there is no ductwork, typical dripping of chrome at weld seams is eliminated.
- **Air:** With a properly installed and operated EED system, emissions are eliminated. Plant can operate under O.S.H.A.'s P.E.L. standards.
- **Air:** Because no exhaust stacks are required, chrome fumes cannot escape into the atmosphere as they could if the scrubber system fails. The EED is environmentally friendly.
- **Water:** Effluent control for treating scrubber solutions is no longer required, eliminating hazardous waste and sludge generation at the treatment facility. Total water usage is reduced.

Regulations:

- Since there are no exhaust stacks with the EED, no exhaust operational reports are required. Stack testing is eliminated resulting in savings of $3,000 to $5,000 annually, as required by local regulatory authorities.

Production Throughput:

- Because EED includes a cover that must be opened, operators become more aware of their work habits. Production throughput will actually improve due this renewed attention to procedures.

VERIFICATION OF THE EED TECHNOLOGY:

The following information is acknowledged and accepted as an EPA Office of Enforcement and Compliance Assurance alternative test procedure as adequate to demonstrate performance and compliance of the EED as applied to hard chromium electroplating and chromic acid anodizing process tanks affected by the Chrome Plating NESHAP. Recognizing the qualitative nature of this performance test method, observed emissions in the EED shall be considered as indications of noncompliance with the Chrome Plating NESHAP.

Theory:

Over 99% of Cr^{+6} molecules are greater than 1 micron in size. Smoke particles are in the range of one micron. The smoke test is conducted to detect any emissions from either the membrane materials or seals. If there are no visual or detectable signs of smoke being emitted from the EED, Cr^{+6} molecules, being larger in size than the smoke particles, will not be emitted.

Applicability and Principle:

Applicability: This alternative method is applicable to all hard chromium electroplating and anodizing operations where an Emission Elimination Device (EED) is used on a tank for reducing or eliminating chromium emissions.

Principle: During chromium electroplating or anodizing operations, bubbles of hydrogen and oxygen gas liberated at the cathode and anode, respectively, and rise to the surface of the tank. As they break the surface, Cr^{+6} molecules, in the form of a mist, become entrained in the air above the tank. The design of the EED completely encloses the air above the tank, the Cr^{+6} molecules either falls back into the solution because of gravity or collects on the inside walls of the EED Adapter Plate and runs back into the solution. A semi-permeable membrane allows the hydrogen and oxygen gasses to escape from the EED. The lit smoke device is used to verify that neither the water vapor nor Cr^{+6} mist is emitted from the EED.

Apparatus:

Smoke device: Adequate to generate 500 to 1000 ft^3 of smoke per 20 ft^2 of tank surface area along with a container to hold the smoke device.

Procedure:

- Place a small metallic container on a stable and flat area in the center of the EED (use a board or like material to span across the buss bars.)
- Place the smoke device into the container.
- With the EED cover partially closed, light the device, and quickly close the cover to prevent the smoke from escaping the EED.
- Once the device has completely burned (approximately 15 secs.) the space beneath the EED unit will now be filled with smoke.
- Inspection of the various seal points of the EED now can be observed for any smoke emission. Record these observations; including the locations and a qualitative assessment of any emission of smoke.
- After all seals and membranes have been inspected, turn on the evacuation unit to purge the smoke from the EED.
- If repairs are in order, complete them, and repeat steps a thru f until satisfactory results are obtained. Satisfactory results being defined as zero smoke emissions.
- Records must be kept of this activity to ensure proper compliance.

COMPLIANCE/WORK PRACTICE STANDARDS:

Initial Compliance Test

Conduct a Smoke Test using approximately 500 - 1000 ft^3 of smoke per 20 ft^2 of tank surface area. The smoke test verifies the design and installation of all seals, which then can be verified weekly by visual inspections as part of workplace standards.

Continuous Compliance Monitoring Program

During hard chromium electroplating, there is a very slight positive pressure that exists inside the EED. An upward movement of the membranes, away from the solution surface, manifests this pressure. When the EED system is adequately sealed and the membranes are intact, this constant pressure results in an upward contour of the membrane. If the system is equipped with more than one membrane segments, all segments achieve a balance in pressure exerted on them. After the electroplating process is completed, an evacuation process is implemented. This evacuation process generates a negative pressure inside the cover, which is manifested by a downward (towards the plating solution) movement of the membranes. While the EED is being evacuated the membranes show a downward contour when the system is adequately sealed and the membranes are intact.

Continuous compliance is demonstrated by using one of the following methods:

When the electroplating tank is in operation and parts are being plated, induce an external pressure to the membrane. This can be done by manually tapping the bulged membrane downwards. By inducing external pressure on a segment of membrane, the balance of positive pressure is shifted to other part of the same membrane and/or to the other membranes. This results in extra movement at this and/or the other membranes when the system is adequately sealed and the membranes are intact. Absence of such movement or rebound of the membrane indicates lack of adequate seal or lack of membrane integrity.

Presence of negative pressure during evacuation/purge (demonstrated by movement of the membrane) shall be verified and logged weekly. If the membrane does not move inward (towards the electroplating solution), the seals and/or membranes are faulty.

<u>Work Practice Standards</u>

- Perform a weekly visually inspection of all seals on the EED for integrity.
- Perform a weekly visual inspection of the membranes for integrity.
- Inspect the membranes monthly for any perforations using a light source that adequately illuminates the membrane.
- **Note**: If any component of the EED is discovered to be faulty, an immediate maintenance action is required. After performing the necessary maintenance, reverify the integrity of the system.
- Monthly cleaning of the evacuation system cartridge filters. Cleaning Procedure:

  a. Remove filter tube from its PVC housing.
  b. Immerse filter into a 50% solution of HCl for 5 min.
  c. Remove and drain, rinse in clean water for 2 - 3 min.
  d. Allow filter to drain, and then air dry for 7 days prior to reinstalling.

CONCLUSION:

The EED System, when operated properly, is a proven alternative control device that will meet or exceed all requirements of the Chrome Plating NESHAP while eliminating the need for conventional ventilation systems and fume suppressants. Due to the simple design and operation of the EED, significant savings are achieved using this technology when compared to conventional exhaust systems. Probably 90-95% of all hard chrome plating and chromic acid anodizing facilities are viable candidates for EED technology.

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