

ESTCP Cost and Performance Report

(CP-0003)



The Use of Wetting Agents/Fume Suppressants for Minimizing the Atmospheric Emissions from Hard Chromium Electroplating Baths

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ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
AIHA	American Industrial Hygiene Association
ALC	Air Logistics Center
APCD	air pollution control device
AMS	Aerospace Materials Specification
cfm	cubic feet per minute
CFR	Code of Federal Regulations
CIHL	Consolidated Industrial Hygiene Laboratory
cm	centimeter
CNO	Chief of Naval Operations
DoD	Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FAA	Federal Aviation Authority
ft ²	square feet
gr/dscf	grains per dry standard cubic foot
HVOF	high velocity oxygen fuel
IH	industrial hygiene
lb	pound(s)
µg/dscm	micrograms per dry standard cubic meter
µg/m ³	micrograms per cubic meter
mg/dscf	milligrams per dry standard cubic foot
mg/dscm	milligrams per dry standard cubic meter
mil	one thousandth of an inch
NAS	Naval Air Station
NADEP	Naval Aviation Depot
NAVAIR	Naval Air Command
NEPMU 2	Navy Environmental and Preventive Medicine Unit
NESHAP	National Emissions Standards for Hazardous Air Pollutants
NIOSH	National Institute for Occupational Safety and Health
NRMRL	National Risk Management Research Laboratory

ACRONYMS AND ABBREVIATIONS (continued)

O&M	operating and maintenance
OAQPS	Office of Air Quality Planning and Standards
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure level
REL	recommended exposure limit
RSL	rising step load
RTI	Research Triangle Institute
UTS	ultimate tensile strength
WA/FS	wetting agent/fume suppressant

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1.0 EXECUTIVE SUMMARY

The Department of Defense (DoD) and numerous commercial electroplaters perform hard chromium electroplating to produce hard surface finishes, typically for use as bearing surfaces. Hard chromium electroplating is conducted using a bath containing concentrated chromic acid. The electroplating activity causes bubbling in the bath. As the bubbles break the surface of the bath, they emit particles of chromic acid mist. Chromic acid contains chromium in its more toxic hexavalent form. Because of the toxicity of hexavalent chromium, these baths are required by the Occupational Safety and Health Administration (OSHA) to be ventilated through an exhaust system, which removes almost all the chromium from the workplace. However, the exhaust system deposits the chromium in the ambient environment surrounding the plating facility. Because of the toxicity of hexavalent chromium, the U.S. Environmental Protection Agency (EPA) limits the amount of chromium that may be emitted to the environment. To comply with these limits, hard chromium electroplating emissions are first passed through an air pollution control device (APCD), typically a wet scrubber/mist eliminator, to remove the chromium from the exhaust air stream. The chromium thus removed becomes part of a wastewater stream (which is also regulated but is not the subject of this investigation).

The primary objective of this investigation was to test the effectiveness of a wetting agent/fume suppressant (WA/FS), Fumetrol® 140, in suppressing the evolution of hexavalent chromium mist from the surface of a hard chromium electroplating tank. The secondary objective was to evaluate the effect that Fumetrol® 140 has on the substrates being plated and on the chromium electroplate. Adding Fumetrol® 140 to the electroplating tank at a concentration of 0.25 percent significantly changes the surface tension of the liquid, reducing the size of the bubbles formed, and thereby reducing the amount of misting. If chromium emissions can be reduced significantly using WA/FS, there will be a savings in the amount of chromic acid purchased, and the need for APCDs may be minimized or eliminated.

For *decorative* chromium electroplaters, EPA already has regulations in place that allow electroplaters to use *either* APCDs or WA/FS. If WA/FS were equally effective for hard chromium electroplating, then it is possible that EPA would promulgate regulations giving hard chromium electroplaters the same option. However, to date, EPA has not formally proposed a similar regulation for hard chromium electroplaters. Such a regulation would eliminate the need to purchase APCDs for new hard chromium electroplating activities. For existing activities that already have APCDs, the internal packing in the APCDs could be removed, lowering the exhaust system pressure drop and associated fan horsepower/electrical requirements. No water would be required in these APCDs, eliminating the costs for water and associated wastewater treatment.

With respect to the in-plant air quality, OSHA is considering tightening its current hexavalent chromium standard by 10- to 100-fold. If this takes place, WA/FS, which was expected to reduce emissions of chromium mist, would also lower the amount of emissions that escape the plating tank exhaust system and end up in the facility air.

For this investigation, the emissions from two DoD hard chromium electroplating tanks were evaluated with tanks at Naval Aviation Depot (NADEP) in Cherry Point, North Carolina, and the Oklahoma City Air Logistics Center (ALC) at Tinker Air Force Base (AFB), Oklahoma.

Emissions of total and hexavalent chromium from the exhaust ducts that ventilate the tanks were sampled and analyzed upstream of the existing APCDs. Sampling was conducted before addition of the WA/FS, as well as after addition. The results were compared to determine if WA/FS addition reduced chromium emissions. Similarly, industrial hygiene (IH) samples were taken at three locations around the hard chromium tanks — directly over the tank surface, in the breathing zone in front of the tanks, and in the breathing zone several feet from the tanks. The IH samples were taken to evaluate the effect of WA/FS on occupational exposure.

Details of the performance assessment are given in Section 4 of this report. It was clearly shown that there was approximately a 20- to 70-fold reduction in total chromium emissions in the tank exhausts when WA/FS was added in the prescribed quantity. In most cases, the exhaust chromium concentration was lower than the current EPA standard for *small* (less than 60 million ampere-hours per year), *existing* hard chromium tanks, which is 30 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). With respect to the 15 $\mu\text{g}/\text{m}^3$ standard for all other chromium electroplating tanks, the decrease in chromium concentration was typically not sufficient to comply with this standard.

With respect to occupational health impacts, all the shop-air concentration data were extremely low compared to the current OSHA standard of 52 $\mu\text{g}/\text{m}^3$ (as chromium). In fact, none of the breathing zone samples taken in or around the electroplating tanks, with or without WA/FS being used, was even close to exceeding the most stringent proposed OSHA standard of 0.5 $\mu\text{g}/\text{m}^3$. Because the chromium concentrations were so low in the shop air, it was difficult to compare the data from sampling a single chromium plating tank when WA/FS was in use to the data when WA/FS was not in use. Nevertheless, averaging the data, it was estimated that the shop air quality with WA/FS was approximately two to four times better than without WA/FS. Also, any potentially negative health effects that might be attributable to Fumetrol® 140 were negligible when compared to the positive health effects of reducing the amount of hexavalent chromium in shop air and in the outside environment. The investigation also showed that there were no adverse effects on plated parts associated with using Fumetrol® 140.

The savings in the loss of chromic acid to the exhaust system for each tank tested is likely to range from \$850 to \$3,200 per year, compared to an annual per-tank cost for replenishing WA/FS of less than \$500 (plus the initial WA/FS cost of approximately \$300). If existing APCDs no longer need to be used, the APCD water/wastewater flow could be curtailed, resulting in additional annual savings in water purchase costs and wastewater treatment costs of at least \$23,000 for each APCD. (Typically, 3 to 5 hard chromium electroplating tanks are ventilated to each APCD). There would also be significant savings in the electrical costs for exhaust fan operation, for APCD operation and maintenance, and for APCD pump operating costs. For an existing system, using an average figure of \$2,000 per year for chromic acid savings, the payback period on the minimal modifications necessary would range from less than 7 months (if the APCD were turned off) to less than 3 years (if the APCD remained in use).

For new DoD installations of hard chromium electroplating, APCDs might not be required if WA/FS were used instead. This would potentially save well over \$140,000 in installed capital costs (this figure does not include the cost of ductwork and fan, which would still be required to ventilate the tank) per APCD (servicing 3 plating tanks), in addition to the aforementioned operating costs.

2.0 TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

A fume suppressant is defined as a chemical added to the electroplating bath that reduces or suppresses fumes or mists at the surface of the bath. [See 40 Code of Federal Regulations Part 63 (40CFR63).] Electroplating baths, particularly hexavalent chromium baths, emit bubbles of hydrogen and oxygen at the bath cathode and anode, respectively. In fact, for hexavalent chromium electroplating baths, 85–90 percent of the electrical energy supplied to the baths produces bubbling. (The other 10–15 percent causes chromium to plate on the substrate metal.) These bubbles (and also the bubbles produced by mechanical aeration of the baths) burst as they rise to the surface of the baths, producing chromic acid mist.

A WA/FS reduces the surface tension of a liquid. When a WA/FS lowers the surface tension of a plating bath, gases escape at the surface of the solution with a diminished “bursting” effect, causing less mist formation (i.e., smaller bubble size, less surface impact). WA/FS chemicals are organic compounds of components with opposing solubility tendencies, typically an oil-soluble hydrocarbon group and a water-soluble ionic group.

Unlike earlier generations of WA/FS, the current generation is perfluorinated compounds that are relatively soluble in water and produce very little foam. Active ingredients include organic fluorosulfonate and tetraethylammonium-perfluorocetyl sulfonate. Unlike earlier generations of WA/FS, there appear to be no adverse effects on the quality of the chromium plate, process hardware, or substrates during hard chrome plating operations. The WA/FS product tested in this demonstration was Fumetrol® 140, a liquid distributed by Atotech USA, Inc. in Rock Hill, South Carolina.

2.2 PROCESS DESCRIPTION

2.2.1 Installation and Operation Requirements

The process of using WA/FS to control emissions of hexavalent chromium from hard chromium electroplating baths is quite simple. It consists of adding approximately 0.25 percent by volume of the Fumetrol® 140 liquid WA/FS to a hard chromium electroplating bath, and allowing the bath contents to reach equilibrium (a few hours). Addition of WA/FS effectively lowers the surface tension of the bath from above 70 dynes/centimeter (cm), as measured by a Du Nouy ring tensiometer, to below 30 dynes/cm. Additional Fumetrol® 140 is added over time as required to maintain the surface tension below 30 dynes/cm.

2.2.2 Design Criteria

There is no capital equipment involved with the application of WA/FS. The only criterion is that the surface tension of the bath be monitored and maintained. Monitoring requires the purchase of a Du Nouy ring tensiometer. The surface tension should be measured once a week initially, decreasing to once a month after the bath maintenance requirements are established. If surface

tension measurements indicate that more WA/FS is required, it should be added to bring the bath to the desired value (below 30 dynes/cm).

Figure 1 shows the hard chromium electroplating tank (or more than one tank) vented to an air scrubber. Water is recycled through the scrubber to remove the chromic acid mist from the air stream. A portion of the recycled water is drained to a wastewater treatment facility where the chromium is ultimately removed from the wastewater as hazardous waste sludge.

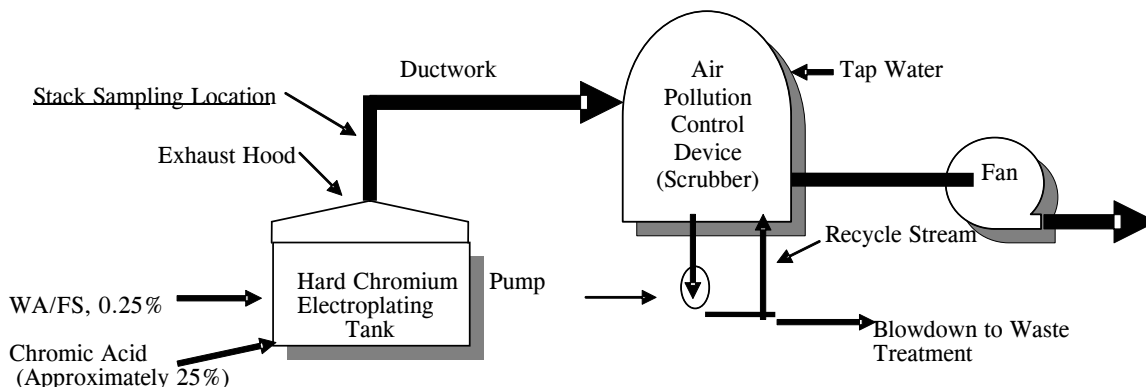


Figure 1. Process Schematic.

2.2.3 Regulatory Standards To Be Met

Numerous air quality regulations at the local, state, and federal levels have affected the hard chromium electroplating industry. OSHA also regulates occupational exposure to hexavalent chromium.

In 1995, EPA promulgated the National Emission Standards for Chromium Emissions from Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks (40CFR63, Subpart N). Under these standards, facilities that perform chromium plating must demonstrate that chromium emissions do not exceed acceptable limits, and must satisfy monitoring, record keeping, and reporting requirements. Table 1 is a synopsis of the current hexavalent chromium surface finishing standards. Table 1 shows that *decorative* chromium electroplaters do not have to meet a quantitative emissions standard if they maintain a specific bath surface tension by the application of WA/FS. EPA's Office of Air Quality Planning and Standards (OAQPS) is considering allowing the use of WA/FS additives for hard chromium electroplating as well, based on work done under the Common Sense Initiative (a joint EPA and American Electroplaters and Surface Finishers program) and studies such as this one.

OSHA currently regulates hexavalent chromium under 29 CFR 1910.1000, Table Z-2, Limits for Air Contaminants. The current permissible exposure limit (PEL) is a ceiling value of $52 \mu\text{g}/\text{m}^3$ of chromium (i.e., $100 \mu\text{g}/\text{m}^3$ as chromic oxide). However, OSHA was petitioned for an

emergency temporary standard in July 1993. Currently, OSHA is expected to issue a proposed hexavalent chromium regulation on October 4, 2004, and a final regulation on January 18, 2006. The standard is expected to be between $0.5 \mu\text{g}/\text{m}^3$ and $5.0 \mu\text{g}/\text{m}^3$. This is a 10- to 100-fold reduction below the current regulatory level.

Table 1. EPA Standards for Chromium Plating and Anodizing Tanks.

Type of Tank	Emission Limitations	
	Small Facility (<60 million amp-hrs/yr)	Large Facility
Hard Chromium Plating Tanks		
All existing tanks	0.03 milligrams per dry standard cubic meter (mg/dscm) [1.3 x 10 ⁻⁵ grains per dry standard cubic foot (gr/dscf)]	0.015 mg/dscm (6.6 x 10 ⁻⁶ gr/dscf)
All new tanks	0.015 mg/dscm (6.6 x 10 ⁻⁶ gr/dscf)	0.015 mg/dscm (6.6 x 10 ⁻⁶ gr/dscf)
Decorative Chromium Plating Tanks Using a Chromic Acid Bath		
All new and existing tanks	0.01 mg/dscm (4.4 x 10 ⁻⁶ gr/dscf) or Surface tension of <45 dynes/cm [3.1 x 10 ⁻³ pounds/foot (lb/ft)]	
Chromium Anodizing Tanks		
All new and existing tanks	0.01 mg/dscm (4.4 x 10 ⁻⁶ gr/dscf) or Surface tension of <45 dynes/cm (3.1 x 10 ⁻³ lb/ft)	

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

EPA's National Risk Management Research Laboratory (NRMRL) tested Fumetrol® 140 WA/FS at Hohman Plating and Manufacturing Incorporated, in Dayton, Ohio, and several other facilities. Hohman falls in the category of a "large facility" for EPA reporting and control technology purposes. (DoD operations fall in the same category.) Two papers, *Use of Fume Suppressants in Hard Chromium Baths—Quality Testing*¹ and *Use of Fume Suppressants in Hard Chromium Baths—Emission Testing*², were developed for technical and end-user publications describing the test results.

During EPA's testing, using OSHA and the National Institute for Occupational Safety and Health (NIOSH) sampling procedures, it was shown that the concentration of hexavalent chromium in the airspace directly above the electroplating tank decreased three orders of magnitude with the addition of WA/FS. During normal operating conditions using WA/FS, worker exposure to hexavalent chromium at the tested facilities was found to be below the current permissible exposure limit of $52 \mu\text{g}/\text{m}^3$ but above the most stringent proposed permissible exposure limit of $0.5 \mu\text{g}/\text{m}^3$.

Material quality testing showed that the Fumetrol® 140 had no negative effects on plating quality. In fact, adding WA/FS tended to increase microhardness. However, there were some

negative outcomes from samples taken from tanks treated with or without the WA/FS (e.g., pitting tests). The inferior quality outcomes were attributed to poor preparation before plating.

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Preliminary tests performed by EPA's NRMRL showed no limitations to plated product quality while using the WA/FS additive.

There are anecdotal stories that WA/FS is not appropriate for hard chrome plating on cast iron since the cast iron already has significant pitting, but EPA tested one cast iron sample and found no effect on material quality. Otherwise, there are no restrictions on types of substrate to be plated.

EPA recently discussed the project with Delta Faucet Company, which uses WA/FS for decorative chrome plating. Delta found that cathode efficiency decreased when using fume suppressants. It is also true for the older suppressants. This is the only other negative comment heard from those using the newest suppressants (i.e., third generation WA/FS). The efficiency loss may slightly change the power requirements for the plating process.

Cost of the technology is a major advantage in that the WA/FS technology is simple and inexpensive. Start-up cost estimates are only \$800 per tank (including the initial WA/FS addition) for the first year. Annual operating costs are expected to decrease to less than \$400 per tank. Cost savings are expected to occur from reduced maintenance of the APCDs; less wear and tear on the ventilation hoods, ductwork, and exhaust fans; savings in chromic acid because less chromic acid mist escapes the bath; savings in water used in APCDs (i.e., air scrubbers); and savings in the cost of treating the wastewater generated using the APCDs. Ultimately, DoD could obtain significant savings if APCDs were no longer required on future plating lines.

DoD is investigating methods of replacing hard chromium electroplating with other more environmentally friendly coating methods. However, NADEP Cherry Point estimates that even after any of the high technology processes currently undergoing research are implemented, approximately 20 to 40 percent of their existing hard chromium electroplating operations will continue. This is because many of the high technology processes cannot plate in non-line-of-sight areas such as recesses and pinch points. Therefore, even if alternative and/or high tech alternative technologies are implemented, there will still be a need for conventional chromium electroplating baths in the foreseeable future.

3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The primary project objective was to provide data to the regulatory arm of EPA to support inclusion of WA/FS addition as an alternative to an emission concentration standard for hard chromium plating. This alternative is currently available to decorative chromium operations. The project demonstrated that Atotech's Fumetrol® 140, a WA/FS, reduces atmospheric emissions during electroplating operations. The intent was to show that if the WA/FS kept the surface tension at or below 30 dynes/cm, atmospheric emissions from the hard chromium electroplating bath would remain below the most stringent hexavalent chromium regulatory limit of 15 micrograms per dry standard cubic meter ($\mu\text{g}/\text{dscm}$). Consequently, WA/FS additives may be an effective alternative to mechanical APCDs such as mesh pad mist eliminators.

A second objective was to demonstrate a significant reduction in fugitive emissions from the tank. Fugitive emissions increase the occupational exposures of workers in the shop. WA/FS additives are reported to reduce occupational exposures below the current PEL of $52 \mu\text{g}/\text{m}^3$ (as chromium) but may not be able to reduce the exposure below the most stringent anticipated PEL of $0.5 \mu\text{g}/\text{m}^3$. However, the demonstration project configuration prevented valid personnel sampling on the individual workers due to the proximity of other plating operations to which workers were also exposed. Stationary area samples were taken instead.

The third objective was to certify that the WA/FS does not negatively affect the integrity of the electroplating process, the hard chromium coating, or the functional properties of the plated components. Critical properties include fatigue characteristics and embrittlement. Hard chromium is plated on platform-critical components at DoD facilities. Successful evaluation required that materials electroplated in hard chromium tanks treated with WA/FS performed as well as materials treated in tanks without WA/FS.

3.2 SELECTION OF TEST SITES/FACILITIES

The plating engineering departments of Army, Air Force and Navy bases that perform hard chromium electroplating were contacted by telephone, and the various electroplating facility engineers indicated that NADEP North Island (San Diego, California) has satisfactorily used Fumetrol® 140 to reduce emissions since 1998. The maximum surface tension they use as their indicator was unclear, but reports range from 25 to 40 dynes/cm. NADEP North Island made their decision to use Fumetrol® 140 after experiencing a temporary shut-down for shop repairs approximately 4 years ago. They transferred their workload to an electroplating job shop that used Fumetrol® 140. The Federal Aviation Authority (FAA) approved the job shop to electroplate new and reworked parts for several DoD prime contractors. Based on FAA approval, NADEP North Island shop and engineering management made a decision to use the additive. After a temporary engineering investigation, NADEP North Island incorporated the product into their local process specifications. To validate the comprehensive performance impact of Fumetrol® 140 for North Island and potential implementations at NADEP Cherry Point, North Carolina and NADEP Jacksonville, Florida, Naval Air Command (NAVAIR) required the evaluation of electroplated hard chromium performance with and without the use of

Fumetrol® 140. This validation was necessary due to the critical nature of components processed through the hard chromium plating tanks at NAVAIR as well as Air Force and Army depots.

At the time of site selection, NADEP North Island was in the process of redesigning its electroplating shop, including the hard chromium lines, and was still in the process of obtaining a renewed air emissions permit. Therefore, it was decided to forgo air emissions (environmental and occupational health) testing at NADEP North Island but include North Island samples as part of the materials testing.

NADEP Cherry Point was also interested in implementing the use of WA/FS if NAVAIR approved of the use of Fumetrol® 140 in hard chromium tanks. Cherry Point was therefore chosen as NAVAIR's primary test site, with North Island serving as a Fumetrol® 140 control for the coating evaluation.

Hill AFB, Utah, evaluated Fumetrol® 101, an earlier generation of WA/FS, with unsatisfactory results, and at the time of site selection was disinclined to try the new generation (Fumetrol® 140). However, later discussion (after validation began) with other Hill AFB staff members indicated that they are extremely interested in the test results from this generation of WA/FS.

Tinker AFB (Oklahoma City, Oklahoma) was willing to participate in the test and served as the Air Force test site. Typically, engine parts that are not subject to the same stresses and mechanical performance requirements as structurally critical parts (e.g., landing gears) are electroplated at Tinker AFB.

Several Army bases were asked to participate, but facility contacts claimed to be satisfied with their progress in reducing hexavalent chromium emissions using their current technologies and declined to participate in the project.

To keep the project manageable, emissions testing was limited to one U.S. Navy shop (Cherry Point) and one Air Force shop (Tinker AFB) that had expressed interest in participating. Electroplating for the material quality testing took place at two Navy facilities (Cherry Point and North Island) and one Air Force facility (Tinker). Work at all three shops was typical of the rework operations performed at DoD facilities.

3.3 TEST FACILITY HISTORIES/CHARACTERISTICS

3.3.1 Characteristics of Test Sites

The facilities chosen for testing were typical DoD electroplating shops on Navy and Air Force depots. The hard chromium electroplating facilities and tanks selected for testing during this project were NADEP Cherry Point, Tank 155, and Air Logistics Center, Tinker AFB, Tank 222.

Cherry Point has five chromium electroplating tanks, all active, between 422 and 810 gallons capacity, which exhaust into a single four-stage polymer mesh pad scrubber, rated at 40,000 cubic feet per minute (cfm). There are approximately 50 tanks total (including cleaning and

rinsing tanks). Cherry Point has the capability to perform type I, II, and III anodizing and nickel, silver, cadmium, and tin plating. Tin-zinc and zinc-nickel plating and chemical-milling capabilities had recently been implemented and a high velocity oxygen fuel (HVOF) coating system was being implemented as a line-of-sight chromium electroplating replacement.

Tinker AFB has eight hard chromium tanks and all have a 1,466 gallon capacity. There are 32 tanks on the chromium plating line. The line exhausts to one of two scrubbers, one for the chromium-containing tanks and the other for the acid/alkaline, acid etch, chromium strip, and other tanks.

NADEP North Island has six chromium plating tanks, five of which are active. These exhaust into a single five-stage composite mesh pad scrubber.

3.3.2 Site Histories

3.3.2.1 NADEP Cherry Point, North Carolina

For more than 50 years Cherry Point has provided maintenance, engineering, and logistics support on a variety of aircraft, engines, and components for all branches of the U.S. Armed Forces, various federal agencies, and 24 foreign nations. Depot-level maintenance performed at Cherry Point is divided into four categories: aircraft, engines, components, and other support.

In April 1996, the Chief of Naval Operations (CNO) recognized the depot for environmental achievements in the industrial installation pollution prevention and recycling categories. In September 1996 and August 1997, North Carolina's Department of Environment, Health, and Natural Resources recognized Cherry Point for excellence in waste reduction. In April 2000, the depot received a CNO environmental award in the Installation Recycling category.

3.3.2.2 Oklahoma City Air Logistics Center, Tinker AFB, Oklahoma

Tinker operates one of the largest electroplating shops in the nation, restoring worn parts and providing corrosion protection to engine and aircraft parts. Source reduction has been the primary goal of the minimization program, although waste control and recycling technologies are also being used.

Tinker's largest organization is the Oklahoma City Air Logistics Center (ALC), one of five depot repair centers in the Air Force Materiel Command. The ALC is the worldwide manager for a wide range of aircraft, engines, missiles, and commodity items. Through the use of aggressive and innovative technologies, Tinker has also become a national leader in pollution prevention.

Tinker is pursuing a multipronged approach to their goal of eliminating chromium and nickel plating. High phosphorus electroless nickel was selected to replace some chromium plating applications, and a process to rejuvenate the solutions was developed. Other innovations include use of HVOF coatings, which were recently approved for chromium substitution of some parts and are being evaluated for expanded use. Tinker has also eliminated chromium anodizing by

using MIL-A-8625 Type 1C, Thin Film Sulfuric Acid anodizing. They are also part of a project looking for non-line-of-sight substitutes for hard chromium plating.

3.3.2.3 NADEP North Island, California

North Island is a tenant command at Naval Air Station (NAS) North Island, in San Diego, California. Their mission includes a complete range of depot level rework operations on designated weapons systems, accessories, and equipment; manufacture of parts and assemblies; engineering services; and assistance in resolving aircraft maintenance and logistics problems. North Island provides a variety of services to the submarines, surface ships, and aviation units of the fleet, including engineering, calibration, manufacturing, and overhaul/repair services.

3.4 PHYSICAL SETUP AND OPERATION

At Cherry Point, the duct sampled was a 20-inch diameter fiberglass reinforced duct that runs horizontally through the basement. The two sampling ports were approximately 8 feet from the nearest upstream restriction, and approximately 4 feet from the nearest downstream restriction. At Tinker, the 22-inch fiberglass ductwork from the sampled tank (Tank 222) runs vertically toward the ceiling. The two sampling ports are about 6½ feet above the nearest upstream restriction and more than 7 feet from the nearest downstream restriction. Figure 2 and Figure 3 show the hard chromium electroplating tanks and emissions sampling equipment used at Tinker (the same equipment used at Cherry Point).

Occupational health sampling (i.e., ambient shop air sampling) was performed at both Cherry Point and Tinker AFB. Some samplers used are shown in Figure 3. Samples were taken a few inches above the surface of the tanks, in the breathing zone directly in front of the tanks, and in the breathing zone a few feet in either direction from the tanks. At each of the sampling locations, two to four samples were taken during each sampling day.

In summary, the concentration of chromium was measured in the air stream in the ductwork exhausting the bath as well as in the shop air surrounding the bath. The concentrations of chromium with and without addition of WA/FS to the bath were compared to determine the relative reduction in emissions and the specific concentration level to which the emissions were reduced. Sampling of emissions in the bath exhaust duct and in the surrounding shop was conducted on 4 different days without WA/FS (three times at Cherry Point, and once at Tinker), and on 10 different days while using WA/FS. Three separate sampling runs were conducted for each day of exhaust duct sampling.

Eight days of sampling were conducted at Cherry Point. The first, second, and fourth days (July 11, 2000; July 12, 2000; and November 15, 2000) were sampled with no WA/FS in the tank. During the other five days (September 21, 2000; November 16, 2000; December 13, 2000; March 27, 2001; and April 17, 2001), WA/FS was present in the tank at the following respective surface tensions: 33, 23, 23, 27, and 27 dynes/cm.

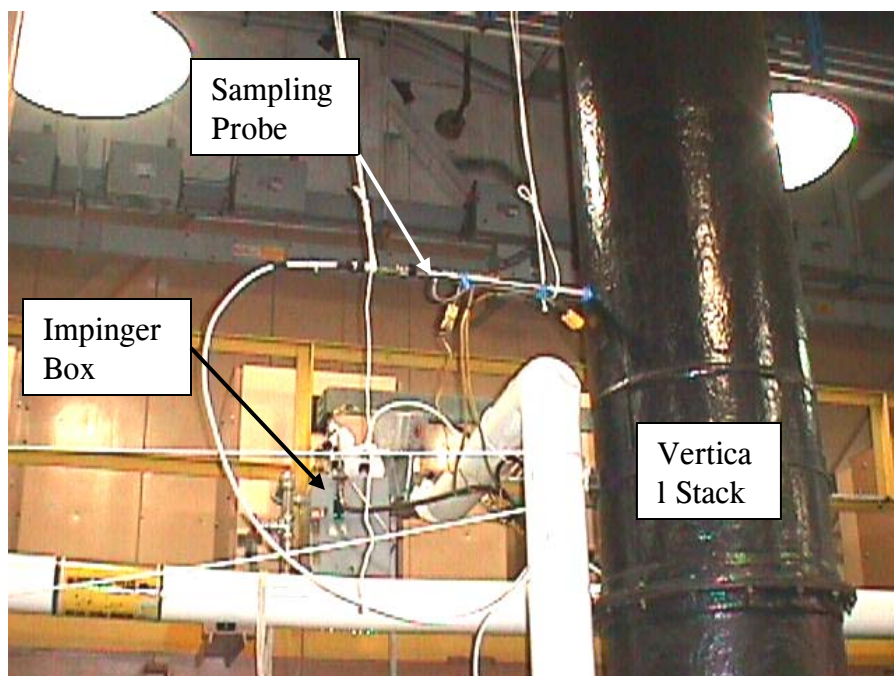


Figure 2. Stack Sampling Assembly at Tinker AFB.

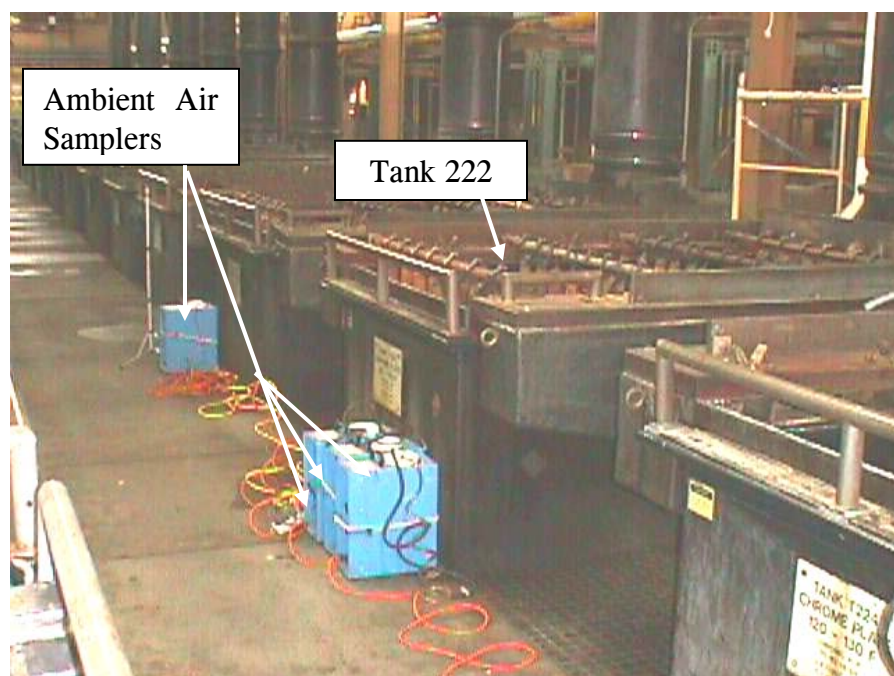


Figure 3. Occupational Health Sampling Equipment at Tinker AFB.

Six days of sampling were conducted at Tinker. The first day (September 12, 2000) there was no WA/FS in the tank. During the other 5 days (October 11, 2000; November 8, 2000; December 6, 2000; July 31, 2001; and August 1, 2001) WA/FS was present in the tank at the following respective surface tensions: 34, 27, 30.5, 27.5, and 27.5 dynes/cm.

3.5 SAMPLING/MONITORING PROCEDURES

Air pollution emissions testing (i.e., stack tests in the ductwork between tanks and the APCDs) was conducted using EPA Method 306, *Determination of Chromium Emissions from Decorative and Hard Chromium Electroplating and Anodizing Operations*³. This is the conventional test protocol for total and hexavalent chromium analysis for point source air emissions. Each emissions test sample was taken during a 2-hour period using isokinetic sampling techniques mandated by Method 306. Three emissions tests were conducted during each sampling day. The results for each sampling day were calculated by averaging the data from each of the three tests taken that day. The testing schedule is shown in Table 2.

Table 2. Sample Location Schedule.

SAMPLE SITES	AIR EMISSION TESTS	DATE
NADEP Cherry Point	without WA/FS, & with polyethylene shield*	July 11, 2000
	without WA/FS	July 12, 2000
	with WA/FS	September 21, 2000
	without WA/FS	November 15, 2000
	with WA/FS	November 16, 2000
	with WA/FS	December 13, 2000
	with WA/FS	March 27, 2001
	with WA/FS	April 17, 2001
Tinker AFB	without WA/FS	September 12, 2000
	with WA/FS	October 11, 2000
	with WA/FS	November 8, 2000
	with WA/FS	December 6, 2000
	with WA/FS	July 31, 2001
	with WA/FS	August 1, 2001

* The first day at Cherry Point was the only time and location that the polyethylene barrier was used.

Occupational health area sampling was conducted using OSHA Method 215, *Hexavalent Chromium in Workplace Atmospheres*⁴ with the most recent modifications. During each test day, samples were taken in three locations: a few inches above the surface of the tanks, in the breathing zone directly in front of the tanks, and in the breathing zone a few feet in either direction from the tanks. At each of the sampling locations, two to four samples were taken during each sampling day.

Material quality testing, except for fatigue testing, complied with Aerospace Material Specification (AMS) QQ-C-320B, *Chromium Plating Electrodeposited*⁵. The standard test includes the ASTM Methods listed in Table 3 and Table 4. Limited equivalence fatigue testing was based on NAVAIR requirements.

Table 3. Test Plan for Materials, Environmental, and Occupational Health Testing.

Parameter	Sample Type	Method Number	Method Title	Method Type	Number of Samples	Controls
Test events per facility, each day, planned at Tinker and Cherry Point						
Stack gas – hexavalent chrome	Time weighted average	EPA 306	<i>Determination of Chromium Emissions from Decorative and Hard Chrome Electroplating and Anodizing Operations</i>	IC/PCR	3ea 2-hr/test events	1 field blank
Worker protection-area samples	Time weighted average	OSHA ID-215	<i>Hexavalent Chromium in Workplace Atmospheres</i>	IC with UV-vis detector and post column delivery system	6 samples 2 @ surface (+1-2"), 2 @ tank breathing zone (BZ), 2@ 10" away from tank	1 of every 5 samples submitted
One test event before and one after adding Fumetrol® 140 at Cherry Point, Tinker, and North Island						
Material quality	Batch 1" x 4" x 0.040" coupons	Fed Spec QQ-C-320B(4)	<i>Chromium Plating (electrodeposited)</i>	Thickness Adhesion Hardness Porosity	10 samples/per test type /site (40 samples per test site)	Pass/fail
Material quality	Batch, notched round bars	Fed Spec QQ-C-320B(4)	Sustained tensile load per ASTM F 519-97	Hydrogen embrittlement	10 samples/per test type /site	Pass/fail
Material quality	Batch, notched round bars	Fed Spec QQ-C-320B(4)	Rising step load per ASTM F 519-97 and ASTM F 1624	Hydrogen embrittlement	10 samples/per test type/site	Pass/fail
Recorded during testing and records reviewed during testing period						
Surface tension	Grab	ASTM D1331-89	Tensiometric	Tensiometer	Per 40 CFR 63	
Other	Grab		<i>Amp-hours, voltage, amps, bath temperature</i>			Per instrument instructions

Table 4. Detailed Test Plan for Material Quality Testing.

Test	Specimens	Method	References	Number of Samples					Test Performer
				North Island with WA/FS	Tinker without WA/FS	Tinker with WA/FS	Cherry Point without WA/FS	Cherry Point with WA/FS	
Hydrogen embrittlement relief	4340 notched round bars per ASTM F 519-97	Sustained load per ASTM F 519-97	QQ-C-320B	10	10	10	10	10	Pax Materials Lab
Hydrogen embrittlement relief	4340 notched round bars per ASTM F 519-97	Rising step load per ASTM F 519-97 and ASTM F 1624	QQ-C-320B	10	10	10	10	10	Pax Materials Lab
Thickness	4130, 1" by 4" by 0.040"	Magnetic thickness testing per ASTM B 499	QQ-C-320B section 4.5.1	10	10	10	10	10	Pax Materials Lab
Adhesion	4130, 1" by 4" by 0.040"	Mandrel bend test ASTM B 571-97 section 3.1	QQ-C-320B section 4.5.2	10	10	10	10	10	NI Materials Lab
Hardness	4130, 1" by 4" by 0.040"	Vickers hardness test per ASTM B 578	QQ-C-320B section 4.5.3	10	10	10	10	10	NI Materials Lab
Porosity	4130, 3" by 10" by 0.040"	Ferroxyl test per QQ-C-320B section 4.5.4	QQ-C-320B section 4.5.4	10	10	10	10	10	Pax Materials Lab

After initial baseline testing without WA/FS (Fumetrol® 140) at both facilities (Cherry Point and Tinker), the WA/FS was added to the tanks, attempting to reach a surface tension value of less than 30 dynes/cm.

3.6 ANALYTICAL PROCEDURES

Research Triangle Institute (RTI), Research Triangle Park, North Carolina, was retained to analyze the stack samples using EPA Test Method 306 (which describes both the stack sampling and the sample analytical methodology). The in-plant air samples were analyzed according to OSHA 215. The analytical method is similar to the EPA Method 306.

Industrial hygiene samples (in-plant air samples collected on filters) were analyzed by the Naval Environmental Health Center, Consolidated Industrial Hygiene Laboratory (CIHL) at Navy Environmental & Preventive Medicine Unit #2 (NEPMU 2), in Norfolk, Virginia. NEPMU 2 held an American Industrial Hygiene Association (AIHA) Accreditation (Laboratory #102170, Certificate #58) for industrial hygiene testing of metals.

The Becker Laboratory at Patuxent River, Maryland, NAVAIR's Aerospace Materials Division's main laboratory, and the Materials Engineering Laboratory, NADEP North Island, in San Diego, performed the materials testing. Becker Laboratory is recognized by the American Association for Laboratory Accreditation for compliance with ISO 9001, *Quality Systems—Model for Quality Assurance in Design, Development, Production, Installation and Servicing*.

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4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

Three types of performance data were developed in conjunction with this study.

- **Stack emissions data.** These are measurements of atmospheric emissions of chromic acid mist from the electroplating bath that are captured by the ductwork leading to the bath's APCD. Samples were collected from Cherry Point and Tinker when plating was being conducted with and without the use of WA/FS.
- **Industrial hygiene data.** These are measurements of the concentration of chromium taken in the shop environment directly over the plating bath and in the breathing zone in front of and a few feet away from the bath. Samples were collected from Cherry Point and Tinker, with and without the use of WA/FS.
- **Plated parts quality data.** To determine if the use of WA/FS had any effect on the quality of the plated parts, parts that were plated with and without the use of WA/FS were subject to six plating quality tests: fatigue, hydrogen embrittlement, hardness, porosity, adhesion, and thickness.

4.2 PERFORMANCE CRITERIA

Performance was measured against applicable regulatory standards for atmospheric emissions and occupational exposure (see Section 2.2.3 for regulatory standards). In addition, emissions/exposures produced during the use of WA/FS were compared to emissions/exposures produced when WA/FS was not used (i.e., the normal/baseline condition). Similarly, the quality of parts that were plated during the use of WA/FS was compared to the quality when WA/FS was not in use.

With respect to stack emissions (i.e., samples taken in the bath exhaust ductwork), the use of WA/FS reduced the concentration of chromium in the exhaust gases 20- to 70-fold compared to operations without the WA/FS. Typically, the exhaust emissions readily complied with EPA regulatory standards for existing, small (less than 60 million ampere-hours per year) hard chromium electroplating shops. However, it does not appear that the reduction in emissions is enough to comply with current regulatory emission standards for new hard chromium electroplating baths or existing baths for large shops.

With respect to occupational exposure to chromium mists, most of the samples (with or without WA/FS) complied with the current regulatory standard (see section 2.2.3). However, OSHA has, for some time, been considering tightening the occupational standard by a factor of 10- to 100-fold. At a 10-fold tightening of the standard, all the samples taken in this study would comply. At a 100-fold tightening, all the breathing zone samples taken (with or without using WA/FS) would comply, as would all the samples taken a few inches above the bath while using WA/FS. On the other hand, most samples taken a few inches above the bath without using WA/FS would

fail the 100-fold regulatory reduction. This benefit makes the use of Fumetrol® 140 a key compliance tool for hard chromium plating facilities.

4.3 DATA ASSESSMENT

4.3.1 Atmospheric Emissions

Stack emissions were sampled and analyzed on 8 days at Cherry Point and on 6 days at Tinker. For 3 days at Cherry Point and 1 day at Tinker, the chromium electroplating baths were in the “baseline” condition, i.e., no WA/FS was added to the baths. For the other days, the baths contained WA/FS at concentrations sufficient to adjust the surface tension of the baths to 23 to 34 dynes/cm. Three 2-hour samples were collected from the exhaust ductwork during each sampling day. The results of those sampling events are summarized in Table 5 in units of milligrams of both hexavalent and total chromium per dry standard cubic meter of air. Figure 4 and Figure 5 present the sampling results.

A review of the summary data in Table 5, Figure 4, and Figure 5 shows that using WA/FS caused a dramatic decrease in the concentration of total and hexavalent chromium from stack emissions to the atmosphere (or to an APCD). At Cherry Point, the average reduction in concentration of total chromium was approximately 70-fold, and at Tinker it was approximately 20-fold.

However, when comparing the emissions data to the current EPA National Emissions Standards for Hazardous Air Pollutants (NESHAP) standard of 0.015 mg/dscm, the Cherry Point average data with WA/FS for total chromium was 0.0348 mg/dscm, and the Tinker average data with WA/FS for total chromium was 0.0245 mg/dscm. Both would be out of compliance if they did not have APCDs installed downstream of the sampling points.

Data are also presented in graphs in the upper right-hand corners of Figure 4 and Figure 5 for the emissions as a function of the electroplating load (i.e., mg of chromium per ampere-hours). The results are also dramatic with respect to the reduction in emissions with WA/FS as compared to without WA/FS. At Tinker, there was some question about whether the amp-hr meters were providing the correct readings. Therefore, some of the ampere-hours emissions data for Tinker may be incorrect.

Table 5. Summary of Chromium Concentrations in Stack Emissions. (mg/dscm)

CHERRY POINT									
Sampling Date	Surface Tension (dynes/cm)	Hexavalent Chromium				Total Chromium			
		Sample # 1	Sample # 2	Sample # 3	Average	Sample # 1	Sample # 2	Sample # 3	Average
7/11/00	72	<i>N/A</i>	<i>6.32</i>	<i>0.737</i>	<i>3.529</i>	<i>N/A</i>	<i>6.804</i>	<i>0.853</i>	<i>3.829</i>
7/12/00	72	<i>3.13</i>	<i>0.912</i>	<i>1.37</i>	<i>1.804</i>	<i>4.06</i>	<i>0.919</i>	<i>1.56</i>	<i>2.180</i>
9/21/00	33	0.0418	0.0299	0.0216	0.0311	0.0482	0.0367	0.0237	0.0362
11/15/00	76	<i>1.49</i>	<i>1.30</i>	<i>1.26</i>	<i>1.35</i>	<i>1.57</i>	<i>1.31</i>	<i>1.21</i>	<i>1.36</i>
11/16/00	23.1	0.0446	0.0482	0.0678	0.0535	0.0431	0.0473	0.0678	0.0527
12/13/00	23.4	0.0170	0.0273	0.0233	0.0225	0.0193	0.0289	0.0243	0.0242
3/27/01	27	0.0313	0.0533	0.0276	0.0374	0.0356	0.0539	0.0349	0.0415
4/17/01	27	0.0215	0.0153	0.0204	0.0191	0.0218	0.0163	0.0209	0.0197

Average without WA/FS: 2.228

2.457

Average with WA/FS: 0.0327

0.0348

NOTE: N/A indicates that no parts were being electroplated during test number 1 on July 11, 2000.

TINKER									
Sampling Date	Surface Tension (dynes/cm)	Hexavalent Chromium				Total Chromium			
		Sample # 1	Sample # 2	Sample # 3	Average	Sample # 1	Sample # 2	Sample # 3	Average
9/12/00	72	<i>0.516</i>	<i>0.286</i>	<i>0.347</i>	<i>0.3833</i>	<i>0.645</i>	<i>0.333</i>	<i>0.443</i>	<i>0.474</i>
10/11/00	34	0.00818	0.0104	0.00624	0.0083	0.00890	0.0125	0.0111	0.0108
11/8/00	27	0.00870	0.00715	0.00295	0.00627	0.00896	0.00642	0.00299	0.00612
12/6/00	30.5	0.0234	0.0186	0.0106	0.0175	0.0240	0.0215	0.0125	0.0193
7/31/01	27.5	0.106	0.0204	0.0337	0.0534	0.109	0.0217	0.0397	0.0568
8/1/01	27.5	0.0242	0.0314	0.0242	0.0266	0.0271	0.0344	0.0262	0.0292

Average without WA/FS: 0.383

0.474

Average with WA/FS: 0.0224

0.0245

NOTE: *Italicized and shaded* rows represent baseline sampling (i.e., without WA/FS).

Figure 4. NADEP Cherry Point Total Chromium Emissions Concentration.

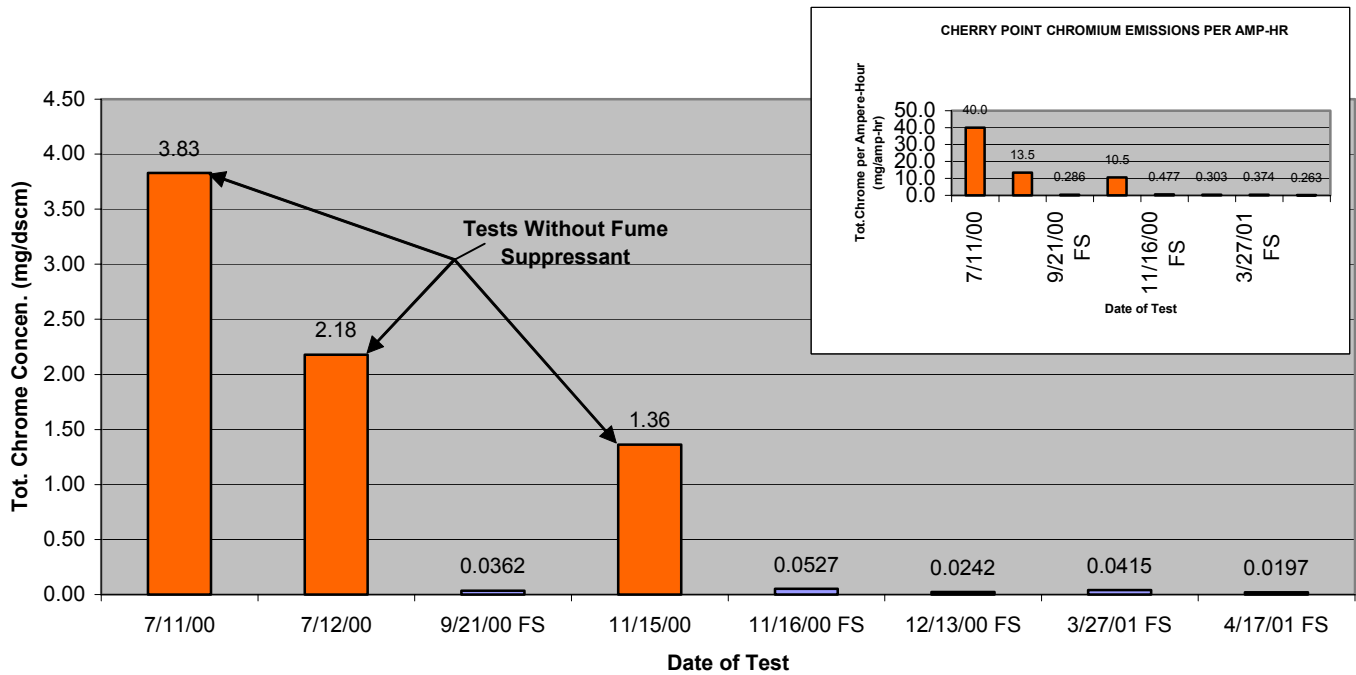
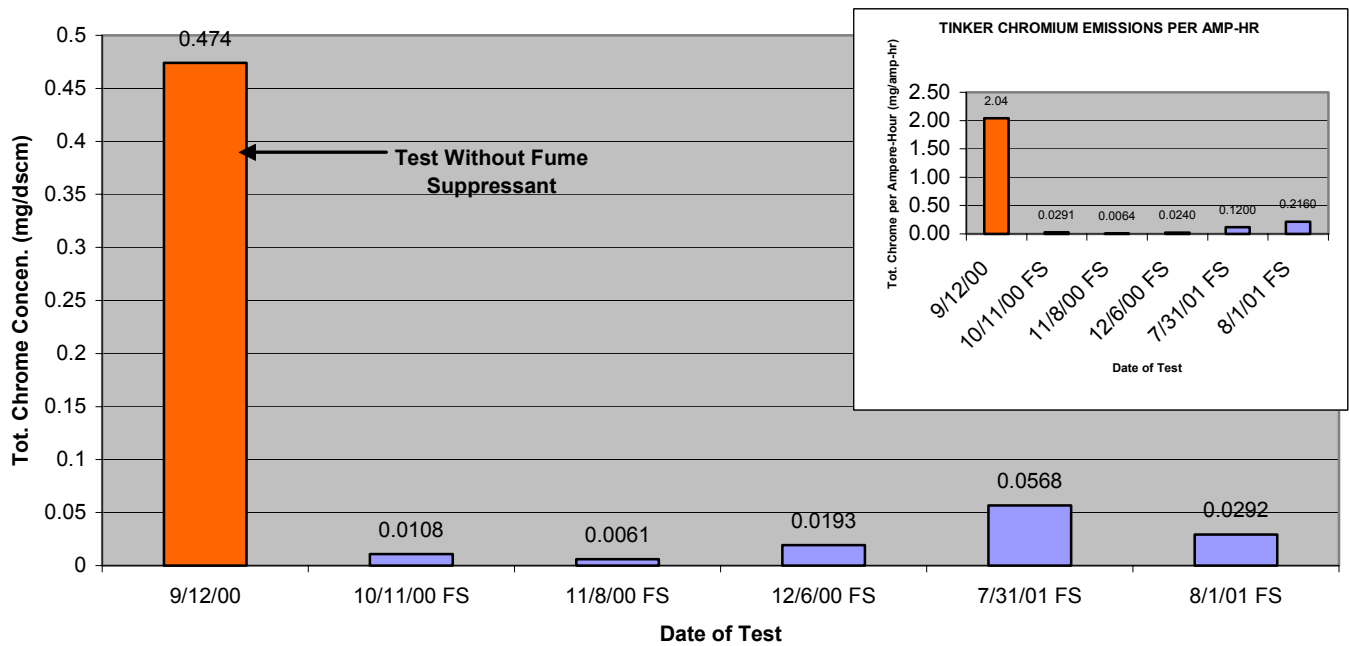


Figure 5. Tinker AFB Total Chromium Emissions Concentration.



4.3.2 Occupational Exposures

Table 6 presents the data from industrial hygiene (IH) sampling. IH samples were taken concurrently with the stack samples at Cherry Point and Tinker. Samples were taken in three locations: (1) a few inches directly above the sampled bath liquid surface (“In Tank”); (2) directly in front of the sampled bath in the breathing zone (“Near Tank Breathing Zone”); and (3) a few feet from the sampled bath in the breathing zone (“Remote Breathing Zone”). It was anticipated that the most concentrated samples would be those taken above the liquid surface, and that the least concentrated would be those “remote” samples taken a few feet from the bath. In fact this was the general trend for all testing *except* at Tinker during the baseline tests (i.e., tests without WA/FS in the bath).

Each value in Table 6 represents an average of two data points, unless otherwise noted. Shaded values represent baseline samples (i.e., when no WA/FS was in the bath). Average concentrations for all testing are shown at the bottom of Table 6, both for the baseline condition and when the baths contained WA/FS. As noted above, the trend was clear from the averages that the hexavalent chromium concentrations decreased as the sampling location become more remote (except for the baseline testing at Tinker). The trend was even more dramatic if the excluded Table 6 “outlier” values, except for the 585 $\mu\text{g}/\text{m}^3$ value, had been included (see Table Notes 3, 4, 5, and 8).

It is also clear that the concentrations of chromium were lowest when the WA/FS was in use (again with the exception at Tinker for samples taken in the breathing zone near the bath). In fact, for the samples taken a few inches from the liquid surface (“In Tank”), the improvement when WA/FS was in use was greater than 20-fold. It was theorized that the improvement was not as dramatic in the breathing zone locations (and is in fact reversed for the noted Tinker “Near Tank” samples) because the concentrations were very low at those locations to begin with, and consequently the influence of other facility, chromium-containing baths became significant.

4.3.3 Quality of Electroplated Parts

4.3.3.1 Hydrogen Embrittlement

Hydrogen embrittlement testing was performed on ASTM F 519 Type 1a.1 notched round bars made from 4340 steel. The bars were chromium plated at all three facilities (Cherry Point, Tinker, and North Island) while using Fumetrol® 140, and from Cherry Point and Tinker with no Fumetrol® 140 (controls). Two types of testing were performed. The first was the standard 00-hour sustained tensile load test per AMS QQ-C-320B, as defined in ASTM F 519, which holds the specimen at 75 percent of ultimate tensile strength (UTS) for 200 hours. The second test was a developmental rising step load (RSL) test that holds the specimen at 75 percent of UTS for 24 hours, followed by 5 percent tensile increases each hour to failure.

All specimens from all sites and tanks passed the 200-hour sustained tensile load test, indicating that Fumetrol® 140 had no deleterious effect on the embrittlement characteristics of high-strength steels plated with hard chromium. For comparison purposes, all test samples survived

Table 6. Industrial Hygiene Sampling Data. (concentrations in $\mu\text{g}/\text{m}^3$)

CHERRY POINT				TINKER			
Hexavalent Chromium Concentration				Hexavalent Chromium Concentration			
Test Date	Remote	Near Tank	In Tank	Test Date	Remote	Near Tank	In Tank
	Breathing Zone	Breathing Zone			Breathing Zone	Breathing Zone	
7/11/00	0.041	0.038	1.450	9/12/00 am	0.115	0.014	0.201
7/12/00	0.033	0.077	1.250	9/12/00 pm	(Note 6)	0.022	0.252
9/21/00 am	0.031	0.024	0.023	10/11/00 am	0.007	0.035	0.023
9/21/00 pm	(Note 6)	0.043	0.043	10/11/00 pm	(Note 6)	0.028	0.033
11/15/00 am	0.056	0.112	2.266	11/8/00 am	0.047	0.014	0.036
11/15/00 pm	(Note 6)	(Note 6)	2.400	11/8/00 pm	(Note 6)	(Note 6)	0.078
11/16/00 am	0.042	0.035	0.070	12/6/00	0.028	0.042	0.100
11/16/00 pm	(Note 6)	(Note 6)	0.120	7/31/01	0.023	0.038	0.053
12/13/00 am	0.014	0.030	0.113	8/1/01 (Note 7)	0.050	0.018	4.23
12/13/00 pm	(note 6)	0.030	0.075				
3/27/01	0.014	0.186	0.073				
4/17/01	0.028	0.014	0.041				
Averages⁹:							
Without FS:	0.043	0.076	1.68		0.083	0.018	2.23
With FS:	0.026	0.060	0.067		0.026	0.031	0.060
NOTES:							
1. Rows with shaded background represent baseline data (i.e., without fume suppressant).							
2. All values reported below various detection limits were averaged as the detection limit divided by the square root of 2 (i.e., 1.414). For example, if non-detect was less than $0.020 \mu\text{g}/\text{m}^3$, it was reported as 0.014 (i.e., $0.020/1.414$). ⁵							
3. Cherry Point, a value of $3.59 \mu\text{g}/\text{m}^3$, was considered an outlier from the 7/11/00 sampling for “Near Tank Breathing Zone” and was not included in the calculations.							
4. Tinker, a value of $585 \mu\text{g}/\text{m}^3$, was considered an outlier from the 9/12/00 am sampling for “In Tank” and was not included in the calculations.							
5. Tinker, 9/12/00 am, “Near Tank Breathing Zone,” two locations were sampled. One had a concentration of $31.52 \mu\text{g}/\text{m}^3$. This value was considered an outlier and was not included in calculations.							
6. Only one set of samples was taken during the day, spanning the entire day (i.e., am and pm). The value shown for “am” represents the entire day.							
7. This baseline sample was taken on Tank 214. All other data were for Tank 222.							
8. Tinker, 8/1/01, “In Tank,” two locations were sampled. One had a concentration of $28.6 \mu\text{g}/\text{m}^3$. This value was considered an outlier, and was not included in the calculations.							
9. To calculate averages, concentrations based on a full-day sampling were given twice the weight as concentrations based on half-day sampling.							
For Reference:							
1. PEL is $100 \mu\text{g}/\text{m}^3$ as chromic oxide ($52 \mu\text{g}/\text{m}^3$ as chromium).							
2. Proposed OSHA PEL ranges between 0.5 and $5 \mu\text{g}/\text{m}^3$.							
3. Conference on Governmental Industrial Hygienists time weighted average for water-soluble hexavalent chromium compounds is $50 \mu\text{g}/\text{m}^3$ as chromium.							
4. NIOSH Recommended Exposure Limit (REL) for hexavalent chromium compounds is $\mu\text{g}/\text{m}^3$ as chromium.							
5. Environmental Health Center, <i>Industrial Hygiene Field Operations Manual</i> , Chapter 4, Section 8a.(3), pages 4-22.							

the initial 24-hour sustained load of the RSL test (not unexpected, due to the success in the 200-hour test).

4.3.3.2 Hardness

Per AMS QQ-P-320B, the Vickers hardness test method was planned to be used to determine coating hardness. However, due to the availability of hardness testing equipment, the materials test laboratory at NADEP Cherry Point performed the hardness test using their standard technique based on the Rockwell C method. Three samples from Cherry Point and Tinker with and without Fumetrol® 140 were chosen at random from a batch of 1" x 4" test coupons. Each sample had 10 hardness tests.

Based on the hardness data in Table 7, there appears to be no statistical difference between the results with or without Fumetrol® 140. Therefore, the use of Fumetrol® 140 in hard chromium electroplating baths appeared to have no detrimental effect on the hardness of the chromium plating. An additional set of tests was run on three samples from the North Island facility using Fumetrol® 140. The results were similar to the Tinker and Cherry Point data.

Table 7. Hardness Tests.

Sample	Source	Hardness (Rockwell C)				
		Average of 10 Tests	Average of the Averages	Standard Deviation	Max	Min
1	Cherry Point—no WA/FS	63.68	62.82	2.86	67.16	57.70
2	Cherry Point—no WA/FS	60.01		3.45	65.23	53.13
3	Cherry Point—no WA/FS	64.78		2.12	67.36	60.81
1	Cherry Point—with WA/FS	63.19	63.02	1.38	64.95	61.04
2	Cherry Point—with WA/FS	61.56		2.86	64.10	54.43
3	Cherry Point—with WA/FS	64.31		4.09	67.36	53.13
1	Tinker—no WA/FS	64.12	64.07	1.084	65.24	61.93
2	Tinker—no WA/FS	64.74		1.105	67.00	63.13
3	Tinker—no WA/FS	63.35		2.413	66.41	58.84
1	Tinker—with WA/FS	63.77	63.91	0.963	64.95	61.93
2	Tinker—with WA/FS	64.27		0.932	65.53	62.55
3	Tinker—with WA/FS	63.68		0.873	64.66	61.93

4.3.3.3 Porosity

The pitting test detailed in AMS QQ-P-320B provides a relative measure of the quality of the electroplated chromium. Since previous generations of fume suppressants increased the porosity of the electroplated chromium, this was an important test to validate the performance of Fumetrol® 140 relative to previous products and the control tanks.

Initial porosity testing was completed on three samples each from Cherry Point and Tinker, with and without Fumetrol® 140, and three samples from North Island. Of the test sets, only the Cherry Point set processed from the control tank with no Fumetrol® 140 showed no pits, and passed the specification criteria. The Fumetrol® 140 set from Cherry Point showed small numbers of pits but also appeared to have red rust on the surface of the chromium from processing. This rust may have been deposited from the unplated areas of the test coupons that were in contact with the chromium plating during handling. All coupons from Tinker had residual red rust on the chromium surface as well, presumably leading to the large number of pits seen. For the North Island set, two coupons were pit-free and one had four pits. As a result of the initial tests, there was no evidence that the Fumetrol® 140 changed the porosity of the chromium plating. Since so many coupons did show positive results, it was decided to run another set of tests using thicker coatings and Cherry Point as the coating source.

For this test, the chromium was plated to 3 mils for both control and Fumetrol® 140 coatings. The test was completed on five specimens of each coating. No difference in porosity was noted between the NADEP Cherry Point plated coatings, with or without Fumetrol® 140 in the plating tanks. The overall porosity of the NADEP North Island coatings from a plating tank with Fumetrol® 140 was less than the Cherry Point coatings. The second round of porosity tests showed no deleterious effect on porosity due to the presence of Fumetrol® 140 in the plating tanks.

4.3.3.4 Adhesion

A bend-to-break adhesion test was used to evaluate the quality of adhesion of the chromium to the substrate. Five random samples of the original sets of 1-mil coatings from Cherry Point (with and without Fumetrol® 140), Tinker (with and without Fumetrol® 140) and North Island (with Fumetrol® 140) were tested. All samples from Cherry Point and Tinker passed the test in that no loss of adhesion was noted after breaking. The North Island samples showed a small degradation in adhesion that was linked to a quality control problem and resolved. The test was repeated using 10 random 3-mil coatings from Cherry Point, five from the control tank and five from the tank with Fumetrol® 140. No samples showed any degradation in adhesion. Based on the results, Fumetrol® 140 was not considered to have an effect on coating adhesion compared to the control coating.

4.3.3.5 Thickness

Thickness is a measurement of how close the plated coating is to the requested thickness and takes into consideration the regularity from sample to sample. From the thickness data in Table 8, there appears to be no statistical difference in requested thickness with and without the use of Fumetrol® 140.

Table 8. Average Thicknesses of Hard Chromium Coatings. (in mils)

Coupon	NADEP North Island with Fumetrol	NADEP Cherry Point with Fumetrol	NADEP Cherry Point without Fumetrol (control)
1	2.4	3.5	2.6
2	2.7	2.5	2.2
3	2.5	3.5	2.3
4	2.6	3.0	1.9
5	2.5	3.0	0.65
Average	2.5	3.1	1.9

4.3.3.6 Fatigue

The potential influence of Fumetrol® 140 on the fatigue characteristics of representative high-strength steels was evaluated using a limited equivalence test. Three alloys were selected based on their use and importance to DoD in critical components. Fatigue specimens were designed and machined out of these alloys per ASTM E 466 and ASTM E 606. The coupons were sent to NADEP Cherry Point for electroplating of hard chromium in production tanks with and without Fumetrol® 140. Plated specimens were tested in the NAVAIR Materials Mechanical Test Laboratory. Analysis of the data indicated that the Fumetrol® 140 had no, or a slightly positive, effect on fatigue performance of the test specimens.

4.4 TECHNOLOGY COMPARISON

Summarizing the information contained in Section 4.3.1, with respect to atmospheric emissions, there was a 20- to 70-fold decrease in emissions from hard chromium electroplating baths when WA/FS was used, as opposed to when WA/FS was not used (i.e., the baseline condition). However, it did not appear that the reduction in emissions was enough to comply with the current 0.015 mg/m³ regulatory emission standard for new facility or existing “large” facility hard chromium electroplating baths.

In summary, Section 4.3.2 describes that, with respect to occupational exposure, there was approximately a 20-fold reduction in the concentration of chromium directly above the electroplating bath when WA/FS was in use. In the breathing zone in front of the bath and a few feet from the bath, concentrations of chromium were extremely low compared to the OSHA PEL, whether WA/FS was used or not. It appeared that breathing zone concentrations were lower when WA/FS was in use.

In summary, Section 4.3.3 describes that, with respect to electroplated product quality, there was no reduction in the acceptability of product quality.

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5.0 COST ASSESSMENT

5.1 COST PERFORMANCE

The cost of implementing WA/FS technology is shown in Table 9 and Table 10. Table 9 is the cost for retrofitting WA/FS at existing facilities, such as the two facilities tested for this report (Cherry Point and Tinker). Table 10 shows the cost to implement WA/FS at new facilities. Start-up costs are considered to be one-time costs; operation and maintenance (O&M) costs are shown on an annual basis for each hard chromium electroplating bath (assuming a bath surface area of approximately 25 square feet (ft²), similar to the baths tested for this report). No demobilization costs were envisioned for either new or existing systems (see Table 10).

The differences between the two tables reflect the fact that a new facility is assumed to not be required to install an APCD in the electroplating bath exhaust system ductwork (i.e., the use of WA/FS would control emissions to a level that would, by itself, comply with air pollution control regulations). For existing facilities, two alternatives are shown (see last footnote to Table 9): (1) WA/FS technology is used in conjunction with the existing APCD (i.e., scrubber) system, and (2) the existing scrubber is, in effect, turned off when using WA/FS technology. The second alternative assumes that emission limits can be achieved by using WA/FS alone.

It should be noted that the \$1,700 credit shown for consumables and supplies in both Table 9 and Table 10 under Operation and Maintenance is included because the use of WA/FS minimizes the loss of chromic acid through the exhaust system (i.e., to the scrubber) from the hard chromium baths. Based on sampling data (see Table 11), 120 to 460 pounds of chromic acid would be saved per year per bath when using WA/FS, at a cost of \$7 per pound. This amounts to an average saving of more than \$2,000 per year per bath (assuming that the baths are in service 50 percent of the time). However, it is necessary to maintain the appropriate surface tension in the bath to obtain the chromic acid savings. An 800-gallon bath should require approximately 2 gallons of WA/FS annually to maintain the proper surface tension. At \$150 per gallon, the annual cost would be \$300. Therefore, the net savings on consumables and supplies is estimated to be \$1,700 (\$2,000 minus \$300).

5.2 COST COMPARISONS OF CONVENTIONAL AND OTHER TECHNOLOGIES

Table 12 summarizes the relative costs and savings shown in Table 9 and Table 10 for three scenarios in which WA/FS technology could be used. Table 9 and Table 10 both compare the use of WA/FS technology to the conventional technology of using a wet scrubber (or similar APCD) in the exhaust ductwork. Table 9 evaluates two scenarios for *existing* hard chromium electroplating baths, and Table 10 evaluates the use of WA/FS in *new* electroplating systems.

Table 9 gives two cost alternatives relating to the use of WA/FS on existing hard chromium electroplating baths. The first alternative uses WA/FS in addition to the existing scrubber. Even though this approach might not appear to be economical, it is in fact economical because the WA/FS prevents the loss of chromic acid plating solution. Specifically (see Table 9 Totals),

Table 9. Costs of Implementing and Using Wetting Agent/Fume Suppressant Technology at Existing Facilities. (per 25-ft² bath)

Startup		Operation & Maintenance		Demobilization	
Activity	Cost (\$)	Activity	Cost (\$/yr)	Activity	Cost (\$)
Labor	0	Labor	0	Removal of equipment and structures	N/A
Planning and contracting	0	Monitoring	1,300	Site restoration	N/A
Site preparation	0	Analytical services	0	Decontamination	N/A
Capital equipment	800*	Equipment/facility modifications	0	Demobilization of personnel	N/A
Construction	0	Utilities	0/(5,710)**		
Permitting and regulatory requirements	0/3,590**	Training to operate technology	0		
		Effluent treatment and disposal	0/(2,000)**		
		Residual waste handling and disposal	0		
		Ancillary equipment	0		
		Consumables and supplies	(1,700)		
TOTALS:					
Start-up (one-time):	800/4,390**	O&M (annual):	(400)/(8,100)**	Demobilization:	0

N/A – not applicable

() – Indicates a negative cost; i.e., a savings.

* Includes \$300 for the cost of the one-time start-up addition of WA/FS to each 800-gallon bath.

** For costs shown as x/y, “x” represents costs if no modifications are made to the existing exhaust systems or APCDs; “y” reflects costs incurred if all APCD internals are removed and scrubber water is turned off.

Table 10. Costs of Implementing and Using Wetting Agent/Fume Suppressant Technology at New Facilities. (per 25-ft² bath)

Startup		Operation & Maintenance		Demobilization	
Activity	Cost (\$)	Activity	Cost (\$/yr)	Activity	Cost (\$)
Labor	0	Labor	0	Removal of equipment and structures	N/A
Planning and contracting	0	Monitoring	1,300	Site restoration	N/A
Site preparation	0	Analytical services	0	Decontamination	N/A
Capital equipment	800*	Equipment/facility modifications	0	Demobilization of personnel	N/A
Construction	(46,000)***	Utilities	(5,710)		
Permitting and regulatory requirements	0	Training to operate technology	0		
		Effluent treatment and disposal	(2,000)		
		Residual waste handling and disposal	0		
		Ancillary equipment	0		
		Consumables and supplies	(1,700)		
TOTALS:					
Start-up (one-time):	(45,200)	O&M (annual):	(8,100)	Demobilization:	0**

N/A – not applicable

* Includes \$300 for the cost of the one-time start-up addition of WA/FS to each 800-gallon bath.

** In fact, there is a distinct cost savings for demobilizing new hard chromium plating operations that use WA/FS, and therefore, do not use scrubbers; i.e., there are no scrubbers and associated equipment to demobilize at the end of the useful life of the hard chromium plating operation. However, these savings are not included in this analysis.

*** Construction cost savings reflects the fact that the cost of capital equipment (a scrubber and associated equipment) plus installation is not required.

Table 11. Analysis of Emissions Data and Projected Cost Savings from Use of Wetting Agent/Fume Suppressant Technology.

Cherry Point Stack Samples

Set Sampling Date	Average Air Flow (dscf/min)/ (dscm/min)	Total Chromium Concentration (mg/dscm)	Emitted Mass of Chromium without WA/FS (mg/min)	Emitted Mass of Chromium with WA/FS (mg/min)	Amount of Chromic Acid Saved (lb/yr) and Cost Savings (\$/yr)
7/11/00	4,890/138	3.83	530		
7/12/00	4,890/138	2.18	302		
9/21/00 FS*	6,760/191	0.0362		6.93	
11/15/00	5,980/169	1.36	231		
11/16/00 FS	6,840/194	0.0527		10.21	
12/13/00 FS	6,240/177	0.0242		4.28	
3/27/01 FS	7,810/221	0.0415		9.18	
4/17/01 FS	7,380/209	0.0197		4.12	
Average Chromium Emission:			354	6.94	456
Cost savings per year @ \$7/lb and 50% bath use:					\$3,194
Tinker AFB Stack Samples					
9/12/00	7,400/210	0.474	99		
10/11/00 FS	7,740/219	0.0108		2.37	
11/8/00 FS	7,480/212	0.0061		1.30	
12/6/00 FS	7,280/206	0.0193		3.98	
7/31/01 FS	6,550/185	0.0568		10.54	
8/1/01 FS	6,520/185	0.0292		5.39	
Average Chromium Emission:			99	4.71	124
Cost savings per year @ \$7/lb and 50% bath use:					\$867

* FS signifies that fume suppressant was used for this series of tests.

Table 12. Summary of Annual Savings When Using Wetting Agent/Fume Suppressant Technology. (dollars per hard chromium plating bath)*

	Existing Hard Chromium Line		New Hard Chromium Line
	WA/FS plus scrubber	WA/FS with scrubber disabled	
Start-up costs	800	4,390	(45,200)
Annualized start-up costs/savings**	95	520	(5,350)
Annual O&M costs/savings	(400)	(8,100)	(8,100)
Total annual cost/savings	(300)	(7,600)	(13,450)
Payback period (years)	2.7	0.6	N/A

* Savings are in parentheses ().

**Annualized costs/savings are calculated based on 10 years equipment life for capital equipment, and a Real Discount Rate of 3.2% per year.

there are one-time start-up costs of \$800, and annual O&M *savings* of \$400. If it is assumed that the bath/scrubber system has a 10-year effective life cycle, and that the Real Discount Rate used by federal government agencies is 3.2 percent per year (OMB Circular A-94),⁶ then the effective annual equivalent cost of the \$800 start-up cost is \$95. Therefore, the effective annual saving per bath of this alternative is approximately \$300 per year (\$400 minus \$95). This savings represents a payback of the \$800 startup costs in fewer than 3 years.

The second alternative presented in Table 9, in which the scrubber system is in effect shut off, will have an effective annual savings per bath of approximately \$7,600. (The \$4,390 start-up costs have an annualized value of \$520, subtracted from the annual O&M savings of \$8,100.) This savings represents a payback period for the \$4,390 start-up costs of less than 7 months. However, it must be emphasized that this alternative may not be viable because, even with the emissions reduction attained by using WA/FS, this study shows that EPA's regulatory emissions limits still cannot routinely be met without a scrubber system (see Section 4.2 and 4.4). Likewise, for the Table 10 costs for new facilities, these savings may not be available if WA/FS cannot attain current emissions limitations without the use of a scrubber system.

Table 12 shows that, for a new installation, one-time start-up costs are approximately \$45,200 *less* than for a conventional system with a scrubber. In addition, approximately \$8,100 in O&M savings occurs every year. The effective annual savings are therefore approximately \$13,450 per bath. (The annualized value of the \$45,200 savings is approximately \$5,350, plus the \$8,100 annual O&M savings.) Since the start-up costs are less than for a conventional scrubber system, the payback period is not relevant.

6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

Annual savings on existing DoD hard chromium electroplating baths for which the APCDs are not disabled would be approximately \$300, with a 2.7 year payback of the minimal start-up costs. If regulatory standards were adopted that allow the APCD to be disabled on an existing bath (because the use of WA/FS would enable the facility to be permitted without APCDs), savings of approximately \$7,600 per year would accrue, a 0.6 year payback period.

Newly constructed hard chromium electroplating baths using WA/FS that can be built without APCDs would cost approximately \$13,500 less per year to operate (including the annualized credit for not having to install APCDs) than systems that do not use WA/FS. The payback period is not relevant because there is an effective negative relative capital cost.

The cost estimates do not include potential savings due to reduced human exposure liability, reduced volumes of chromic acid in the depots' hazardous material supply chain, and costs to comply with proposed OSHA PELs for hexavalent chromium that current environmental control measures may not be able to meet.

6.2 PERFORMANCE OBSERVATIONS

This project demonstrated that a third-generation wetting WA/FS additive to hard chromium electroplating baths reduced hexavalent chromium airborne emissions to the environment and employee occupational exposures in the electroplating shop. Further, emissions of hexavalent chromium were possibly low enough that regulatory agencies may not require the use of APCDs on exhausts from hard chromium electroplating operations. (Currently, EPA does not require APCDs for *decorative* chromium electroplating operations that use the appropriate amount of WA/FS.) This project also demonstrated that the WA/FS has no negative effect on electroplating quality or the base metals.

There was a dramatic 20- to 70-fold decrease in atmospheric emissions from hard chromium electroplating bath surfaces (i.e., emissions to the APCD) when the WA/FS Fumetrol® 140 was used as a bath additive.

With respect to occupational exposure, when using WA/FS there was generally a significant reduction in breathing zone hexavalent chromium concentration in the vicinity of the chromium electroplating bath. The reduction was not as dramatic as with emissions to the APCD, because breathing zone chromium concentrations were already very low prior to use of WA/FS.

Fumetrol® 140 did not degrade the material characteristics of the electroplated chromium or the steel alloys on which it was deposited.

6.3 SCALE-UP

Scale-up testing is not required for the implementation of Fumetrol® 140 at other DoD facilities. The testing described in this report was done with full-size hard chromium electroplating tanks, exhaust systems, etc. The tank production loading used during the testing was typical for high loads. With proper WA/FS concentration maintenance (using a tensiometer for measurement of surface tension), production-type chromium electroplating baths should perform exactly as they did in this investigation.

6.4 OTHER SIGNIFICANT OBSERVATIONS

The question often raised about the emission of mist from electroplating tanks is whether the misting is primarily from the electrical activity at the anodes and cathodes (i.e., the production of hydrogen and oxygen gases), or from mechanical aeration of the tanks to facilitate mixing. The answer became apparent inadvertently during the first day of baseline testing (i.e., testing without WA/FS) at Cherry Point (July 11, 2000). During the first of the three tests on that day there was no electroplating load in the tank. However, the tank was being aerated. The emissions from that test were 0.0454 mg/dscm of hexavalent chromium. The two following tests, under the same conditions, except with loads in the tank, were 6.32 and 0.737 mg/dscm, respectively, more than one order of magnitude higher than with aeration alone. These data suggest that emissions from electrolytic activity during hexavalent chromium electroplating are far more significant than from mechanical aeration. This phenomenon is probably less pronounced in nonhexavalent chromium electroplating operations. Hexavalent chromium plating has very poor cathode efficiency—less than 15 percent, whereas almost all other electroplating operations exceed 90 percent efficiency. Poor efficiency manifests itself by the creation of hydrogen gas at the cathode instead of producing a coating of the desired metal.

6.5 LESSONS LEARNED

It was the original intention of this study to do one baseline test (i.e., without WA/FS) at each of the facilities tested (Cherry Point and Tinker). Subsequent testing at both facilities was expected to be only with WA/FS in the baths. At Cherry Point, however, the facility was not able to reduce the surface tension to below the desired 30 dynes per cm range in the bath being tested (Tank 155). After the baseline test, 33 dynes per cm appeared to be as low as the facility could achieve by adding WA/FS. Consequently, the bath was changed out and replaced with fresh components. Another baseline test was run (on November 15, 2000), and then WA/FS was added for subsequent testing. At that time fresh bath surface tensions between 23 and 27 dynes cm were achieved.

When Tank 155 was originally put into service, and during several years of use, tap water was used to make up for evaporation and dragout. Therefore, it was concluded that the buildup of dissolved salts (e.g., magnesium, calcium, trace metals, and anions) from the tap water reduced the ability of the WA/FS to effectively lower the surface tension. This experience suggests that surface tension reduction may not be achievable in chromium electroplating baths with excessive amounts of contamination, or unless dragout and evaporation are replaced with distilled or

deionized water, as they are at Tinker and North Island. (Cherry Point also recently converted to deionized water.)

6.6 END-USER ISSUES

There are no significant end-user issues with respect to chromium plated product quality associated with using WA/FS. However, EPA has issued a proposed rule (65 FR 62319, 18 October 2000), *Perfluorooctyl Sulfonates: Proposed Significant New Use*, that could affect the use of the WA/FS (Fumetrol® 140) tested for this project. The proposed rule requires that manufacturers of perfluorooctyl sulfonate compounds notify EPA before commencing the manufacture of these substances. The EPA is concerned that these compounds, which appear to be the primary active ingredient in Fumetrol® 140, may be “hazardous to human health and the environment.” This proposed rule has no immediate effect on the use of WA/FS. However, it is conceivable the proposed rule might lead to banning or reducing the use of such compounds for certain uses. The recommended dosage of Fumetrol® 140 for hard chromium electroplating tanks is only 0.25 percent by volume. Therefore, it is unlikely that such low concentration use would ever be regulated for hard chromium operations. This is especially true because the function of Fumetrol® 140 is to significantly reduce the environmental and occupational exposure to a known carcinogen, hexavalent chromium.

Other technologies are constantly being evaluated for the purposes of minimizing or eliminating the need for hexavalent chromium-based electroplating, or minimizing emissions from such plating. Thus far, none of these technologies has been successfully implemented in applications that are currently served by conventional hard chromium electroplating. Some examples are:

- **Tank Lids/Covers.** Covering hard chromium electroplating tanks during plating operations reduces the amount of ventilation required, thus reducing the amount of contaminated air exhausted from the plating operation. However, this approach is not popular because it enhances the possibility of explosive situations (i.e., hydrogen buildup) and interferes with the ability to operate the plating baths on an uninterrupted basis (i.e., electroplating must cease every time the cover is removed to add a part to the bath).
- **HVOF Thermal Spray Systems.** This is a technology that allows the application of chromium to metal substrates through high temperature techniques. However, the application is limited to line-of-sight coatings, whereas electroplating provides for more uniform coatings. Consequently, HVOF may somewhat reduce the need for hard chromium electroplating but is not expected to ever be able to eliminate it. NADEP Cherry Point estimates that 20 to 40 percent of existing hard chrome operations would continue even after implementation of HVOF.
- **Trivalent Chromium Electroplating.** Chromium can be electroplated from a trivalent chromium bath (e.g., chromium sulfate). Trivalent chromium is much less toxic than hexavalent chromium. However, thus far, trivalent chromium techniques do not yield the quality of coating or the rate of deposition that is available from hexavalent plating.

- **Alternative Coatings.** On an R&D basis, several nickel/cobalt alloys have been evaluated as alternatives to chromium coatings. Much study is still required to determine if the coating quality is as good as chromium when subjected to real-world conditions.

6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

Currently DoD hard chromium electroplating tanks have air emission permits regulating discharges to the atmosphere. Using WA/FS will not, under current EPA regulations, eliminate the need for these permits. Even though the use of WA/FS will undoubtedly lower the amount of chromium exhausted to APCDs, it will probably not be any less time consuming to obtain new or renewal permits from permitting agencies. However, DoD should persist in efforts to convince EPA to allow the use of WA/FS *instead of* APCDs, as the EPA has done for *decorative* chromium electroplaters. If these efforts are successful, there is the potential for large savings in being able to “turn off” existing APCDs, or in not having to install APCDs on new hard chromium electroplating tanks.

Results of the current project suggest that hard chromium electroplaters would be able to meet the proposed $5.0 \mu\text{g}/\text{m}^3$ OSHA workplace concentration value for hexavalent chromium but not the $0.5 \mu\text{g}/\text{m}^3$ proposed value, whether or not WA/FS were used. The results also suggested that under the more stringent $0.5 \mu\text{g}/\text{m}^3$ standard all *breathing zone* samples would still comply, whether or not WA/FS were used. However, if WA/FS were not used, it is quite likely that hard chromium operations would not be able to meet the $0.5 \mu\text{g}/\text{m}^3$ standard for exposures just above the bath surface.

With respect to OSHA compliance relative to in-plant emissions of hexavalent chromium, WA/FS undoubtedly lowers the amount of hexavalent chromium available for respiration by workers. This might allow hard chromium electroplating tanks to operate with less exhaust volume and still comply with OSHA regulations (current or proposed). This benefits new hard chromium installations but probably results in no practical savings for existing installations. Existing installations (or new installations whose ventilation systems are designed to current flow standards) could still benefit from use of WA/FS through lower workman compensation liability with respect to hexavalent chromium respiratory illness claims.

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APPENDIX A

POINTS OF CONTACT

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