Appendix C

Methodology for Estimating Hexavalent Chromium Emissions from Thermal Spraying

C.1. Introduction

Hexavalent chromium emissions from thermal spraying can be estimated by direct measurement of facility exhaust gases or by performing calculations based on material usage. Measurement of exhaust gases is generally the preferred method for individual facilities, but conducting stack exhaust tests can be costly. Therefore, we have developed calculation methods that can be used to estimate hexavalent chromium emissions for different types of thermal spraying processes and the associated air pollution control devices. The following sections describe the process that was used to develop emission estimation methods for thermal spraying.

C.2. Hexavalent Chromium Fumes from Thermal Spraying

Hexavalent chromium and hexavalent chromium compounds are classified as toxic air contaminants, but hexavalent chromium compounds are not generally present in thermal spraying materials as a raw ingredient. The types of chromium that are listed as ingredients include:

- Chromium CAS # 7440-47-3
- Chromium +3 (trivalent) CAS # 16065-83-1
- Chromium Oxide CAS # 1308-38-9

Even though hexavalent chromium compounds are not originally present in thermal spraying materials, numerous stack tests have measured emissions of hexavalent chromium from thermal spraying facilities. This indicates that a conversion occurs during the thermal spraying process to change chromium from an elemental or trivalent state to a hexavalent state. A supplier of thermal spraying materials has found that hexavalent chromium may be produced when materials are exposed to the high temperatures that are involved in many thermal spraying processes (Praxair, 2002). In addition, a thermal spraying industry report states that vaporized metallic chromium can cause a small fraction of the chromium to oxidize and form chromates that contain a hexavalent form of chromium (Smith, 1994). This conversion to hexavalent chromium was measured during Sawatari's study of a plasma metal spraying process with chromium metal (Sawatari, 1986). Researchers used a METCO 7MC plasma metal sprayer and 99.9% chromium powder to generate fumes that were then analyzed to determine the hexavalent chromium content. Total chromium was determined with an atomic absorption spectrometer. Hexavalent chromium was determined by the colorimetric method, using an ultraviolet-visible (UV-Vis) spectrophotometer. Results indicated that metallic chromium was undetectable in the fumes (less than 0.5% of the total), but the fumes did contain 30% hexavalent chromium compounds as shown in Table C-1.

Table C-1:
Chromium Compounds in Plasma Spraying Fumes

Name of Compound	CAS #	MW*	% of Total
Dichromium Trioxide (Cr_2O_3) [corundum structure]	1308-38-9	152	25%
Chromium (VI) Trioxide (CrO_3)	1333-82-0	100	**3%**
Mixed Oxide Fraction Containing:			
Dichromium (III) Trioxide (Cr_2O_3)	1308-38-9	152	45%
Chromium (VI) Trioxide (CrO_3)	1333-82-0	100	**27%**
		Total =	100%

*MW = Molecular Weight, grams/mole

In another study, researchers used a plasma spraying gun to generate metal fumes from chromium powder. Total chromium was determined with an atomic absorption spectrometer. Hexavalent chromium was determined by the colorimetric method, using an ultraviolet-visible (UV-Vis) spectrophotometer. Chemical analysis determined that 26.4% of the total chromium was hexavalent and the residue was trivalent (Serita, 1990). These results are consistent with the values obtained from Sawatari's study.

The California Occupational Safety and Health Administration (Cal/OSHA) conducted additional research on plasma spraying activities (Gold, 2000). They conducted personal air sampling during two days of plasma spraying activities and measured the concentrations of hexavalent chromium, total chromium, and nickel. Hexavalent chromium was measured using the following analytical methods: NIOSH 7600 (visible absorption spectrophotometry), NIOSH 7604 (ion chromatography conductivity detection), and OSHA 215 (ion chromatography with UV-Vis detector). For the first day, the hexavalent chromium concentration was 0.074 mg/m^3 for two different samples, while the total chromium concentration was 0.110 mg/m^3 for one sample and 0.230 mg/m^3 for the other sample. On the second day, hexavalent chromium levels were much higher, measuring 0.646 mg/m^3 for one sample and 7.230 mg/m^3 for the other sample, while total chromium was 10.172 mg/m^3 and 27.258 mg/m^3, respectively. Based on these results, it is possible to estimate the percentage of total chromium that is in the hexavalent form (e.g., 0.074 /0.110 mg/m^3 = 67%). The average percentage of hexavalent chromium is 33%, which is consistent with the results from the Sawatari and Serita studies.

Hexavalent chromium emissions were also measured during a NIOSH Health Hazard Evaluation at a thermal spraying facility (NIOSH, 1989). Air samples were collected while workers conducted electric arc spraying with wires made of stainless steel, bronze, and alcro (aluminum, chromium, and iron). These samples were analyzed for a variety of metals, including hexavalent chromium, total chromium, and nickel. Hexavalent chromium was measured using the analytical method of NIOSH 7600 (visible absorption spectrophotometry.) During twelve sampling events, hexavalent chromium was detected in concentrations ranging from 0.12 to 0.34 mg/m^3 at the face of the ventilation hood. Total chromium concentrations ranged from 1.82 to 2.22 mg/m^3 and the average percentage of hexavalent chromium was 11%. These results confirm that hexavalent chromium is generated during electric arc spraying, but the percentage of hexavalent chromium in the fumes is lower than has been measured for plasma spraying. This may be because plasma spraying generates much higher temperatures and particle velocities than electric arc spraying.

As these studies demonstrate, the formation of hexavalent chromium during thermal spraying has been documented for a variety of sources, but the quantities that are emitted can vary widely, depending on the type of process and the type of control device. Some stack tests have found that more than 90% of the total chromium being measured consists of hexavalent chromium, while other tests have found less than 5%. The most conservative approach for estimating statewide emissions would be to assume maximum conversion to hexavalent chromium and complete consumption of all materials sold in California during 2002. However, ARB staff has developed a method that involves estimating emissions by compiling data from a variety of sources and a range of control devices. The following sections describe the different sources that were used to develop emission factors and estimate hexavalent chromium emissions on an annual basis and an hourly (average and maximum) basis.

C.2.1. Particle Sizes

Emissions and control device efficiencies are dependent on the size of the particles that are generated by thermal spraying processes. Some research has been done to measure particle sizes for thermal spraying processes and the results indicate that particle diameters can range from less than one micron to more than 100 microns. In Serita's study, fume particles from a plasma spraying gun were examined with a scanning electron microscope. The mass median aerodynamic diameter and the geometric standard deviation of the chromium fumes were 2.1 um and 2.00 um, respectively. Those of the nickel fumes were 3.7 um and 1.74 um, respectively (Serita, 1990). Chadwick's study also used a scanning electron microscope to examine fume particulate generated by electric arc, plasma and detonation gun spraying. This study found that particles were of two distinct types: crystalline/angular particles with diameters from 5 um to 20 um and smaller spherical particles ranging from <1 um to 10 um. Both plasma and detonation gun spraying produced a high proportion of particles with a diameter <2 um (Chadwick, 1997.) Both Chadwick's and Serita's studies indicate that metal fumes from thermal spraying contain a large portion of particles that are less than 5 um. We also found data on the "dust" that is generated by thermal spraying. Table C-2 contains particle size distributions for a variety of thermal spraying processes and the results indicate that 90% of the dust particles are larger than 5 microns (Smith, 1994). The analytical method that was used to measure these particles was not provided.

Table C-2:
Typical Particle Size Distributions in Dust of Thermal Spray Processes

Process	1 um	>1-5 um	5-10 um	10-50 um	50-100 um	>100 um
Flame/Wire Metallizing	2	8	10	20	40	20
Wire-Arc (Zinc)	-	1	2	21	-	76
Wire-Arc (Aluminum)	10	-	3	-	87	-
Powder/Flame	1	9	20	30	30	10
HVOF	1	9	30	55	5	-
Plasma	3	7	30	40	20	-

(Smith, 1994)

C.3. Hexavalent Chromium Emission Factors - Summary

The general approach for estimating emissions involves multiplying emission factors by usage rates. Emission factors were obtained from a variety of sources, based on the type of process, the form of material being used (i.e., powder or wire), and the type of control device. In some cases, emission factors were taken directly from stack test results, while other factors were derived from a combination of stack test results, research data, and data on control efficiencies. Table C-3 summarizes the emission factors that were used and Section C.4 describes how these factors were derived.

Table C-3:
Emission Factor Summary – Hexavalent Chromium

Process	Emission Factors (lbs Cr^{+6}/lb Cr sprayed)			
	0% Ctl. Eff. (Uncontrolled)	90% Ctl. Eff. [1] (e.g. Water Curtain)	99% Ctl. Eff. (e.g. Dry Filter)	99.97% Ctl. Eff. (e.g., HEPA Filter)
Single-Wire Flame Spray[2]	4.68E-03	4.68E-04	4.68E-05	1.40E-06
Twin-Wire Electric Arc Spray[2]	6.96E-03	6.96E-04	6.96E-05	2.09E-06
Flame Spray[3]	6.20E-03	1.17E-03	6.20E-05	1.86E-06
HVOF[3]	6.20E-03	1.17E-03	6.20E-05	1.86E-06
Plasma Spray[4]	1.18E-02	6.73E-03	2.61E-03	2.86E-06
Other Thermal Spraying[5]	7.17E-03	2.05E-03	5.70E-04	2.01E-06

1. Listed below the control efficiencies are examples of control devices that may meet the control efficiency.
2. Emission factors based on Battelle study.
3. Emission factors based on SDAPCD stack test data for flame spraying.
4. Emission factors based on stack test results compiled by CATEF, SCAQMD, and SDAPCD.
5. For "Other Thermal Spraying" processes, we used an average of the emission factors for the listed thermal spraying processes.

C.4. Emission Factor Development

The following sections describe how emission factors are derived from various sources for different types of thermal spraying processes and control devices. In each case, emission factors are developed for operations that had no air pollution control devices (i.e., uncontrolled) and for operations that had control devices (i.e., controlled).

C.4.1. Emission Factors: Flame Spraying & Electric Arc Spraying with Wire

Emission factors for wire spraying are based on a study that was conducted by Battelle for the American Welding Society. The study was primarily focused on measuring fumes from welding, but it also included using an enclosed fume collection chamber to measure the quantities of fumes generated by combustion flame spraying with stainless steel wire, and twin-wire electric arc spraying with stainless steel wire (AWS, 1979.) Results of the study are summarized in Table C-4.

Table C-4:
Fume Generation Rates - Flame Spraying & Electric Arc Spraying with Wire

Process	[wt. of fumes] / [wt. of metal sprayed] (grams/kg)	Total Chromium Content in Fumes (weight %)	Type of Wire
Single-Wire Flame Spray	16.6	8-15	316 Stainless Steel (16-18 % Cr)
Twin-Wire Electric Arc Spray	19.75	10-20	Proprietary Stainless Steel (17-18 % Cr)

(AWS, 1979)

The results of this study can be used to determine the maximum pounds of total chromium fumes that are generated for each pound of chromium sprayed.

[max. wt. of total chromium in fumes] = [wt. of fumes]*[max. total chromium content in fumes]
[min. wt. of total chromium sprayed] = [wt. of metal sprayed]*[min. chromium content of metal]

Flame Spray (wire):
[max. wt. of total chromium in fumes] = [16.6 grams]*[15%] = 2.49 grams
[min. wt. of total chromium sprayed] = [1 kg metal]*[16%] = 0.16 kg = 160 grams
max. wt. of total Cr in fumes per lb. of total Cr sprayed = [2.49 g]/[160 g] = 1.56E-02 g Cr/g Cr sprayed
= 1.56E-02 lb Cr/lb Cr sprayed

Electric Arc:
[max. wt. of total chromium in fumes] = [19.75 grams]*[20%] = 3.95 grams
[min. wt. of total chromium sprayed] = [1 kg metal]*[17%] = 0.170 kg = 170 grams
max. wt. of total Cr in fumes per lb. of total Cr sprayed = [3.95 g]/[170 g] = 2.32E-02 g Cr/g Cr sprayed
= 2.32E-02 lb Cr/lb Cr sprayed

Since the study only measured total chromium, we used the conclusions of the Sawatari study and other studies to estimate that 30% of the total chromium consists of hexavalent chromium. Listed below are the uncontrolled emission factors for wire spraying processes.

Flame Spray (wire): [1.56E-02]*[30%] = **4.68E-03** lb Cr^{+6}/lb chromium sprayed

Electric Arc: [2.32E-02]*[30%] = **6.96E-03** lb Cr^{+6}/lb chromium sprayed

To determine controlled emission factors, we used the following equation:

Eqn. 1: [Controlled Emission Factor] = [Uncontrolled Emission Factor][1 – Control Efficiency]*

Controlled emission factors for wire were developed for the following levels of control:

Control Efficiency Levels	
90%	(e.g., a water curtain)
99%	(e.g., dry filter)
99.97%	(e.g., a HEPA filter)

The actual control efficiency for a control device at a particular facility can depend on specific parameters (e.g., particle size, filter media, etc.), but the control efficiencies listed above are consistent with general industry estimates. Calculations for controlled emission factors are provided below:

Flame (wire) –

90% (e.g., water curtain): [4.68E-03 lb Cr^{+6}/lb wire]*[1 – 0.90] = **4.68E-04** lb Cr^{+6}/lb Cr
99% (e.g., dry filter): [4.68E-03 lb Cr^{+6}/lb wire]*[1 – 0.99] = **4.68E-05** lb Cr^{+6}/lb Cr
99.97% (e.g., HEPA filter): [4.68E-03 lb Cr^{+6}/lb wire]*[1 – 0.9997] = **1.40E-06** lb Cr^{+6}/lb Cr

Electric Arc –

90% (e.g., water curtain): [6.96E-03 lb Cr^{+6}/lb wire]*[1 – 0.90] = **6.96E-04** lb Cr^{+6}/lb Cr
99% (e.g., dry filter): [6.96E-03 lb Cr^{+6}/lb wire]*[1 – 0.99] = **6.96E-05** lb Cr^{+6}/lb Cr
99.97% (e.g., HEPA filter): [6.96E-03 lb Cr^{+6}/lb wire]*[1 – 0.9997] = **2.09E-06** lb Cr^{+6}/lb Cr

C.4.2. California Air Toxic Emission Factors – Thermal Spraying

ARB has developed a database of California Air Toxic Emission Factors (CATEF), based on source test data that were compiled for the Air Toxics Hot Spots Program. Source test reports were reviewed to verify the validity of the test methods and results. The validated report data were then used to develop the CATEF emission factors. The CATEF II database can be accessed on the ARB website (http://www.arb.ca.gov/emisinv/catef/catef.htm) and it includes a search function that enables users to identify emission factors for specific Source Classification Codes (SCCs). For thermal spraying, the CATEF II database contains emission factors for general thermal spraying of powdered metal (SCC 30904010) and plasma spraying of powdered metal (SCC 30904020).

CATEF contains thermal spraying emission factors for hexavalent chromium and total chromium, as shown in Table C-5. The factors are based on the quantity of material sprayed. To determine the emission factor based on the quantity of chromium metal sprayed, we used the following equation:

Eqn. 2:
$$\text{Emission Factor, } \frac{\text{lbs } Cr^{+6}}{\text{lb chromium}} = \text{Emission Factor, } \frac{\text{lbs } Cr^{+6}}{\text{lb material}} \times \frac{1}{\text{wt\% chromium in material}}$$

Different factors are provided based on the type of material that was sprayed and the air pollution control device (APC Device). In some cases, the APC Device is listed as an air filter, but no data were provided regarding control efficiency. Therefore, we have assumed that the air filters have a control efficiency of 99%, which is a low-end, conservative assumption for the efficiency of a dry filter system.

Table C-5:
Emission Factors – CATEF: Thermal Spraying Processes

Process*	APC Device	Material Type		Hexavalent Chromium Emission Factors		Total Chromium Emission Factors	
		Description	Wt % Cr	(lbs Cr^{+6}/lb matl used)	(lbs Cr^{+6}/lb Cr used)	(lbs total Cr/ lb matl used)	(lbs total Cr/ lb Cr used)
General Thermal Spray	None	8.5% Cr	8.5%	3.34E-05	3.93E-04	3.82E-03	4.49E-02
Plasma Spray	None	75%Cr_3C_2, 20%NiCr, 5% Cr	Unk.	1.63E-02	-	3.75E-01	-
Plasma Spray	None	80%Ni, 20%Cr	20%	2.58E-04	1.29E-03	1.86E-03	9.30E-03
Plasma Spray	None	100% Chromium Oxide	68%	8.90E-03	1.31E-02	1.42E-01	2.09E-01
Plasma Spray	Air Filter	70%Ni, 4%Cr	4%	1.81E-04	4.53E-03	1.86E-04	4.65E-03
Plasma Spray	Air Filter	49% Ni, 44%Cr	44%	3.01E-04	6.84E-04	4.03E-04	9.16E-04

* General Thermal Spraying of Powdered Metal – SCC 30904010
Plasma Arc Spraying of Powdered Metal – SCC 30904020
"Unk." – The total weight percent for chromium is unknown, because the chromium weight percentage in the Nickel-Chromium (NiCr) alloy was not specified.

Average CATEF hexavalent chromium emission factors were calculated as follows:

Plasma Spraying – Uncontrolled: (1.29E-03 + 1.31E-02)/2 = 7.20E-03 lbs Cr^{+6}/ lb Cr used
Plasma Spraying – Air Filter: (4.53E-03 + 6.84E-04)/2 = **2.61E-03** lbs Cr^{+6}/ lb Cr used

The uncontrolled CATEF value was then combined with factors from other sources to develop an overall average emission factor for plasma spraying (see Section C.4.5.)

C.4.3. SDAPCD Emission Factors for Plasma Spraying & Flame Spraying

The San Diego County Air Pollution Control District (SDAPCD) has compiled the following emission factors for various plasma spraying and flame spraying facilities, based on stack test data (SDAPCD, 1998).

Table C-6:
SDAPCD Emission Factors – Hexavalent Chromium and Nonhexavalent Chromium

SDAPCD Method #	Process	Control Device	Emission Factors	
			(lb Cr^{+6}/lb Cr sprayed)	(lb non-hex Cr/lb Cr)
M01	Plasma Spray	HEPA	3.94E-06	3.31E-05
M02	Plasma Spray	HEPA	2.19E-06	1.35E-05
M03	Plasma Spray	HEPA	3.07E-06	2.32E-05
M04	Plasma Spray	Water Curtain	1.02E-03	2.70E-04
M05	Plasma Spray	Water Curtain	2.83E-03	2.08E-02
M06	Plasma Spray	Water Curtain	1.93E-03	1.05E-02
M08	Flame Spray	HEPA	**1.86E-06***	1.52E-04
M09	Flame Spray	Water Curtain	**1.17E-03***	7.15E-02

* Bold highlighting indicates a value that appears in the emission factor summary table.

For flame spraying facilities, the following controlled emission factors were used from SDAPCD Methods M08 and M09 –

HEPA Filter: **1.86E-06** lbs Cr^{+6}/lb chromium sprayed
Water Wash Booth: **1.17E-03** lbs Cr^{+6}/lb chromium sprayed

To determine an uncontrolled emission factor for a flame spraying facility, we used the following equation:

Eqn. 3: [Uncontrolled Emission Factor] = [Controlled Emission Factor]/[1 – Control Efficiency]

The uncontrolled emission factor for flame spraying was calculated as shown below:

Emission Factor for Flame Spraying with a HEPA Filter = 1.86E-06 lb Cr^{+6}/lb Cr sprayed
Estimated Control Efficiency for a HEPA Filter = 99.97%
[Uncontrolled Emission Factor] = [1.86E-06]/[1 – 0.9997] = **6.2E-03** lb Cr^{+6}/lb Cr sprayed

The emission factor for flame spraying with a dry filter was calculated as shown below:

Uncontrolled Emission Factor for Flame Spraying = 6.2E-03 lb Cr^{+6}/lb Cr sprayed
Control Efficiency = 99% (e.g., a dry filter)
[Controlled Emission Factor @ 99%] = [6.2E-03]*[1 – 0.99] = **6.2E-05** lb Cr^{+6}/lb Cr sprayed

The emission factors for flame spraying were also used to estimate emissions from HVOF processes, because they are both combustion-based operations that achieve comparable temperatures.

The emission factors in Table C-6 are based on stack test data from several thermal spraying facilities in the San Diego area. ARB staff reviewed these stack test results and selected tests that had the strongest staff evaluations. In addition to these tests, SDAPCD provided results from two stack tests that were conducted in 2002 at a plasma spraying facility. For plasma spraying, results from the following eight tests were selected to develop an average emission factor. All of the tests in Table C-6 used ARB Method 425 to measure hexavalent chromium emissions.

Table C-6:
Stack Test Results from Plasma Spraying Facilities in SDAPCD

Test #	Control Device	Material Sprayed During Test		Emissions	Emission Factor	
		Spray Rate (lb/hr)	Wt.% Chromium	(lbs Cr^{+6}/hr) per ARB Method 425	(lbs Cr^{+6}/ lb Cr sprayed)	(lbs total Cr/ lb Cr)
#1	HEPA	19.1	20.3%	1.037E-05	2.67E-06	2.36E-05
#2	Water Wash Booth	1.24	25.5%	5.23E-04	1.66E-03	1.64E-03
#3	HEPA	13.4	20%	1.03E-05	3.94E-06	3.70E-05
#4	Water Wash Booth	11.5	20%	6.15E-04	2.67E-04	6.72E-04
#5	HEPA	7.27	19%	8.19E-06	5.96E-06	2.02E-05
#6	HEPA	9.37	19%	6.59E-06	3.74E-06	1.62E-05
#7	HEPA	10.09	19%	8.28E-07	4.32E-07	6.42E-05
#8	HEPA	9.8	19%	8.29E-07	4.44E-07	1.06E-04
			Average:	HEPA	**2.86E-06**	4.45E-05
			Average:	Water Wash	9.64E-04	1.16E-03

(ERM, 1995; SCEC, 1998; SCEC, 1998a; SCEC, 2001; SDAPCD, 2002; SDAPCD, 2004)

The average value for the water wash booth in Table C-6 was combined with other data to develop an overall average emission factor for plasma spraying (see Section C.4.5.)

C.4.4. SCAQMD Emission Factors for Plasma Spraying

The South Coast Air Quality Management District (SCAQMD) worked with Pacific Environmental Services to develop an emission inventory for metal welding, cutting, and spraying operations. In May, 2000, Pacific Environmental Services completed an emission inventory report which contained metal spraying emission factors for total chromium (PES, 2000). The emission factors for total chromium were based on stack tests that were conducted at six facilities in the SCAQMD and the SDAPCD from 1987 to 1991. All of the facilities conducted plasma spraying during the stack tests. The report did not recommend an emission factor for hexavalent chromium, because the authors felt that the stack tests were conducted before improvements in laboratory methods allowed for reliable discrimination between total and hexavalent chromium. However, the report did refer to the previously cited Sawatari study which found that the fumes from plasma spraying contain approximately 30% hexavalent chromium (Sawatari, 1986).

The SCAQMD report concluded that the data could be reduced to two emission factors: one factor for a facility with a HEPA filter ($1.0x10^{-5}$ lb total Cr/lb Cr sprayed), and another factor for all other facilities ($5.1x10^{-2}$ lb total Cr/lb Cr sprayed). For the purposes of this report, we have reviewed the available stack test data and have used the results from 10 test runs at facilities with water curtains and 2 test runs at uncontrolled facilities to support development of our emission factors. The tests were conducted from 1989 to 1991. Listed below are average emission factors for total chromium and hexavalent chromium, based on the stack test data in the SCAQMD report (see Table C-7).

Table C-7:
Emission Factors – SCAQMD Plasma Spraying

Control Devices	Emission Factors		Test Methods
	(lb total chromium/ lb Cr sprayed) [1]	(lb Cr^{+6}/ lb Cr sprayed) [2]	
Water Curtain	4.15E-02	1.25E-02	ARB Method 425 SCAQMD Method 205.1
Uncontrolled	5.44E-02	1.63E-02	Unknown

1. These values are based on stack test results in the SCAQMD report (PES, 2000.)
2. These values are based on the assumption that 30% of the total chromium is in the hexavalent form.

C.4.5. Summary of Average Plasma Spraying Emission Factors

CATEF, SDAPCD, and SCAQMD provided emission factors for plasma spraying processes. We used average values from these sources for our emission factor calculations, as shown below:

Table C-8:
Average Emission Factors – Plasma Spraying

Reference	Control Device	Emission Factor (lb Cr^{+6}/lb Cr)	Average Emission Factor (lb Cr^{+6}/lb Cr)
SDAPCD	Water Curtain	9.64E-04	**6.73E-03**
SCAQMD	Water Curtain	1.25E-02	
CATEF	Uncontrolled	7.20E-03	**1.18E-02**
SCAQMD	Uncontrolled	1.63E-02	

C.4.6. Thermal Spraying Emission Data from Other States

ARB staff contacted regulatory agencies in the following states to gather information on their methods for estimating emissions from thermal spraying sources:

Connecticut	Michigan	Pennsylvania
Florida	New Jersey	Texas
Georgia	New York	Virginia
Massachusetts	Ohio	Wisconsin

Most of the states that we contacted have permitting thresholds that allow smaller facilities to be exempt from obtaining an air permit. For example, some states do not require permitting or toxics screening for facilities that emit less than 1 ton/yr of hazardous air pollutants. Since many thermal spraying facilities fall below this threshold, the available permit data were generally restricted to relatively large thermal spraying operations. Stack testing was not required in most cases, so emissions were frequently estimated using the following equation:

Eqn. 4: Emissions, lbs PM/yr = [Material Usage, lbs/yr][1- T.E.]*[1 - Dropout]*[1 – C.E.]*

where

Emissions, lbs PM/yr = Pounds of particulate matter emissions per year
T.E. = Transfer Efficiency, which is the fraction of sprayed material that adheres to the part surface. Material that does not adhere to the surface is called overspray.
Dropout = The fraction of particles that drop out of the overspray before it is sent through the control device. This drop out can occur in the booth or the ductwork.
C.E. = Control Efficiency, which is the fraction of pollutants that are not emitted into the air due to the control device.

Equation #4 can be rearranged to yield an emission factor equation, as shown below:

$$\text{Eqn. 5: Emission Factor, } \frac{\text{lbs PM}}{\text{lbs matl./yr}} = \frac{\text{[Emissions, lbs PM/yr]}}{\text{[Material Usage, lbs/yr]}} = [1-\text{T.E.}]*[1-\text{Dropout}]*[1-\text{C.E.}]$$

ARB has used this equation to compare the emission factors from other states with those developed by ARB. The following sections contain information that we obtained from other states for some of the thermal spraying facilities that were identified. We've also included some emission factor comparisons, which demonstrate that ARB's emission estimation methods are generally comparable to the methods used by other states.

Connecticut

Sources Identified - Staff members identified one Title V source that operates two thermal spraying booths, one for plasma spraying and one for HVOF spraying.

Control Devices – Both booths are equipped with HEPA filter systems, rated at 99.99% and 99.97% efficiency.

Permit Limits - Maximum application rates are 15 lb/hr for each booth. The permit contains mass limits for total suspended particulate (TSP) and concentration limits for hazardous air pollutants. For plasma spraying, the TSP emissions limit is 5.25E-04 lb TSP/hr while the HVOF process has no hourly limit. Both processes have annual TSP limits of 2.3E-03 tons per 12 consecutive months. To control toxic emissions, the permit contains maximum allowable stack concentrations that are equivalent to 150 ug Cr^{+6}/m^3 for the plasma spraying and 6.8 ug Cr^{+6}/m^3 for the HVOF process. These limits were determined in accordance with state air toxic regulations.

Stack Testing/Modeling - No stack testing or air dispersion modeling was required, because the facility emits less than 3 tpy of PM.

Emission Factors -

$$\text{Emission Factor, } \frac{\text{lbs TSP}}{\text{lbs matl./yr}} = \frac{[5.25\text{E-04 lb TSP/hr}]}{[15 \text{ lbs material/hr}]} = \frac{3.5\text{E-05 lb TSP}}{\text{lb material}}$$

Since total chromium is a component of the thermal spraying material, this emission factor also applies to total chromium emissions. If it is assumed that the total chromium contains 30% hexavalent chromium (i.e., 0.3 lbs Cr^{+6}/lb Cr), the following emission factor for hexavalent chromium can be derived:

Emission Factor = [3.5E-05 lbs total Cr/lb Cr sprayed]*[0.3 lbs Cr^{+6}/lb Cr] = [**1.05E-05** lbs Cr^{+6}/lb Cr]

This Connecticut emission factor lies between ARB's average HVOF/Plasma Spray emission factor for a control device with 99% efficiency and ARB's emission factors for a control device with 99.97% efficiency. Therefore, it appears that Connecticut's emission estimation methodology is reasonably consistent with ARB's methods.

Florida

Sources Identified - Staff members identified one thermal spraying facility that operated multiple booths.

Control Devices – The booths used two types of control devices – wet impingers (95% efficiency) and dry dust collectors (99% efficiency).

Permit Limits – ARB did not obtain a copy of the local permit.

Stack Testing/Modeling - No stack testing or air dispersion modeling was required.

Emission Factors - Emissions were calculated based on a 60% transfer efficiency (T.E.) and a 50% dropout rate. For a booth with a wet impinger (95% control efficiency), the emission factor would be -

$$\text{Emission Factor, } \frac{\text{lbs PM}}{\text{lbs matl./yr}} = [1\text{- T.E.}]*[1 - \text{Dropout}]*[1 - \text{C.E.}] = [1\text{-}0.6]*[1\text{-}0.5]*[1\text{-}0.95] = 1.00\text{E-02}$$

Since total chromium is a component of the thermal spraying material, this emission factor also applies to total chromium emissions. If it is assumed that the total chromium contains 30% hexavalent chromium, the following emission factor for hexavalent chromium can be derived:

Emission Factor = [1.00E-02 lbs Cr/lb Cr]*[0.3 lbs Cr^{+6}/lb Cr] = [**3.0E-03** lbs Cr^{+6}/lb Cr sprayed]

This value is between the ARB overall average emission factor for a control device with 90% efficiency and a control device with 99% efficiency, as summarized in Table C-3. Therefore, these results are consistent with ARB's methods.

New York

Sources Identified – Staff members identified one Title V source that operates four thermal spraying booths for a combination of HVOF and plasma spraying. One booth contains three thermal spraying units. The source is primarily a research facility, but it is permitted to conduct manufacturing, if needed.

Control Devices – Control devices include a baghouse/filter (99%+); fabric filter (95%)/Dollinger filter (98%); and a water curtain (90%).

Permit Limits – Maximum spray rates range from 10 lbs/hr to 1,050 lbs/hr for the highest capacity process. Annual usage limits range from 10,000 lbs/yr to 250,000 lbs/yr.

Stack Testing/Modeling - No stack testing or air dispersion modeling was required.

Emission Factors - Emissions were calculated based on transfer efficiencies (50% or 75%, depending on booth), a 90% dropout rate, the efficiencies of the control devices, and other assumptions. For the largest unit which vents to a baghouse/filter, 0.5% of quantity sprayed is emitted (i.e., the emission factor is 5.0E-03 lbs PM/lb matl.) Since the material being sprayed contains chromium, this 0.5% emission factor also applies to the chromium being sprayed (5.0E-03 lbs Cr/lb Cr sprayed). If it is assumed that the total chromium contains 30% hexavalent chromium, the following emission factor for hexavalent chromium can be derived:

Emission Factor = [5.0E-03 lbs Cr/lb Cr]*[0.3 lbs Cr^{+6}/lb Cr] = [**1.5E-03** lbs Cr^{+6}/lb Cr sprayed]

This value is between the ARB HVOF emission factor for a control device with 90% efficiency and a control device with 99% efficiency, as summarized in Table C-3. Therefore, these results are reasonably consistent with ARB's methods.

Ohio

Sources Identified – Staff members identified four permitted thermal spraying facilities, one of which was a Title V source with three plasma spraying booths.

Control Devices – The booths were vented to baghouses with 99% control efficiency.

Permit Limits – The maximum material usage rate is 8 lbs/hr and the annual operating limits are either 1,814 hours/yr or 3,267 hours/yr, depending on the booth. Hourly particulate emissions are limited to 0.551 lbs PM/hr for all of the booths. Maximum allowable annual emissions are either 0.5 tpy or 0.9 tpy, depending on the booth.

Stack Testing/Modeling - No stack testing or air dispersion modeling was required.

Emission Factors - Emissions were calculated based on a 65% transfer efficiency (T.E.) and a 99% control efficiency. No assumption was made regarding dropout percentage (i.e., dropout = 0.)

$$\text{Emission Factor, } \frac{\text{lbs PM}}{\text{lbs matl./yr}} = [1\text{- T.E.}]*[1 - \text{Dropout}]*[1 - \text{C.E.}] = [1\text{-}0.65]*[1\text{-}0]*[1\text{-}0.99] = 3.50\text{E-}03$$

The primary pollutant of concern for this facility was nickel, but it is possible to develop an estimated emission factor for chromium as well. If total chromium was a component of the thermal spraying material, the emission factor would also apply to total chromium emissions. If it is assumed that the total chromium contains 30% hexavalent chromium, the following emission factor for hexavalent chromium can be derived:

Emission Factor = [3.50E-03 lbs Cr/lb Cr]*[0.3 lbs Cr^{+6}/lb Cr] = [**1.05E-03** lbs Cr^{+6}/lb Cr sprayed]

This value is between the ARB Plasma Spray emission factor for a control device with 99% efficiency and a control device with 99.97% efficiency, as summarized in Table C-3. Therefore, these results are consistent with ARB's methods.

Pennsylvania

Sources Identified – Staff members identified a Title V permit for a facility that conducted HVOF spraying on print rollers, using a nickel-chromium-copper material.

Control Devices – Emissions are controlled with a HEPA filter that has 99.97% control efficiency.

Permit Limits – Material usage is limited to 1,800 lbs/yr.

Stack Testing/Modeling – No stack testing or air dispersion modeling was required.

Emission Factors – Emissions were calculated based on 92% transfer efficiency, because the roller faces are flat and uniform. No assumption was made regarding dropout percentage (i.e., dropout = 0.)

$$\text{Emission Factor, } \frac{\text{lbs PM}}{\text{lbs matl./yr}} = [1\text{- T.E.}]*[1 - \text{Dropout}]*[1 - \text{C.E.}]=[1\text{-}0.92]*[1\text{-}0]*[1\text{-}0.9997] = 2.40\text{E-}05$$

Since total chromium is a component of the thermal spraying material, this emission factor also applies to total chromium emissions. If it is assumed that the total chromium contains 30% hexavalent chromium, the following emission factor for hexavalent chromium can be derived:

Emission Factor = [2.40E-05 lbs Cr/lb Cr]*[0.3 lbs Cr^{+6}/lb Cr] = [**7.2E-06** lbs Cr^{+6}/lb Cr sprayed]

This value is slightly larger than ARB's HVOF emission factor for a control device with 99.97% control efficiency, as summarized in Table C-3.

C.5. Emission Calculations - Annual

This section describes how emission factors were used to estimate annual hexavalent chromium emissions from thermal spraying processes. The general approach involved multiplying emission factors by annual usage rates, as shown in the following equation:

Eqn. 6: $[\text{Emissions, lbs } Cr^{+6}/\text{year}] = [\text{Emission Factor, lbs } Cr^{+6}/\text{lb Cr}] * [\text{Usage, lbs Cr/year}]$

Emission factors were described in Section C.4 and were summarized in Table C-3.

ARB staff estimated annual emissions using two approaches: (1) potential to emit, based on manufacturer sales data, and (2) actual emissions, based on usage data as reported by individual facilities. When calculating the potential to emit, we used material sales data from ARB's 2003 Thermal Spraying Material Survey (ARB, 2004.) This survey collected sales quantities from thermal spraying materials manufacturers for calendar year 2002. The survey focussed on materials containing chemicals of concern (e.g., chromium and nickel). Based on this survey, more than 70 tons of thermal spraying materials containing chromium were sold or distributed in California during 2002. A report of the manufacturer survey results can be obtained on ARB's website (http://www.arb.ca.gov/coatings/thermal/thermal.htm). When calculating actual emissions, we used material throughput data from thermal spraying businesses, that was obtained from ARB's 2004 Thermal Spraying Facility Survey. The total estimated usage quantity provided by thermal spraying facilities was significantly less than the sales data provided by manufacturers. Since some facilities only provided rough estimates of their usage, we believe that the manufacturer's data are more accurate and yield a more reliable estimate of statewide usage for determining the potential to emit.

Data from ARB's 2003 Thermal Spraying Material Survey provided information on the annual material sales and ingredient percentages. We used these data to calculate the amount of chromium in each material and the potential annual usage of such materials, as shown in the following equations:

Eqn. 7: For products with Chromium

$$[\text{Chromium Qty, } \frac{\text{Lbs}]}{\text{Yr}} = [\text{Material Sales, } \frac{\text{lbs}]}{\text{yr}} * [\text{Wt\% Chromium}]$$

Eqn. 8: For products with Chromium Oxide (Cr_2O_3)

$$[\text{Chromium Qty, } \frac{\text{lbs}]}{\text{yr}} = [\text{Material Sales, } \frac{\text{lbs}]}{\text{yr}} * [\text{Wt\% } Cr_2O_3] * \frac{[104 \text{ g } Cr_2]}{[152 \text{ g } Cr_2O_3]}$$

The manufacturer survey also identified the types of thermal spraying processes associated with each product, which allowed us to select the appropriate emission factors. Some thermal spraying materials were designated as being suitable for two types of processes (e.g., flame spray and plasma spray).

For these multi-use products, an average emission factor value was used, as shown in the following example calculations:

Average Emission Factor Calculation - Uncontrolled Flame Spray & Plasma Spray:
(6.20E-03 + 1.18E-02)/2 = 9.00E-03 lbs Cr^{+6}/lb Cr sprayed

Example Annual Emissions Calculation - Uncontrolled Flame Spray & Plasma Spray:
[10,000 lbs Cr sprayed]* [9.00E-03 lbs Cr^{+6}/lb Cr sprayed] = 90 lbs Cr^{+6}/yr

To calculate potential emissions, we multiplied the applicable emission factor times the quantity of chromium sold. Table C-9 summarizes the California sales in 2002 for thermal spraying products that contain chromium and the associated quantity of chromium contained in those products. Table C-9 also contains the associated processes, emission factors, and emissions values. Potential statewide emissions of hexavalent chromium vary widely, depending on the type of control device used. For example, if all facilities used control devices with 99.97% control efficiency, statewide emissions would be only 0.1 lb/yr. However, statewide emissions would be almost 300 lbs/yr, if all facilities were uncontrolled. Therefore, it is important to identify a control effectiveness when estimating statewide emissions. ARB's 2004 Thermal Spraying Facility Survey provided information on the percentage of facilities that use control devices and the types of devices that were used. The results of this survey indicate that 87% of the thermal spraying facilities in California that use materials containing chromium have a control device. The most common type of control device at these facilities is the dry filter cartridge. Based on this information, the following assumptions were made:

- 87% of the thermal spraying material is used at controlled facilities with dry filters
- 13% of the thermal spraying material is used at uncontrolled facilities
- [Controlled Emissions] = [87%]*[Sales, lbs Cr]*[Emission Factor, lbs Cr^{+6}/lb Cr sold]
- [Uncontrolled Emissions] = [13%]*[Sales, lbs Cr]*[Emission Factor, lbs Cr^{+6}/lb Cr sold]

The survey data indicated that some facilities have HEPA filters (generally more efficient than dry filters) and some facilities have water curtains (usually less efficient than dry filters), so the assumption that controlled facilities use dry filters provides a reasonable representation of the average control efficiencies statewide.

Based on these assumptions, 18 tons of chromium were potentially used at thermal spraying facilities and the potential to emit is 66 pounds for hexavalent chromium statewide in 2002. Table C-9 provides details of potential material usage and potential to emit quantities, based on the manufacturer survey.

To calculate actual emissions, we multiplied the applicable emission factor times the quantity of chromium usage reported by individual facilities. Actual emissions were estimated to be 9.4 pounds, based on facility usage data, process descriptions, and control device information as provided by facilities. It is expected that our estimates of actual emissions and the potential to emit represent lower and upper boundaries for statewide emissions. Therefore, we estimate that annual hexavalent chromium emissions from thermal spraying are in the range of 9.4 – 66 pounds. The difference between estimates of maximum potential emissions and actual emissions may be due to the following factors: 1) materials sold in one year may be used over multiple years; 2) some materials sold to California distributors may be redistributed out of State; and 3) some businesses that conduct thermal spraying may not have been captured by the ARB facility survey.

For this thermal spraying ATCM, we estimated the potential emission reductions based on data from the ARB 2004 Thermal Spraying Facility Survey, the ARB 2003 Thermal Spraying Materials Survey, and the proposed ATCM control efficiency requirements. For a facility with no existing control devices, the proposed ATCM would require at least a 99% reduction in emissions. For the largest facility in the State, the proposed ATCM would require that the control device efficiency be increased from a minimum of 81% to at least 99.97%. Overall, the proposed ATCM is expected to reduce hexavalent chromium emissions by nearly 80 percent (7 to 50 lbs/yr.)

Table C-9:
Thermal Spraying Sales & Potential to Emit Summary - Hexavalent Chromium

Process	Material	Sales of Products Containing Chromium (lbs) [1]	Qty. of Chromium in Products (lbs Cr)	Potential to Emit (lbs Cr^{+6}/yr) [2]
Flame Spray	Powder	6,788	713.4	0.6
Flame Spray/Other	Powder	PD	2,415.0	2.8
Flame Spray/Plasma Spray	Powder	PD	736.5	1.7
HVOF	Powder	7,731	3,279.0	2.8
HVOF/Flame Spray/Plasma Spray	Powder	PD	2,860.7	5.3
HVOF/Plasma Spray	Powder	10,918	5,307.9	12.4
Plasma Spray	Powder	14,780	6,962.3	26.5
Plasma Spray/Other	Powder	PD	22.8	0.1
Powder Subtotal =		**63,612**	**22,298**	**52.1**
Single-Wire Flame Spray	Wire	PD	1,330.1	0.9
Twin-Wire Electric Arc	Wire	PD	13,036.6	12.6
Wire Subtotal =		**79,708**	**14,367**	**13.4**
GRAND TOTAL =		**143,320**	**36,664**	**65.6**

1. "PD": Protected data (fewer than three companies reported sales).
2. Assume 13% of products are used at Uncontrolled facilities and 87% of products are used at facilities with a dry filter control device.

C.6. Emission Calculations –Hourly

When performing health risk assessments, it is typically necessary to identify the average hourly emissions and the maximum hourly emissions. The average hourly emissions are used when calculating the possible impacts from long-term chronic exposure, while the maximum hourly emissions are used to calculate impacts from short-term acute exposures. Reference Exposure Levels (RELs) for short-term acute exposures have not yet been established for hexavalent chromium. Therefore, we did not estimate acute risk for hexavalent chromium, based on the maximum hourly emissions.

Annual average hourly emissions were estimated using the following equation:

Eqn. 5: $$[\text{Annual Avg. Hourly Emissions, lbs } Cr^{+6}/\text{hour}] = \frac{[\text{Annual Emissions, lbs } Cr^{+6}/\text{yr}]}{[350 \text{ days/yr}]*[\text{Daily Operating Hours, e.g., 8 hrs/day}]}$$

These values are converted into units of grams/second for the risk assessment calculations, using the following equation:

Eqn. 6: $$[\text{Hourly Emissions, g/s}] = \frac{[\text{Hourly Emissions, lb } Cr^{+6}]}{[\text{hr}]} * \frac{[453.59 \text{ g}]}{[1 \text{ lb}]} * \frac{[1 \text{ hr}]}{[60 \text{ min}]} * \frac{[1 \text{ min}]}{[60 \text{ sec}]}$$

C.6.1. Annual Average Hourly Emissions

Annual average hourly emissions vary, depending on individual facility operating schedules and other parameters. However, we can estimate statewide annual average hourly emissions, based on the total annual emissions statewide. According to the ARB 2004 Thermal Spraying Facility Survey, 30 facilities reported the use of materials that contain chromium.

$$[\text{Annual Avg. Hourly Emissions}] = \frac{[65.6 \text{ lbs } Cr^{+6}/\text{yr}]}{[350 \text{ days/yr}]*[8 \text{ hrs/day}]*[30 \text{ facilities statewide}]} = \frac{7.81\text{E-04 lbs } Cr^{+6}}{\text{hr}}$$

$$[\text{Hourly Emissions, g/s}] = \frac{[7.81\text{E-04 lbs } Cr^{+6}]}{[\text{hr}]} * \frac{[453.59 \text{ g}]}{[1 \text{ lb}]} * \frac{[1 \text{ hr}]}{[60 \text{ min}]} * \frac{[1 \text{ min}]}{[60 \text{ sec}]} = \frac{\mathbf{9.8E\text{-}05} \text{ grams } Cr^{+6}}{\text{second}}$$

This statewide average, based on manufacturer sales data, is at the high end of the values that are based on individual facility data, as reported in the 2004 ARB Thermal Spraying Facility Survey. For most facilities that reported chromium usage, the annual average emissions were between 1E-09 g/s and 1E-05 g/s, with one outlier at approximately 1E-03 g/s. Since the total sales reported by manufacturers was greater than the total usage reported by individual facilities, it is not surprising that annual average emissions based on manufacturer sales would be higher than emissions based on individual facility data.

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