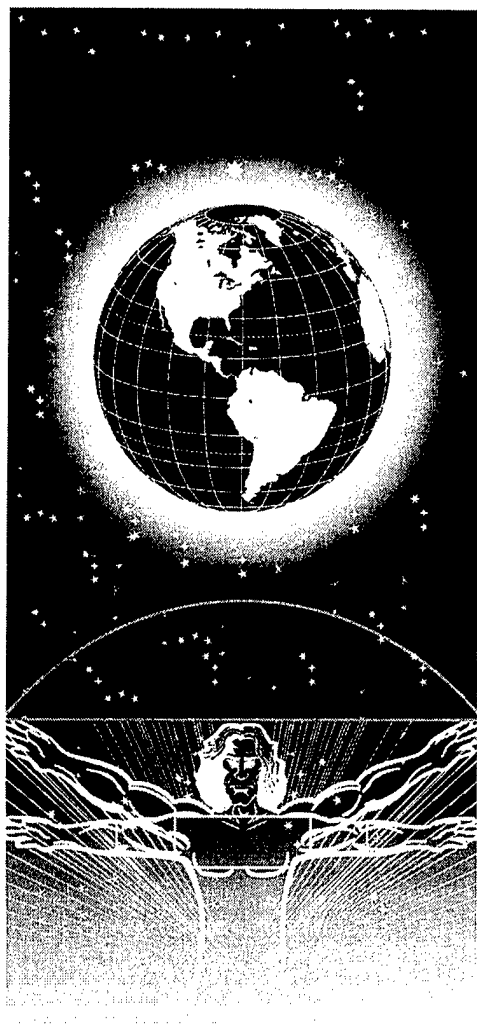




UNITED STATES AIR FORCE IERA

Chromate Sampling Methods and Data Analysis

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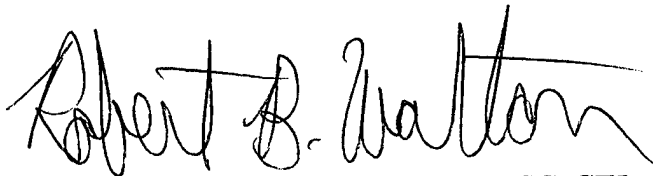
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I. Health Effects

A. The major health issues surrounding occupational exposure to chromates (hexavalent chromium, Cr (VI), CrO₃, are very well summarized in the National Institute for Occupational Safety and Health (NIOSH) publication "criteria for a recommended standard, Occupational Exposure to Chromium VI", 1975. It should be noted that this NIOSH report dealt mainly with the metallurgical, refractory, and plating processes and very little attention was placed on painting related processes. Metallurgical and refractory processes are physically demanding requiring the workers to be exposed to numerous metals, including chrome in various valence states, which are superheated. Workers are exposed to dusts and fumes composed of numerous metals including chrome. In the plating industry, workers are exposed to soluble chromates. These workers have significant skin and potential respiratory exposures to chromates.

B. NIOSH developed their recommended standard for chromate exposure based upon numerous epidemiological reports found in the peer review literature. It is generally accepted that workers in the metallurgical, refractory, and plating industry have increased incidents of nasal septum perforation, chronic rhinitis, and chronic pharyngitis, and skin ulcerations in areas of direct contact with soluble chromates. Finally, workers in these industries also have an increased incidence of respiratory tract related cancers.

C. In the Air Force, metallurgical and refractory processes are essentially non-existent while, with the exception of logistic bases, chrome plating operations are rare and never full time duties. The vast majority of chromate exposure in the Air Force results from painting/depaint operations. The NIOSH criteria document for chromate exposure does not directly relate typical Air Force worker exposure, painting and depainting, to projected illnesses. Therefore, to better understand the potential health effects of painting and depainting operations, a review of the literature with respect to these activities was accomplished.

D. In the private sector, the occupation of painter includes both painting and depainting and all associated related tasks. Unlike the Air Force, painters in the private sector work continuously with paints, solvents, pigments and etc over a lifetime. In the Air Force, the typical painter transitions into supervisory/managerial roles and are removed from continuous occupational exposures. Chen ["A Meta-Analysis of Painting Exposure and Cancer Mortality" 1998] reviewed journal articles from between 1966 to 1995 that reported occupational illnesses related to the painting industry. Chen found that the overall health of painters was not different from the general population. When Chen reviewed only the area of cancer, he reported that the risk to painters for developing cancer was elevated. Specifically, he found painters had the greatest increase in leukemia and liver cancer and a statistical increase in esophagus, stomach, bladder, and lung cancers as compared to the general population. Chen was not able to correct his results for tobacco and alcohol use.

E. What are some of the probable causes of the increase cancer rates reported by Chen? Consideration must be given to the time frame of the study. Painters in the 60's and 70's worked with aromatic solvents including benzene. This could certainly explain the increase in leukemia. The cancers related to the digestive tract are normally associated with life style, alcohol use and diet. The issue of lung cancer is more complex.

F. Numerous studies have shown the single leading cause of lung cancer is cigarette smoking, greater than 85% of all cases. Therefore it is important that smoking history be accounted for during any study involving potential causes of lung cancer. Gibb [Lung Cancer Among Workers in Chromium Chemical Production, 2000] performed a historical study on illnesses associated with the chromium production industry. In this study, 2100 workers that worked in the facility from 1950 to 1974 were contacted and health status queried. Of the 2100 workers, 86 percent had a smoking history. Of the smoking group, 116 developed lung cancer while only 4 non-smokers developed lung cancer. Based upon the statistical analysis, the rate of lung cancer observed for the smokers was not statistically significant however; the number of lung cancers observed in the non-smoking group was significant. Gibb concluded that an exposure to hexavalent chromium would lead to an increase potential for lung cancer. A similar study design in the painting industry accomplished by Dunn [Cancer Experience of Several Occupational Groups Followed Prospectively, 1965] concluded in similar findings.

G. Several researchers have concluded that the probability of increased lung cancer is associated with exposure to chromates and the painting occupation. In general, the predicted increase in lung cancer is in the 20 to 40 percent higher than none exposed control groups. The researchers assumed that the non-smokers increase in lung cancer were the result of occupational exposure while also assuming the inability to measure the increase in lung cancer in smokers was masked by the cigarette smoking. These assumptions are unsubstantiated and mostly unchallenged.

H. The non-smoking painters certainly had chronic occupational exposures to chromates and also experienced increase lung cancers. In the last three years, several studies have been published that report non-smokers that work with or otherwise chronically exposed to passive cigarette smoke have an increase in lung related cancers, Mayne [Previous Lung Disease and Risk of Lung Cancer Among Men and women Nonsmokers, 1999], Rapiti [Passive Smoking and Lung Cancer in Chandigarh India, 1999], Zhang [Environmental Tobacco Smoking, Mutagen Sensitivity, and Head and Neck Squamous Cell Carcinoma, 2000], and the World Health Organization [Passive Smoking Does Cause Lung Cancer, Do Not Let Them Fool You, 1998]. The effect of passive cigarette smoke was not taken into account in any of the epidemiological studies investigating the effects of hexavalent chrome.

I. It is Air Force policy that worker chemical exposures will be maintained within the guidelines of the ACGIH and OSHA. The following graph depicts nearly 1000 air samples results taken during sanding operations across the Air Force.

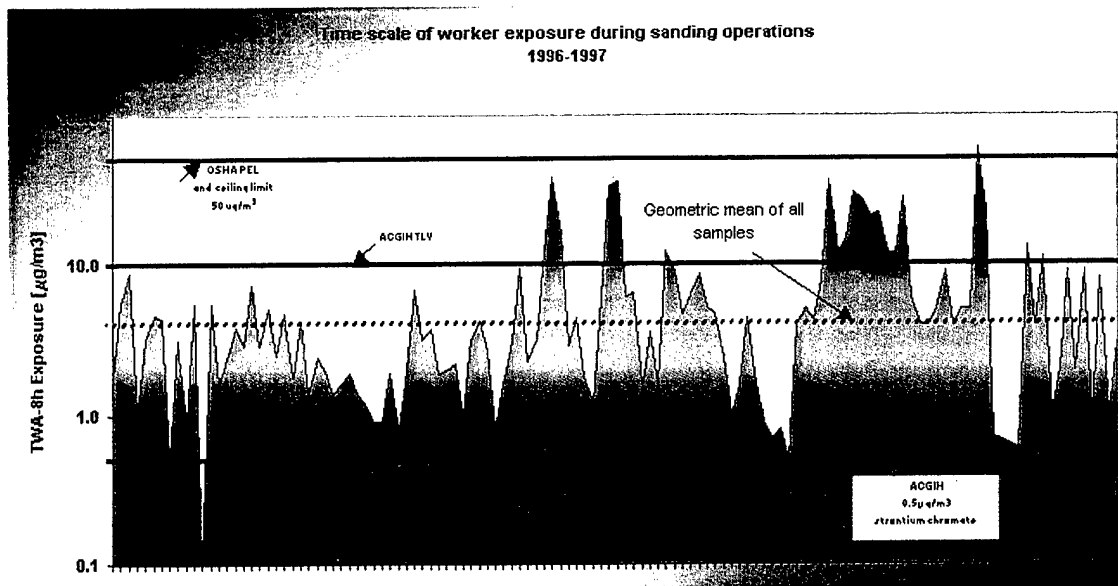


Figure 1. Time scale of worker exposure during sanding operations

J. It is clear that Air Force workers are exposed to less than the OSHA PEL and generally less than the ACGIH generic TLV for chromates. It is also clear that the SrCrO_4 standard is not obtainable. The typical Air Force worker's exposure to hexavalent chrome and overall working environment is far less severe than the workers in the reported studies. To date, no reported adverse health effects that can be related to chromate exposure have been observed in the Air Force corrosion control community.

II. Chromate Standards

A. In the Air Force, compliance with both the OSHA and ACGIH Standards is required. The OSHA Ceiling Standard, 29 CFR 1910.1000 Table Z-2, for chromic acid and chromate (as CrO_3) is $1.0 \text{ mg}/10 \text{ M}^3$ ($0.1 \text{ mg}/\text{M}^3$ as CrO_3). OSHA has not published a PEL or STEL for individual chromates. For completeness, the OSHA definition of a ceiling value **for a substance listed in Table Z-2** is "Acceptable ceiling concentrations." An employee's exposure to a substance listed in Table Z-2 shall not exceed at any time during an 8-hour shift the acceptable ceiling concentration limit given for the substance in the table, except for a time period, and up to a concentration not exceeding the maximum duration and concentration allowed in the column under "acceptable maximum peak above the acceptable ceiling concentration for an 8-hour shift". No values are listed under the "acceptable maximum peak above the acceptable ceiling concentration for an 8-hour shift" for chromates. Therefore, if an air sample exceeds the OSHA standard of $0.1 \text{ mg}/\text{M}^3$ as CrO_3 , regardless of the length of time the sample was taken, a violation of the OSHA Standard occurs.

B. The ACGIH Standard is somewhat more complex. The following table summarizes all the ACGIH 8-hour TLV-TWA values.

TABLE 1. ACGIH 8-hour TLV-TWA values

Substance	8-hr TLV-TWA
Water soluble Cr ⁺⁶	0.05 mg/M ³
Insoluble Cr ⁺⁶	0.01 mg/M ³
PbCrO ₄ - as Pb	0.05 mg/M ³
PbCrO ₄ - as Cr	0.012 mg/M ³
SrCrO ₄ - as Cr	0.0005 mg/M ³
ZnCrO ₄ - as Cr	0.01 mg/M ³

C. The ACGIH considers chromates "Confirmed Human Carcinogens" based upon epidemiological studies (health effect section). Water-soluble chromates are found in plating operations and alodine wash processes. The applicable 8-hr TLV-TWA is 0.05 mg/M³.

D. The ZnCrO₄ and Insoluble Chromate are the same and therefore, the same method can be used to assess worker exposure. The difficulty arises with the SrCrO₄ standard. To apply the SrCrO₄, the percentage or fraction of SrCrO₄ must be known relative to the total chromates present. This isn't difficult for applying paints and primers; the information is contained in the MSDS. It is difficult for repainting operations since no MSDS is available to ascertain the makeup of the paint and primer already on the surface. Also, the color should not be used to definitely determine the type(s) of chromate present.

III. Selecting Sampling Media

A. Sampling for chromates can be a bit confusing. Prior to discussing sampling strategy, it is important to understand the two main analytical methods typically used when quantifying chromate exposures. The first method is a general metals screen, NIOSH Method 7300. The second method is a specific analysis for hexavalent chrome; NIOSH Method 7600, OSHA 215, and OSHA 103. The recommended sampling rate is 2 liters per minute for all the methods. Sometimes you will need to sample for both chromates and metals simultaneously since on occasions multiple chromates with different exposure standards can be found in the work environment. Specifically, the ACGIH lists a generic standard for chromates and specific different standards for strontium chromate and lead chromate. The OSHA lists just one standard for all chromates. The issues of standards are addressed elsewhere.

B. NIOSH Method 7300 is used to determine elemental metals. Metals tied in compounds will also be detected. NIOSH Method 7300 will detect both the chrome and strontium in strontium chromate along with any other chrome and strontium in the work environment. NIOSH Method 7300 requires the sample be collected on a 0.8 micrometer, cellulose ester membrane filter. Since lead, strontium, zinc, nor chromates have size selective TLVs, the sample should be collected using a 37 mm, close faced, cassette.

C. NIOSH Method 7600, OSHA method 215, and OSHA method 103 are used to determine only hexavalent chrome. These methods cannot be used to differentiate

between different kinds of chromates, i.e. strontium chromate, lead chromate, and all other chromates. The NIOSH method 7600, OSHA method 215, and OSHA method 103 all require the samples to be collected with a 37-mm diameter polyvinyl chloride (PVC) filter (5-um pore size) contained in a polystyrene cassette. To reiterate, chromates do not have a size selective TLV therefore, the sample should be collected using a 37 mm, close face, cassette.

D. For additional information on the NIOSH sampling methods 7300 and 7600, refer to the NIOSH Manual of Analytical Methods; at the time of this writing the web site address is <http://www.cdc.gov/niosh/nmam/nmammenu.html>. For additional information on the OSHA methods, refer to the OSHA Analytical Methods that can be found at <http://www.osha-slc.gov/dts/sltc/methods/toc.html#C>.

E. Personal air sampling is performed to assess the potential exposure of an individual to a given contaminant in the air. IAW AFOSH Standard 48-8 "Controlling Exposures to Hazardous Materials", these personal air samples must comply with nationally recognized standards, i.e. OSHA, NIOSH, and ACGIH criterion.

F. Traditionally, particulates are collected using a 37 mm cassette, close face. This is the method clearly defined by OSHA in the OSHA Field Manual. Most particulate samples collected at an Air Force base would be collected using this method. The following diagram is taken from the OSHA technical manual:

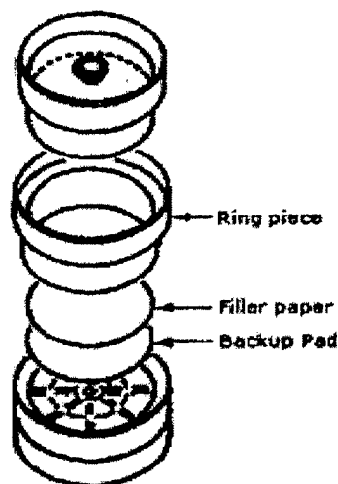


Figure 2. Exploded view of three-piece cassette. Shows correct placement of back-up pad

G. In some cases, the area where the particulate deposits in the body is important. Air sampling devices and standards has been developed to sample in specific cases where size selective sampling is desired. Three ranges of particle sizes are defined: inhalable, thoracic, and respirable. An inhalable fraction includes all particles, based on aerodynamic diameter, which would deposit in the nasopharyngeal (nose and top of throat), tracheobronchial (bronchial and throat), and pulmonary (lungs) regions. The thoracic fraction includes areas where particles would only deposit in the tracheobronchial and pulmonary regions while the respirable fraction includes only particles that would deposit in the pulmonary region. In the following table, a partial list of substances with selective size TLVs:

TABLE 2. Partial List of Substances with Size Selective Standards

Substance	Type	TLV (mg/M ³)
Asphalt	Inhalable	5.0
Cadmium	Total	0.01
Cadmium	Respirable	0.002
Coal dust (anthracite)	Respirable	0.4
Coal dust (bituminous)	Respirable	0.9
Dichloropropionic acid	Inhalable	5.0
Diquat	Inhalable	0.5
Diquat	Respirable	0.1
Flour dust	Inhalable	0.5
Graphite (except fibers)	Respirable	2.0
Kaolin	Respirable	2.0
Mica	Respirable	3.0
Nickel	Inhalable	Variable on form
Paraquat	Total	0.5
Paraquat	Respirable	0.1
PNOC	Inhalable	10.0
PNOC	Respirable	3.0
Silica, crystalline	Respirable	0.05
Quartz	Respirable	0.05

H. By reviewing the preceding table it is apparent that the respirable size selective standard is most applicable to the Air Force. The personal cyclone is the most common device used to obtain a respirable air sample. If for any reason an inhalable sample is desired, several sampling devices are commercially available including the IOM inhalable dust sampler. **Note:** The OSHA Technical Manual only references traditional and respirable air sampling techniques.

I. For chromates, no size selective sampling standard exist, therefore IAW Air Force doctrine, air samples should be collected using the traditional method. One additional point must be made; the IOM is a mass sampling device only. Any chemical analysis performed on an IOM filter/cassette is inheritably invalid. No validated method exists to extract the contaminant from the IOM sampling device. If chemical analysis is accomplished on an IOM sample, the pursuing analytical results are unusable for comparison to any standard. Contacting the IOM supplier, SKC Inc, substantiated this position. SKC does not have nor know of any validated method to extract contaminant off the IOM sampling device. NIOSH, ACGIH, nor OSHA has published any validated analytical techniques with respect to chemical analysis of an IOM sample.

IV. Calculations

Note: For the purposes of calculations, the chromate values were determined assuming NIOSH method 7600 was used. However, OSHA methods 103 and 215 results could be substituted for the NIOSH method 7600 results without any changes in the calculations.

If you are evaluating a painting or priming operation and know that only one chromate compound exists in the paint or primer (MSDS), sample using NIOSH method 7600. The difficulty arises when the types of chromates are not known such as in depainting operations. Determining overall chromate (also known as hexavalent chrome, CrO_3 , Cr^{+6}) exposure or individual chromate exposure can be accomplished using several different methods, NIOSH Method 7600 is used to determine chromate while NIOSH Method 7300 is used to determine total metals. Some methods are much more conservative and therefore leads to much higher exposures assessment. The Air Force currently does not have a policy on which method must be used. When making your selection, please be aware of IAW AFD 90-9 "Operational Risk Assessment". It is no longer AF policy that the most conservative method be used; rather, an objective base risk management methodology that includes cost should be employed.

A. Method 1 (The AFIERA does not recommend using this method)

Since SrCrO_4 has the lowest TLV of all the chromates, assume all the hexavalent chrome is attached to Sr. You would then use NIOSH Method 7600 to sample for chromates and compare the results to the SrCrO_4 standard. This is extremely conservative and can lead to very conservative recommendations that could cost the Air Base a great deal of money and time.

Example

You collect two air samples, each 8-hours in duration, using NIOSH Method 7600. The results are 0.0225 mg/M^3 and 0.00048 mg/M^3 as Cr. The ACGIH standard is 0.0005 mg/M^3 . The first sample is above the OEL while the second sample is below.

B. Method 2 (The AFIERA does not recommend using this method)

When sanding or bead blasting a surface, paint, primer, and metal dusts from the surface of the metal are generated. You can assess quantitatively the concentration of all the metals using NIOSH Method 7300. In corrosion control activities, you can safely assume hexavalent chrome is attached only to Pb, Sr, and Zn. Therefore, with respect to determining chromate exposure, use only the Pb, Sr, and Zn results. To perform the calculations, you will need the molecular weights (MW) of Cr (52.0), Pb (207.2), Sr (87.6), and Zn (65.4). The ratio of Cr to Pb, Cr to Sr, and Cr to Zn in chromates is one mole to one mole. Therefore, you can calculate the equivalent Cr value by

$$\text{X chromate (as chrome)} = \text{X} * \frac{\text{MW of Cr (52)}}{\text{MW of X}}$$

where X is the conc from the 7300 analysis

This method assumes all the Pb, Sr, and Zn is bound to chromate. Therefore, this assessment still overestimates the chromate exposure.

Example

In the following table, assume the second column represents the analytical results (NIOSH Method 7300) from 8-hour samples

TABLE 3. Example of 8-hour samples

Element	Concentration from 7300 analysis mg/M ³	MW of metal	Chromate, As Cr mg/M ³	Standard mg/M ³
Pb*	0.01270	207.2	0.00319	0.0120
Pb*	0.00067	207.2	0.00017	0.0120
Sr	0.00849	87.6	0.00504	0.0005
Sr	0.00301	87.6	0.00179	0.0005
Sr	0.00048	87.6	0.00028	0.0005
Sr	0.00006	87.6	0.00003	0.0005
Zn	0.01010	65.4	0.00803	0.0100
Zn	0.00042	65.4	0.00033	0.0100
Zn	0.00310	65.4	0.00246	0.0100
Zn	0.00098	65.4	0.00078	0.0100

* Remember to apply the lead standard also

C. Method 3 (AFIERA recommended method)

The standard method for determining chromates is NIOSH Method 7600 while NIOSH Method 7300 determines total metal. Unfortunately, NIOSH Method 7600 is non-specific in terms of the associated metal. Therefore, to keep from overestimating the chromate exposure, the total chromate reported can be proportioned between the Pb, Sr, and Zn based upon the NIOSH Method 7300 results.

Example

To assist in explaining this process, the following table and steps are provided:

TABLE 4. Results from NIOSH Method 7300 and NIOSH Method 7600:

Metal	Result (mg/m ³)	Molecular Weight	NIOSH Method
Lead (Pb)	0.0127	207.2	7300
Strontium (Sr)	0.00849	87.6	7300
Zinc (Zn)	0.0101	65.4	7300
Hexavalent Chromium Cr(VI))	0.0025	52.0	7600

Step 1: Divide each metal result by the respective molecular weight to find the number of moles. (Mole is a unit of measure; equal to the molecular weight in grams)

Pb: $0.0127 \div 207.2 = 0.0000613$ (Result A)

Sr: $0.00849 \div 87.6 = 0.0000969$ (Result B)

Zn: $0.0101 \div 65.4 = 0.000154$ (Result C)

Step 2: Sum moles for each metal ($A + B + C = D$)

$0.0000613 + 0.0000969 + 0.000154 = 0.000312$ (Result D)

Step 3: Divide each metal's number of moles (A,B,C) by the total moles (D)

Pb: $A \div D$ is $\frac{0.0000613}{0.000312} = 0.196 = 19.6\%$ (Result W)

Note: To check this calculation, the sum of W,Y,Z should be 1.0 (100%)

Sr: $B \div D$ is $\frac{0.0000969}{0.000312} = 0.311 = 31.1\%$ (Result Y)

Zn: $C \div D$ is $\frac{0.000154}{0.000312} = 0.494 = 49.4\%$ (Result Z)

Step 4: Multiply the hexavalent chromium (Cr(VI)) result from NIOSH Method 7600 by each of the percentages (W,Y,Z) to determine the concentration of each chromate.

Pb: $W \times \text{Cr(VI)}$ is $19.6\% \times 0.0225 \text{ mg/m}^3 = 0.00441$ PbCrO_4 as Cr

Sr: $Y \times \text{Cr(VI)}$ is $31.1\% \times 0.0225 \text{ mg/m}^3 = 0.00697$ SrCrO_4 as Cr

Zn: $Z \times \text{Cr(VI)}$ is $49.4\% \times 0.0225 \text{ mg/m}^3 = 0.0111$ ZnCrO_4 as Cr

Step 5: Calculate the time-weighted average

V. Methods for Reducing Chromate Exposures

A. Chromate exposure in the Air Force is normally related to corrosion control and plating processes. The corrosion control process can be further reduced to the application and removal of paints and primers and the application of alodine. For clarification, alodine is a weak mixture of chromic acid, hydrofluoric acid, and ferricyanide used to form a chrome oxide film on a metal surface to prevent corrosion. Mitigating exposure to chromates follows classical industrial hygiene protocols: substitution, engineering, and administrative controls.

B. Chrome plating requires the use of chromic acid; substitution is not an option. Engineering controls, mechanical ventilation specifically designed for plating operations, is the only practical method of controlling worker exposures to chromic acid. The most difficult aspect of using mechanical ventilation to control worker exposure is maintaining the mechanical system. Depending on the design of the ventilation system, the chromic acid can cause severe deterioration of all the system ultimately leading to worker exposure. It is imperative to periodically inspect the ventilation system to ensure adequate performance. Also, even with a properly designed and maintained ventilation system, workers still must have access to chemical goggles, splashguards, gloves and aprons.

C. The alodine process is most often used to treat a recently depainted aircraft. The alodine coating preserves the integrity of the surface until primer and paint can be applied. No known substitute is available for the current alodine formulation. The alodine mixture can be wiped or sprayed onto the surface of the aircraft. Spraying alodine onto an aircraft should be avoided whenever possible. Spraying alodine may generate inhalable aerosols and can certainly lead to skin contact. Wiping the alodine solution onto the airframe is the most desirable method. This can be accomplished with a sponge, sponge mop etc. When wiping alodine onto a surface, ensure proper PPE is used to avoid skin contact. For small areas, an alodine SEMPEN can be used. When using a SEMPEN no PPE should be required.

D. The application of chromate containing primer and paint is a major source of worker exposure. The Air Force is actively pursuing an acceptable substitute for chromates. However, until these substitutes are proven effective, chromates containing primers and paints will continue to be used. In the interim, several methods can be used to reduce worker exposures to chromates. This includes

1. Use of tie-coat. The tie-coat does not act as a corrosion inhibitor, and is not really a primer per se, but more of an adhesive. Its purpose is to bind or "tie" the polyurethane overcoat to the scuff-sanded surface, thus the name "tie-coat." You can only use the tie-coat on scuff-sanded surfaces.
2. Apply the primer or paint using a roll or brush. This method offers several advantages to include reducing airborne exposure levels to the worker and the environment leading to reduced levels of PPE.

3. Maintain proper spray gun air cap pressure. Proper air cap pressures will help limit excessive over spray generation.
4. Apply minimum amount of chromate containing coating
5. Minimize the number of workers in the area.

E. Chromate does not need to be in every layer of primer and paint to maximize corrosion control. Discussions with the Air Force Corrosion Control office indicate that only one layer of coating needs to contain chromates. Normally, the chromate is best placed in the primer coat.

F. Engineering controls are only effective in reducing exposure if the engineering controls are used properly. To maximize the effectiveness of a ventilation system, the painter should spray with the airflow traveling from behind, across the spray gun, and pass the object being painting. At worse, the painter would spray paint perpendicular to the direction of the airflow. Painters should never positions themselves in line with respect to the airflow; each successive painter would be exposed to the cumulative over spray of all the preceding painters. Finally, even with engineering controls, the best method to reduce exposure to chromates is to have all non-essential personnel leave the application area.

G. Another major source of exposure to chromates is the removal (depainting) operation. Depainting can be accomplished either by chemical (stripping) or physical (blasting or sanding) methods. In chemical stripping, exposures to chromates are not a concern. Blasting operations (beads, wheat, CO₂ etc) are normally very well defined processes in terms of engineering controls, PPE, isolation from all other processes, and personal exposures. Scuff sanding is a very common process. The worker uses a mechanical sander or just sand paper to "scuff" the surface. We have found that the worker exposure during scuff sanding can vary widely depending on worker technique and available engineering controls. Based on these observations, the following is a list of actions that can be taken to minimize worker exposure during scuff sanding operations.

1. Use of a vacuum sander. Ventilated sanders typically have a number of holes located in the rotary disc through which particulates are drawn.
2. Workers should keep the surface of the sander as flat as possible to the aircraft.
3. Avoid attaching more than one sander to the HEPA vacuum and limit the hose length, since either one greatly decreases air flow to sanders.
4. A central vacuum system will provide a greater airflow to the sander than a portable HEPA vacuum.
5. Ensure the sandpaper is compatible with the sander; it should have the same number of hole(s) as the sander and the hole(s) should be properly aligned.
6. Measure the air velocity at the holes and multiply by the area of the holes. If the tool has a shroud measure velocities at several places around the shroud and multiply by the area through which the air is drawn; add this value to the airflow through the holes. Sanders should have a minimum airflow of 10 cfm/in² of disc diameter.

7. A portable HEPA vacuum will, in all likelihood, provide ventilation rates much lower than recommended; a central vacuum system, if properly operating, will probably provide better ventilation rates.
8. Ensure the exhaust hoses are in good repair.