

The author hereby certifies that the use of any copyrighted material in the thesis manuscript entitled:

Dissociation of Hexavalent Chromium from Primer Paint Particles
into Simulated Mucus Fluid

beyond brief excerpts is with the permission of the copyright owner, and will save and hold harmless the Uniformed Services University of the Health Sciences from any damage, which may arise from such copyright violations.

Michael P. Moran
Capt, U.S. Air Force, BSC
Department of Preventive Medicine and Biometrics
Uniformed Services University of the Health Sciences

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

This paper is declared the work of the U.S. Government and is not subject to copyright protection in the United States.

“The views expressed in this article are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense or the U.S. Government.”

20050722 065

Abstract

Title: Dissociation of Hexavalent Chromium from Primer Paint Particles into Simulated Mucus Fluid

Michael Patrick Moran, Master of Science in Public Health, 2005

Directed By: Peter T. LaPuma, LtCol, USAF, BSC
Assistant Professor, Department of Prev Med and Biometrics

The military relies heavily on chromate primer paints to protect equipment from corrosion. Epidemiological studies link chromate exposure to cancer however limited studies suggest exposure to chromate paint particles does not increase the risk of lung cancer. The particle size and paint type may hinder chromate released into lung fluid. To simulate particle deposition in the mucosal layer of the lungs, a viable cascade impactor collected paint particles into porcine-based simulated lung fluid (SLF). Samples were tested after 24 hours for dissolved and total chromate to determine the fraction of Cr⁺⁶ that dissociated from the particles into the Porcine-SLF. In strontium chromate paints, 0.65–2.1 microns sized particles released significantly less chromate than 2.1–7.0 micron sizes. Barium chromate paints only released 3-7% of its chromate, while strontium based paints released from 20-90%. This method demonstrates a technique to evaluate the bioavailability of contaminants from any type of aerosols.

Dissociation of Hexavalent Chromium from Primer Paint Particles into Simulated
Mucus Fluid

By

Michael Patrick Moran

Thesis submitted to the Faculty of the Graduate School of the
Uniformed Services University of the Health Sciences in partial fulfillment
of the requirements for the degree of

Master of Science in Public
Health

2005

Advisory Committee:
LtCol Peter T. LaPuma, Chair
CDR Gary Hook
LCDR Gary Morris

Acknowledgements

First and foremost, I would like to thank my wife and children for their love and patience. I could not have done this without their support and understanding, especially when my time with them was limited.

I would like to thank my advisor Lieutenant Colonel Peter LaPuma for his endless enthusiasm and encouragement. I am thankful for the long hours sacrificed to help shape and improve the thesis document. I also want to thank the other committee members Commander Gary Hook and Lieutenant Commander Gary Morris for their assistance.

Personnel at Armed Forces Radiobiology Research Institute were extremely helpful: Terry Cogswell, Terry McMahan, David McClain, and Blaise LeBlanc. Thank you for your assistance and space provided in which to perform my experiment.

A special thank you to Craig Petersen and Chris Athanasopoulos from Deft Coatings. Thank you for supporting my research project by providing the primer paint and chromate materials. Many thanks to Maureen Donovan for your time and support. Your guidance was invaluable in producing the simulated lung fluid used in this research project.

Finally, thank you to the Air Force Research Laboratory Pollution Prevention Research & Development Program Office for funding this research..

Table of Contents

Abstract.....	iii
Acknowledgements.....	v
Table of Figures.....	viii
Table of Equations.....	viii
1 Introduction.....	1
1.1 Background.....	1
1.1.1 Hexavalent Chromium (Cr ⁺⁶).....	1
1.1.2 Regulatory Pressure.....	1
1.1.3 Military Relevance.....	2
1.1.4 Low Lung Cancer Incidence Among Painters.....	3
1.1.5 Simulated Lung Fluid.....	5
1.2 Research Question And Objectives.....	7
2 Literature Review.....	8
2.1 Overview.....	8
2.2 Human Lung Fluid (Mucus).....	8
2.3 Mucociliary Clearance.....	11
2.4 Factors Affecting Bioavailability from Particles.....	12
2.4.1 Particle Size.....	12
2.4.2 Solubility.....	13
2.4.3 Residence Time.....	14
2.4.4 Paint Matrix.....	15
2.5 Health Effects.....	15
2.5.1 Chromate Production Industry.....	15
2.5.2 Chromate Pigment Production Industry.....	16
2.5.3 Painting Industry.....	17
2.6 Particle Collection.....	18
3 Methodology.....	24
3.1 Porcine-SLF.....	25
3.1.1 Porcine-SLF Preparation.....	26
3.1.2 Centrifugation.....	26
3.1.3 Dialysis.....	27
3.2 Mix Paint.....	27
3.2.1 Solvent (02-Y-040A).....	28
3.2.2 Polyurethane (09-Y-002).....	28
3.2.3 Water-Sr (44 GN-072).....	28
3.2.4 Water-Ba (44-GN-007).....	29
3.3 Particle Collection.....	29
3.3.1 Paint Booth.....	29
3.3.2 Cascade Impactors.....	30
3.3.3 Particle Collection System.....	30
3.4 Sample Preparation.....	32
3.5 Centrifuge.....	32
3.6 Cold Digest.....	33

3.7	Hot Digest.....	33
3.8	Sample Analysis.....	34
3.8.1	Inductively Coupled Plasma (ICP) Device.....	36
3.8.2	Calibration Standards.....	37
3.8.3	Internal Standard.....	38
3.9	Solubility in SLF.....	38
3.10	Detection Limits.....	39
4	Results.....	40
4.1	Statistical Analysis.....	41
4.1.1	Particle Size Comparison.....	43
4.1.2	Paint – Paint Comparison.....	43
4.1.3	Base Paint Comparison.....	44
4.2	Particle Penetration in Porcine-SLF.....	48
4.3	Quality Control.....	49
5	Discussion.....	52
5.1	Limitations.....	54
5.2	Future Work.....	54
	Appendix A Cr ⁺⁶ Dissociation Percentages.....	56
	Appendix B Summary of Mean Dissociation (Figure 4-1).....	58
	Appendix C Normal QQ Plots.....	59
	Appendix D Sample Data for % Cr ⁺⁶ Calculation.....	61
	Appendix D-1 Solvent Paint (Deft 02-Y-040A).....	62
	Appendix D-2 Polyurethane Paint (Deft 09-Y-002).....	68
	Appendix D-3 Water-Sr Paint (Deft 44-GN-072).....	74
	Appendix D-4 Water-Ba Paint (Deft 44-GN-007).....	80
	Appendix E MSDS for Solvent Paint part A & B.....	86
	Appendix F MSDS for Polyurethane Paint part A & B.....	88
	Appendix G MSDS for Water-Sr Paint part A & B.....	90
	Appendix H MSDS for Water-Ba Paint part A & B.....	92
	Bibliography.....	94
	Vita.....	99

Table of Figures

Figure 1-1: Dissociation of Chromate in Mucus.....	4
Figure 2-1: Comparison of Mass of Cr per Mass of Dry Paint [53].....	13
Figure 2-2: Particle Impaction Theory [72].....	19
Figure 2-3: Six Stage Andersen Sampler.....	21
Figure 2-4 Particle Size Cut-offs for Tisch TE-10-800 Viable Cascade Impactor.....	23
Figure 3-1 Method Overview.....	25
Figure 3-2 Particle Collection System.....	31
Figure 3-3 ICP Settings.....	37
Figure 3-4 Method Detection Limits.....	39
Figure 4-1 Mean and 95% Confidence Intervals for Cr ⁺⁶ Dissociation (μg dissociated/ μg total).....	41
Figure 4-2 QQ Plot for Particle Sizes within Water-Sr Paint.....	42
Figure 4-3 One way ANOVA Particle Size Comparison (Horizontal bar indicates “no significant difference” between underlined groups).....	44
Figure 4-4 One way ANOVA Paint Type Comparison (Horizontal bar indicates “no significant difference” between underlined groups).....	45
Figure 4-5 Cr ⁺⁶ Dissociation: Paint Mix (solvent) vs. Base Paint (mean with 95% CI).....	46
Figure 4-6 Cr ⁺⁶ Dissociation: Paint Mix (polyurethane) vs. Base Paint (mean with 95% CI).....	46
Figure 4-7 Cr ⁺⁶ Dissociation: Paint Mix (Water-Sr) vs. Base Paint (mean with 95% CI).....	47
Figure 4-8 Cr ⁺⁶ Dissociation: Paint Mix (Water-Ba) vs. Base Paint (mean with 95% CI).....	47
Figure 4-9 Solvent Cr:Sr Ratio.....	50
Figure 4-10 Polyurethane Cr:Sr Ratio.....	50
Figure 4-11 Water-Sr Cr:Sr Ratio.....	51
Figure 4-12 Water-Ba Cr:Ba Ratio.....	51

Table of Equations

Equation 2-1 Inertial Parameter Ψ	20
--	----

1 Introduction

1.1 Background

1.1.1 Hexavalent Chromium (Cr^{+6})

Chromium (Cr) is a metal that can exist in several different valence states ranging from -2 to $+6$. The hexavalent state is a stable form of Cr but it is not naturally occurring in the environment. Cr^{+6} is used as a pigment (i.e. textiles, paints, plastics etc.) and in metal plating. It may also be liberated during welding operations. Cr^{+6} is the active ingredient in most primer paints used to protect the metal skins of aircraft from corrosion processes. Cr^{+6} used for corrosion control typically is in the form of a chromate salt (bound to metals such as barium (Ba), strontium (Sr) and zinc (Zn)), and is a suspended solid within a paint matrix [1].

1.1.2 Regulatory Pressure

There has been a substantial amount of data collected through animal studies and human epidemiological studies that demonstrate that Cr^{+6} is a potent lung carcinogen, most of which has been collected and reviewed by the Occupational Safety and Health Administration (OSHA) in support of a more stringent chromate standard [2]. The American Conference of Governmental Industrial Hygienists (ACGIH) was the first organization to establish a threshold limit value (TLV) to control workplace exposures to Cr in 1946. In 1974, the ACGIH classified certain chromates as confirmed human carcinogens. The National Institute of Occupational Safety and Health (NIOSH) recommended workplace exposure limits for several chromate compounds considered to

be carcinogenic. In 1988 NIOSH recommended to OSHA that all chromate compounds be considered carcinogenic [3]. In 1990, the International Agency for Research on Cancer (IARC) concluded that there was sufficient evidence that chromate compounds found in industries such as the chromate production, chromate pigment production and Cr plating, were carcinogenic in humans [4]. Despite the mounting evidence, OSHA did not alter the exposure limit for chromates established in 1970, even though this limit was originally established to control irritancy and nasal tissue damage [2].

OSHA has been sued in 1997 and again in 2002 for failure to establish a new standard for Cr^{+6} in a timely manner [2]. In response to this latest pressure, in October 2004 OSHA published a proposal for a more stringent standard to protect worker's health from chromate exposures. If approved, the current ceiling limit of 100 ug/m^3 (as CrO_3) will be lowered to an 8 hour time-weighted average (TWA) of 1.0 ug/m^3 (as Cr^{+6}) for all chromate compounds. For comparison, the proposed standard is equivalent to 2.0 ug/m^3 (as CrO_3) or 50 times less than the current ceiling concentration.

1.1.3 Military Relevance

The Department of Defense (DoD) must maintain and protect its equipment for long periods of time. Military aircraft operate in extremely harsh environments, which threaten to degrade their structural integrity through oxidative processes. Billions of dollars are invested in DoD's aircraft. Aggressive corrosion control practices are needed to prevent the deterioration of aircraft surfaces which threaten equipment life and may hinder mission success [5].

Chromate paints provide superior protection and out perform non-chromate alternatives. As the aircraft flexes, stress fractures may form and it is theorized that

chromate is released from the paint matrix to bind with the exposed metal. This hinders further corrosion of the metal [1, 6]. Because of this long-term protection, the military services rely heavily on chromate paints to protect their aircraft from the harsh conditions in which military aircraft must operate.

In spite of its protective properties, research is being conducted to find a suitable replacement for chromate paints because of regulatory pressure. In 1997, the DoD Joint Group on Pollution Prevention (JGPP) investigated nine non-chromate primers to replace the chromate primers now in use [7]. After lab testing, two primers were selected for operational testing that is currently on going. Cr^{+6} is a recognized human carcinogen and is heavily regulated [1, 4, 8-10]. Even with the OSHA required booth ventilation of 100 feet per minute, models predict that military painting operations can reach concentrations significantly greater (over $500 \mu\text{g}/\text{m}^3$ as Cr^{+6}) than the proposed OSHA TWA of $1 \mu\text{g}/\text{m}^3$ (as Cr^{+6}) [11, 12]. One study showed that 25% of measured airborne exposures from Air Force aircraft priming operations are likely to exceed $500 \mu\text{g}/\text{m}^3$ (as Cr^{+6}) with a 95% upper confidence limit of $948.9 \mu\text{g}/\text{m}^3$ (as Cr^{+6}) [13]. The more stringent permissible exposure limits will make compliance difficult in military painting facilities.

1.1.4 Low Lung Cancer Incidence Among Painters

There is uncertainty over the bioavailability of chemical constituents to the human receptor. Most risk assessment methods do not consider the aerosol type or formulation of inhaled particles prior to assigning a toxicological value. In order for chemicals to reach the lung tissue, they must first enter the respiratory system. In the tracheobronchial region, inhaled particles are trapped within the mucosal fluid and removed from the lung via the mucociliary escalator. The majority of particles are removed within 24 hours. The

mucosal fluid along with the trapped particles, are then deposited into the gastrointestinal (GI) tract, which is not considered to be a significant pathway of concern for Cr^{+6} [14-20]. In order to cause cancer, Cr^{+6} must reach the DNA of the lung tissue. To do this, Cr^{+6} must dissociate from a paint particle into the mucosal fluid and be transported into the cells of the lung tissue, see Figure 1-1.

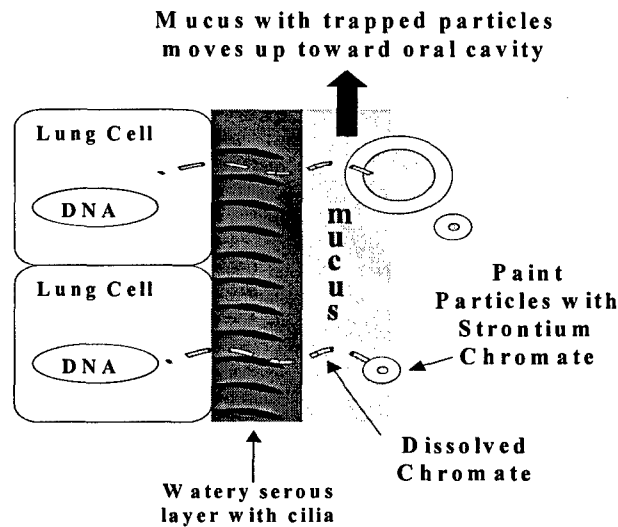


Figure 1-1: Dissociation of Chromate in Mucus

Many factors may affect the amount of chemical released from a particle into the mucosal fluid such as particle size, chemical solubility, and interaction with proteins/mucins. If only 10% of a chemical dissociates from a particle into the surrounding lung fluid, the dose to the lung tissue is only 10% of the total mass inhaled. In comparison, if another type of particle releases 100% of the mass inhaled, then the dose to the lung tissue is 10 times greater than the particle that only releases 10%. A method to measure the fraction of particles dissociated into lung fluid would aid in

determining the actual dose received from a chemical based upon its aerosol type.

Currently, such a method does not exist.

Most of the epidemiological and risk assessment data for Cr^{+6} comes from industries other than painting such as chromate pigment production, welding, leather tanning and Cr plating industries [2]. These industries have well-documented data showing a clear link between exposure and lung cancer. However, this is not the case for the painting industry. There have been only four epidemiological studies looking at chromate-containing paints and lung cancer. Two of the studies showed no increase in the rate of cancer among painters using chromate-containing paints [21, 22]. Although a third study noted a significant increase in respiratory cancer [23], smoking was not accounted for as a possible confounder. The cohort studied by Alexander [22] included 1,064 aerospace painters who had varying exposures to Cr^{+6} paints and found no excess lung cancer (15 observed, 19.5 expected). Alexander hypothesized that the paint matrix may make the Cr^{+6} less biologically active. Chiazzo looked at chromate painters in the automotive industry and found no increase in cancer rate [21].

1.1.5 Simulated Lung Fluid

In this study, paint particles will be collected into a porcine-based simulated lung fluid (Porcine-SLF) to quantify the mass of Cr^{+6} that dissociates from the particles. More complicated models such as *in vivo* animal models are difficult and expensive because bronchial diameters, air speeds and bronchial tree design will deposit particles in animal lungs much differently than in human lungs. Also, uniformly distributing particles with a specific size distribution is very challenging. In this study, the particles will be collected into Porcine-SLF and separated based on particle size with a cascade impactor. It is

common practice of design to collect particles based on the human lung inhalation dynamics using a cascade impactor (described in more detail in Chapter 2.6).

Collecting particles directly into Porcine-SLF is a unique application for studies involving biological availability. It allows a more realistic evaluation because it captures many aspects of particle behavior in lung fluid. Dynamics such as particle and fluid surface interaction, and paint component interaction with lung fluid components (i.e. lipids, enzymes, etc.) will all influence particle and lung fluid interaction. There are also influences from different particle sizes such as the degree of the liquid paint surrounding the chromate salt or the degree of dryness or curing that occurs in particles of different size. The lung fluid constituents may disrupt the curing process of various types of paint. Collecting freshly generated paint particles into Porcine-SLF will simplify the evaluation of Cr^{+6} dissociation from paint particles. In this research, we will learn if the paint matrix causes a hindrance to the release of Cr^{+6} into the Porcine-SLF and how it relates to particle size. Once this method is developed, it may serve as a screening tool to study the biological availability of chemicals from other aerosols such as lead or radon from dust particles or chemical uptake via dust inhalation.

Since particle deposition location within the lung is size dependent, cancer risk could more accurately be assessed knowing the size specific release rate of Cr^{+6} . Due to air quality concerns, there is regulatory pressure to reduce solvent emissions from industrial operations. Water-based primers may be beneficial to air quality but if they release more Cr^{+6} than solvent based paints, they may negatively impact human health in other ways. A method to evaluate chemical release from aerosols into lung fluid does not currently exist.

1.2 Research Question And Objectives

This study is designed to answer the following questions:

1. Does particle size influence the fraction of Cr^{+6} that dissociates from sprayed paint particles into simulated lung fluid?
2. Does the type of paint (e.g. solvent versus water based) have an influence on the release rate of Cr^{+6} from paint particles?

2 Literature Review

2.1 Overview

Cr^{+6} continues to be a source of concern for occupational and environmental professionals. Many studies have looked at the health risk effects from exposure to Cr^{+6} . These studies have influenced regulators to draft more stringent regulations to reduce exposures to Cr^{+6} compounds. Data suggests that the paint matrix may hinder the bioavailability of Cr^{+6} and recent studies have been performed to determine what factors may affect the bioavailability of Cr^{+6} to the human lung. This chapter will review the findings from these studies and summarize the results from pertinent epidemiological studies related to chromate/pigment production. This chapter discusses the lung fluid secretions that line the tracheobronchial region as well as the composition of lung fluid. Also, the role lung fluid plays in the mucociliary apparatus will be discussed. The viable cascade impactor and its ability to capture and separate inhalable particles into Porcine-SLF will also be covered in this chapter.

2.2 Human Lung Fluid (Mucus)

The human lung is covered by a thin layer of an airway surface liquid (ASL). The depth of this layer varies depending on location within the respiratory tract but ranges from 5 – 10 μm . The ASL consists of two distinct layers of fluid, the periciliary sol and a mucus gel layer. The periciliary sol layer is primarily water and electrolytes and this layer is closest to the lung cells. It is hypoosmolar, containing slightly less sodium and chloride ions than plasma, and it is slightly acidic [24, 25]. Its depth is assumed to be equivalent to

the height of the epithelial cilia [26]. The mucus gel layer floats on top of the sol layer closest to the lumen side of the lung bronchioles. The mucus gel layer consists primarily of high molecular weight glycoproteins or mucins. Mucins vary in size ranging from 3 million to 32 million daltons [27]. Mucus also contains non-mucin substances which contribute to its unique properties such as proteoglycans, lipids, IgA immunoglobulins, lysozyme [28], peroxidase [29-31], lactoferrin, DNA [32], actin [33] and others compounds like surfactant [34].

Mucins consist of a protein core with many oligosaccharide side chains. These side chains comprise 70 – 80 % of the mucin mass. These molecules link end to end forming very long chains. The structure can be compared to a bottlebrush. Mucins have a straight peptide backbone surrounded by bristle-like oligosaccharide side chains and a non-glycosylated region “handle” at the end of the backbone. These long molecules polymerize through the disulfide linkages in the non-glycosylated regions and are attracted to each other through ionic and sugar-sugar interactions to form a gel-like material [35]. The chains become entangled with one another and create a random coil conformation within the mucus layer. This unique structure of mucin contributes significantly to the viscous and elastic properties of mucus [36, 37]. The elastic properties are important for clearance by cilia as it transmits energy without energy loss and the viscous nature of mucus permits it to be moved up towards the oral cavity. A balance must be maintained between these two factors for optimal mucociliary clearance to occur [38].

Mucus is secreted into the airway lumen from two different locations: epithelial cells and submucosal glands [39]. In the airway epithelia, glycoproteins (mucins) are

manufactured within the golgi apparatus of goblet and serous cells. Goblet cells are not unique to humans. Several other species, including pigs, have goblet cells that produce mucins as well [40]. The submucosal glands, found within the trachea and bronchioles, contain mucous and serous cells that also produce the large mucin molecules.

Submucosal glands can also be found in other mammal species to include pigs [41].

Mucins are also found in the fluid lining the gastrointestinal tract and around the cervix.

Gastric, respiratory and cervical mucins are similar in nature and have the same hydrodynamic properties, i.e. high intrinsic viscosity and frictional ratio [42]. The frictional ratio reflects the influence of shape and hydration on hydrodynamic drag of a molecule.

Mucus exists in two phases, condensed and expanded. Mucus is produced within the cell and is maintained in the condensed phase. Once the mucus is secreted into the airway, it is hydrated and rapidly expands to several hundred times its original volume [27, 34]. Although mucus is primarily water, it floats atop of the periciliary sol layer. The larger expanded mucous molecules cannot penetrate between the cilia [26].

A gastric pig mucin (Porcine-SLF) was used as the simulated lung fluid for this study. Human lung fluid is very complex and extremely difficult to obtain or reproduce, while Porcine-SLF is readily available and it has viscous and elastic properties similar to human mucus. Porcine-SLF has been used to study the effect of serum albumin on the viscosity of mucin [43] and the respiratory uptake of pharmaceuticals through the mucous layer [44]. The preparation of the Porcine-SLF is discussed in more detail in section 3.2.1.

2.3 Mucociliary Clearance

The mucociliary apparatus' primary role is to protect the deeper regions of the lungs from foreign substances. Its main functions are to trap inhaled particles, act as a chemical screen (antioxidant properties) and provide a biological barrier [34]. The respiratory tract contains a ciliated epithelium from the trachea to the terminal bronchioles. The cilia range in length from 6 μm in the trachea to 3.6 μm in the bronchioles and they are 0.1 – 0.2 μm in diameter [34]. The cilia are located within the periciliary fluid, which provides a low viscosity medium to allow cilia movement. The tip of the cilia contacts the overlying mucus gel, and the rhythmic beat of the cilia forces the mucus outward towards the oral cavity. The mucus travels approximately 4 – 5 mm per minute [45]. In healthy individuals, the mucus is then removed from the body via swallowing and processed through the gastrointestinal tract [46]. Similarly, the nasal passage removes trapped particles by the mucociliary apparatus. The nasal passage contains ciliated mucosa that transports mucus to the back of the throat where it is also swallowed. In healthy individuals, all nasal mucus is swallowed [47].

There are two phases of mucosal clearance, an initial or fast phase and a slow phase. The initial phase removes trapped particles from the tracheobronchial tree via the mucociliary apparatus. Based on mucus velocity rates in the tracheobronchial tree, particles are removed within 24 hours [48-50]. The slow phase may take weeks to months to remove particles. The slow phase removes particles that have reached deep into the alveolar region and are removed via non-ciliary mechanisms such as lung macrophages, which are phagocytic cells in the lungs [51].

2.4 Factors Affecting Bioavailability from Particles

As stated previously, Cr^{+6} must be taken up by cells and bind to DNA which could cause genetic damage and lead to cancer. In order to be taken up into lung cells, the Cr^{+6} must dissociate from an inhaled paint particle, penetrate through the mucus layer and then the more watery periciliary sol layer to get to the cell membrane for possible intracellular uptake. Several factors could influence this process: paint particle size, solubility of Cr^{+6} in lung fluid, residence time of the particle in lung and particle composition.

2.4.1 Particle Size

During spraying, liquid paint is discharged from the spray gun nozzle using pressurized air. The air shears the liquid paint into tiny droplets of varying size [52]. The mass fraction of Cr^{+6} is not uniformly distributed among the resulting particle sizes. Fox [6] discovered that paint particles less than 2.5 microns had a lower mass fraction of Cr^{+6} than particles greater than 2.5 microns. Subsequent studies had similar findings, suggesting that larger particles contain a disproportionately greater portion of chromate than smaller particles [1, 53]. Novy [53] showed that there was a decrease in Cr^{+6} mass corresponding to a decrease in mass median aerodynamic diameter (MMAD), see figure 2-1. The results were consistent for chromate paint from two separate manufacturers. The mass fraction of Cr^{+6} may influence the rate at which Cr^{+6} will dissociate from paint particles of different size. Although previous data is not conclusive, trends suggest that Cr^{+6} dissociates more rapidly from smaller particles [54].

2.4.2 Solubility

In order for Cr^{+6} to dissociate from the paint particle, the surrounding fluid must be below the saturation concentration of the chromate salt. The saturation concentration of strontium chromate (SrCrO_4) in water is 1200 ppm @ 15 °C [55]. SrCrO_4 is likely to be less soluble in a lung fluid simulant. Morgan [56] determined the solubility of SrCrO_4 in a modified Gamble solution to be only 240 ppm @ 37 °C. The modified Gamble solution is a mixture of salts in water designed to simulate the sol layer of human lung fluid. The rate of dissociation will approach zero as the concentration nears the solubility limit.

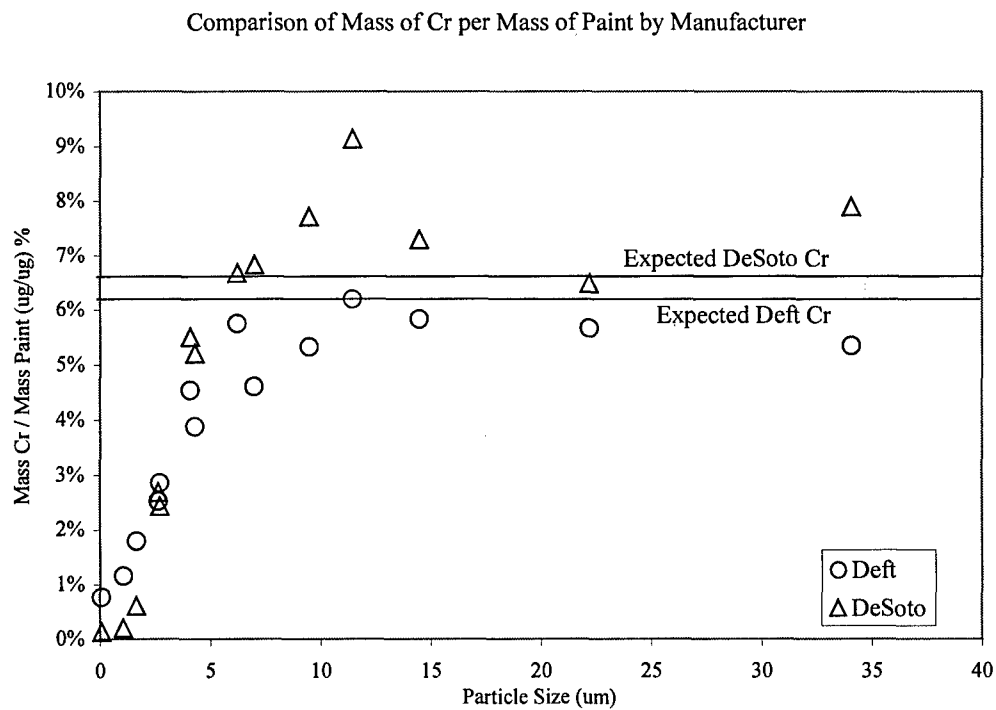


Figure 2-1: Comparison of Mass of Cr per Mass of Dry Paint [53]

2.4.3 Residence Time

The length of time a particle is in contact with lung fluid may affect the amount of chromate that can dissociate into the lung fluid. Three studies looked at the effect of residence time on the dissociation rate of chromate. Morgan [56] analyzed chromate paint samples captured in a modified Gamble solution after 6, 24 and 48 hours residence time. There was no significant difference in the fraction of Cr^{+6} that dissociated from the particles as a function of residence time. Using the same Gamble solution, Kauth [57] looked at residence times of 24 and 48 hours for chromate paint from two different manufacturers. Again, no significant difference was noted between the residence times in either paint. Schilke [54] performed a more comprehensive study of residence times using deionized water. He looked at three separate paint matrix types (solvent, water-based and polyurethane) and used residence times of 1 and 24 hours. Schilke found that particles release most of the chromate within the first hour with minimal changes after 24 and 48 hours. The solvent-based paint released 70% after 1 hour and 85% after 24 hours. The water-based paint released 74% and 84% after the 1st and 24th hour respectively. The polyurethane paint released almost all of its chromate, 94% after the 1st hour and 95% after 24 hours. The polyurethane results may have been overestimated due to losses of particles to glassware walls. Since residence time appears to have very little impact on dissociation between 24 and 48 hours, a residence time of 24 hours was selected for this study, which correlates with the time required for most particles to be removed from the lung (fast clearance) via the mucociliary escalator.

2.4.4 Paint Matrix

The characteristics of the paint vary depending on the matrix in which chromates reside, i.e. polyurethane primers have better flexibility than the other paints. The interaction between the paint matrix and the chromate compound may differ between paint types and potentially affect the rate of dissociation of Cr^{+6} from paint particles. Previous work indicates that there is no difference in dissociation rate of Cr^{+6} between water-based and solvent-based primers [54]. The polyurethane-based primer had a significantly higher dissociation rate than water or solvent-based paints. But, as mentioned, wall losses potentially caused overestimation of the dissociation rate and definitive conclusions could not be made.

2.5 Health Effects

The primary health effect attributed to Cr^{+6} is lung cancer, although it also leads to asthma and perforation to the nasal epithelia and skin [2]. Many epidemiological studies have been conducted linking Cr^{+6} exposures to lung cancer in several industries; however, three studies indicate that painters using Cr^{+6} paints do not experience an increased risk of lung cancer. This section will review studies from industries (chromate production, chromate pigment production industries) that demonstrate an increased cancer risk from Cr^{+6} exposure followed by studies from the painting industry.

2.5.1 Chromate Production Industry

Two main chromate production plants were studied, Baltimore, Maryland [58, 59] and Painesville, Ohio [60, 61]. At the Baltimore plant, Hayes identified 1,803 workers employed between 1945 and 1974 who had a minimum of 3 months of exposure to

sodium chromate and dichromate salts from three production departments: milling (dust particles), dichromate department (mists) and special products (chromic acid mists) and followed them up to 1977. A new production facility was added to the Baltimore plant in 1950 with process improvements to minimize worker exposure. The Hayes study included exposures from the old and new facility. Hayes found a ratio of observed to expected (O/E) cancer deaths of 2.0 ($p < 0.01$). Gibbs followed 2357 male workers at the same Baltimore plant but only used workers from the new plant. Workers studied were hired between 1950 and 1974 and followed up to 1992. Gibbs reports an O/E of 1.86 ($p < 0.01$). Both studies found increased risk of cancer with increasing length of exposure. Mancuso and Luippold found similar results at the Painesville plant (sodium chromate, dichromate and calcium chromate dust particles). Luippold reported O/E of 2.41 ($p < 0.01$) and Mancuso observed an increased lung cancer death rate with cumulative Cr exposure.

2.5.2 Chromate Pigment Production Industry

Several studies were conducted at chromate pigment production plants. These plants produced pigments typically containing lead and zinc chromate. Workers were exposed to chromates both as chromate dust and from chromates within the liquid paint pigment. Workers had the highest exposures from dusts generated during the milling process and moderate exposure from washing and drying processes. Davies [62] found an O/E of 2.2 at factory A and O/E of 4.4 at factory B from the total of 1,152 British chromate workers. The cancer rate was higher for those working in the plant with higher chromate exposure levels. Others studies such as Langard [63] and Deschamps [64] found similar results. As with the previous studies, there was overwhelming evidence

linking chromate exposure to increased cancer rates and increased risk was associated with increased exposure.

2.5.3 Painting Industry

Only four epidemiological studies have been conducted on actual painters of chromate primers/paints. Alexander [22] studied 1505 painters employed between 1974 and 1994. Painters had a minimum of six months of employment to be included in the study. Estimates of lung cancer risk were calculated based on duration of employment in chromate-exposure jobs and cumulative exposures from industrial hygiene data. The resulting overall O/E for painters was 0.8 and found to be "not significant". Boice [65] found no evidence of increased lung cancer risk among 77,965 workers (including 1216 painters) from aircraft manufacturing plant. Exposure categories were formed using job codes and job titles with exposure assessments based on worker interviews and walk-through surveys. The painters had an O/E of 1.1 and it was also "not significant". The results of both the Alexander and Boice studies were judged by OSHA to be inconclusive [2]. The Alexander cohort was small, lacks smoking data, 26% were lost to follow-up and had a young-aged cohort population. A lack of air sampling data in the Boice study limited the ability to accurately predict Cr⁺⁶ exposures to individual workers. Dalager [23] studied 977 male spray painters potentially exposed to zinc chromate and found an excess respiratory cancer risk (21 observed, 11.4 expected). This study also lacked smoking data, which is a possible confounder as smoking is prevalent among painters. Chiazze [21] evaluated painters in the automotive manufacturing industry who were potentially exposed to chromate pigments. The cohort consisted of 226 painters from five

companies who died between 1970 and 1976. No significant increase of lung cancer was observed. OSHA did not evaluate the Dalager or the Chiazze study [2].

All the previous studies of Cr production and pigment plants involve workers who potentially were exposed to chromates as a dust particulate made of chromate salts. Although the studies involving painters have some limitations, the lack of increased cancer risk from multiple studies suggests that something hinders Cr⁺⁶ from producing cancer in painters. It is possible that the paint matrix hinders Cr⁺⁶ from reaching the DNA of lung cells.

2.6 Particle Collection

One of the important components of this study was to identify a method that would capture fine aerosol particles from the overspray of a painting operation and deposit them into a simulated lung fluid. It is desirable to have the collection of particles mimic human respiration as closely as possible. Deposition of particles in the lung is determined by its aerodynamic diameter and not by a particles' physical dimensions [66]. The collection device must be capable of separating particles based on their aerodynamic diameters into discrete particle size ranges. Additionally, the sampling device must be able to deposit collected particles into a sampling media representative of human lung fluid. Prior work done to quantify Cr⁺⁶ desorption from paint particles did not separate particles or deposit them into simulated lung fluid. Impingers were used to collect all particle sizes directly into deionized water [67].

Viable cascade impactors were designed to collect bacteriological particles onto a suitable media that promotes the growth of deposited particles. They also separate the particles based on size. In the mid 1950's, Ariel Andersen pioneered the development of

the viable impactor in conjunction with the U.S. Army Chemical Corps at Dugway Proving Grounds, Utah. The viable impactor used the design features of existing cascade impactors [68-71] which were capable of accurately sizing airborne particles. The design was modified to incorporate a petri dish to hold culture media to collect viable bacteriological particles.

The cascade impactor operates under the principle of inertia. Particles are drawn through aerosol jets, which are aimed at a flat surface. As shown in Figure 2-2, the air passes through the jets and changes direction toward the outer walls as the air approaches the flat surface. Then, the air stream becomes parallel with the flat surface. Larger particles with sufficient inertia will not be able to turn as readily and will impact the flat surface. Smaller particles with less inertia will escape impactation and continue to flow

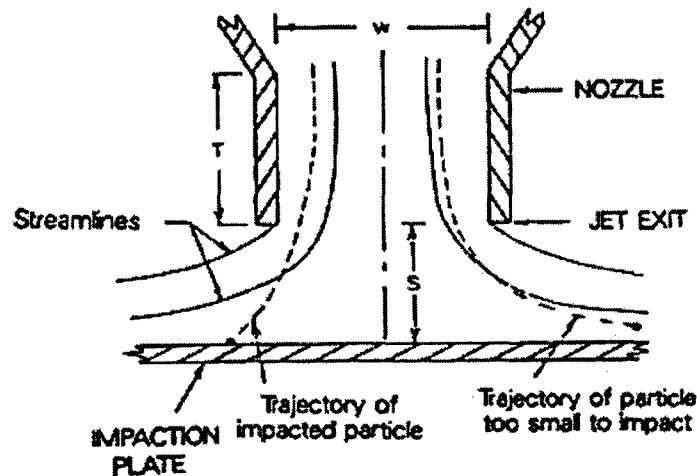


Figure 2-2: Particle Impaction Theory [72]

toward the lower stages. At progressively lower stages, the jets continue to get smaller which increases the velocity. Therefore, particles of smaller size cascade onto lower stages based on less inertia.

According to Ranz [72], jets operating under a specific set of conditions will have a specific range of particle sizes that will be collected. Its ability to separate particles into discreet size ranges makes the cascade impactor extremely useful for collecting particles with inertial properties that are of interest in the human respiratory system. The collection efficiency is a function of a dimensionless inertial parameter ψ .

$$\psi = \frac{C \rho_p v_o D_p^2}{18 \mu D_c} \quad [72].$$

v_o	relative velocity (cm/s)
ρ_p	particle density (g/cm ³)
D_p	particle diameter (cm)
μ	gas viscosity (poise)
D_c	diameter of the round jet (cm)
C	Cummingham slip correction factor

Equation 2-1 Inertial Parameter Ψ

Several factors may affect the collection efficiency of an impactor such as the shape of the jet (round jets have sharper particle range cutoffs) and a high ratio of jet spacing to jet width can reduce efficiency and increase particle range cutoffs [72]. The jet velocity may permit particles to become re-entrained, reducing the collection efficiency. Proper design and operational conditions will minimize or eliminate these effects. Andersen's viable impactor [73] consisted of six stages with each stage having 400 holes of equal diameter. Each stage also contains a petri dish for the collection of particles and would be filled with an appropriate medium based upon the bacteriological particle being collected, see figure 2-3. A vacuum pump draws air through the instrument at a constant rate of 1 cfm.

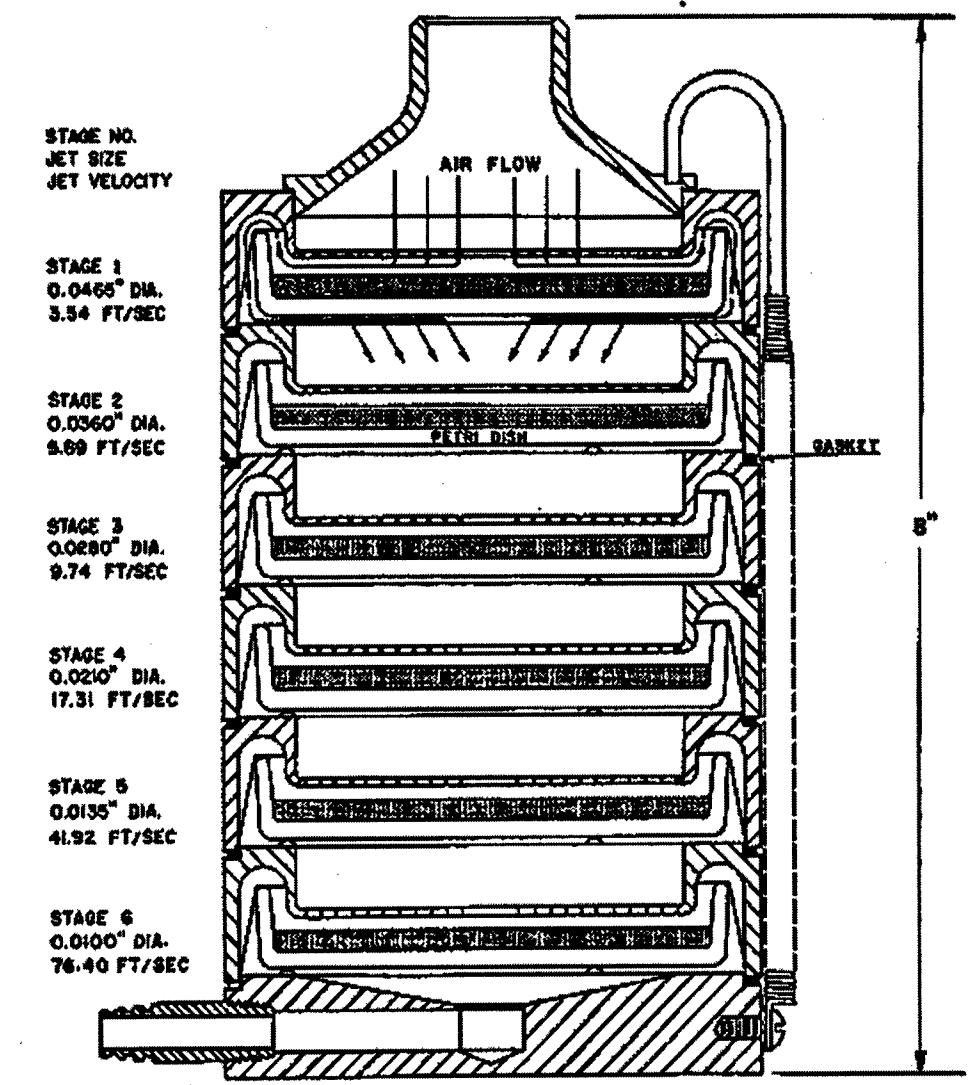


Figure 2-3: Six Stage Andersen Sampler

Andersen's design of 400 holes per stage eliminates dead spaces by evenly distributing the air across the petri dish. The high air flow through the jets prevents particles from collecting on any surface other than the collection medium, thus eliminating the potential of wall loss [73]. The petri dish material was investigated and Andersen [73] found that electrostatic charges from plastic petri dishes reduced collection

efficiency by about 20 percent. Therefore, glass petri dishes are typically used in viable cascade impactors.

Ranz and Wong [72] recommend that the spacing between the jet and sample media be within four jet diameters. This distance was impractical due to the small diameters in the lower stages. Experiments were run to optimize the amount of sample medium placed in the petri dish (90 mm inner diameter x 12 mm height), 27 mL was found to be the optimum amount [73]. Finally, cascade impactors are prone to overlapping particle sizes between stages. One of the factors that determines if a particle will be impacted is the particles nearness to the axis of the jet [72]. The Andersen design of 400 jets per stage confined particle travel along the axis of the jet and significantly minimizes possible overlap. Cascade impactors continue to be widely used today. They are the preferred instrument for the collection and determination of aerosol particle size distribution [74]. A wide variety of impactors have been approved to monitor compliance with EPA's particulate matter standard [PM_{10} and $PM_{2.5}$] [75]. Additionally, cascade impactors are prevalent in the pharmaceutical industry. They are typically used to analyze aerosols from pressurized meter-dose inhalers. Particle distribution data from the impactor is then used to determine the likely deposition location of the active therapeutic agent within the respiratory tract [76]. Andersen's viable sampler design continues to be the basis for bioaerosol sampling. NIOSH method 0800 recommends a viable impactor for sampling bioaerosols [77].

This study used a six-stage viable cascade impactor from Tisch Environmental (TE-10-800). The Tisch impactor is based on the Andersen design having 400 round jets per stage. The jet diameters range from 1.18 mm on the first stage to 0.25 mm on the sixth

stage. The large number of jets reduces the jet velocity, minimizes turbulent flow and results in sharper cutoffs between stages. Table 2-1 lists each stage and its corresponding particle size collection range.

Stage	Jet Diameter (mm)	Particle Size Range (Microns)
1	1.18	7.0 and above
2	0.91	4.7 – 7.0
3	0.71	3.3 – 4.7
4	0.53	2.1 – 3.3
5	0.34	1.1 – 2.1
6	0.25	0.65 – 1.1

Figure 2-4 Particle Size Cut-offs for Tisch TE-10-800 Viable Cascade Impactor

3 Methodology

In order to investigate the dissociation of Cr^{+6} from paint particles within human lung fluid, an innovative method was developed to mimic the human lung as closely as possible. The method consists of four distinct phases:

- Paint particle collection,
- Dissolved Cr analysis,
- Total Cr analysis,
- ICP analysis and calculations.

Figure 3-1 provides a conceptual overview of all four phases. Paint particle collection (steps 1 – 4) consists of capturing respirable particles from the overspray of a painting operation and depositing the particles into Porcine-SLF. A viable cascade impactor was used to separate particles within the respiratory range (0.65 microns to 7 microns). The porcine-SLF was created from purified gastric pig mucin that's designed to mimic human lung mucus.

Following a 24-hour incubation (average particle retention time within the lung), the sample in each petri dish was split into two parts: Dissolved Cr and Total Cr. The Dissolved Cr samples (steps 5 –6) were processed to determine the amount of Cr^{+6} that dissociated into the Porcine-SLF from the paint particles. The Total Cr samples (step 7) were processed to determine the total amount of Cr^{+6} present in the sample within particles and dissociated from particles.

Finally, the amount of Cr^{+6} in all samples was determined using Inductively Coupled Plasma – Optical Emission Spectrometer (ICP) (step 8). The ratio between Dissolved Cr^{+6} ions and the Total Cr^{+6} will be used to calculate the percentage of Cr^{+6} dissociated into the Porcine-SLF.

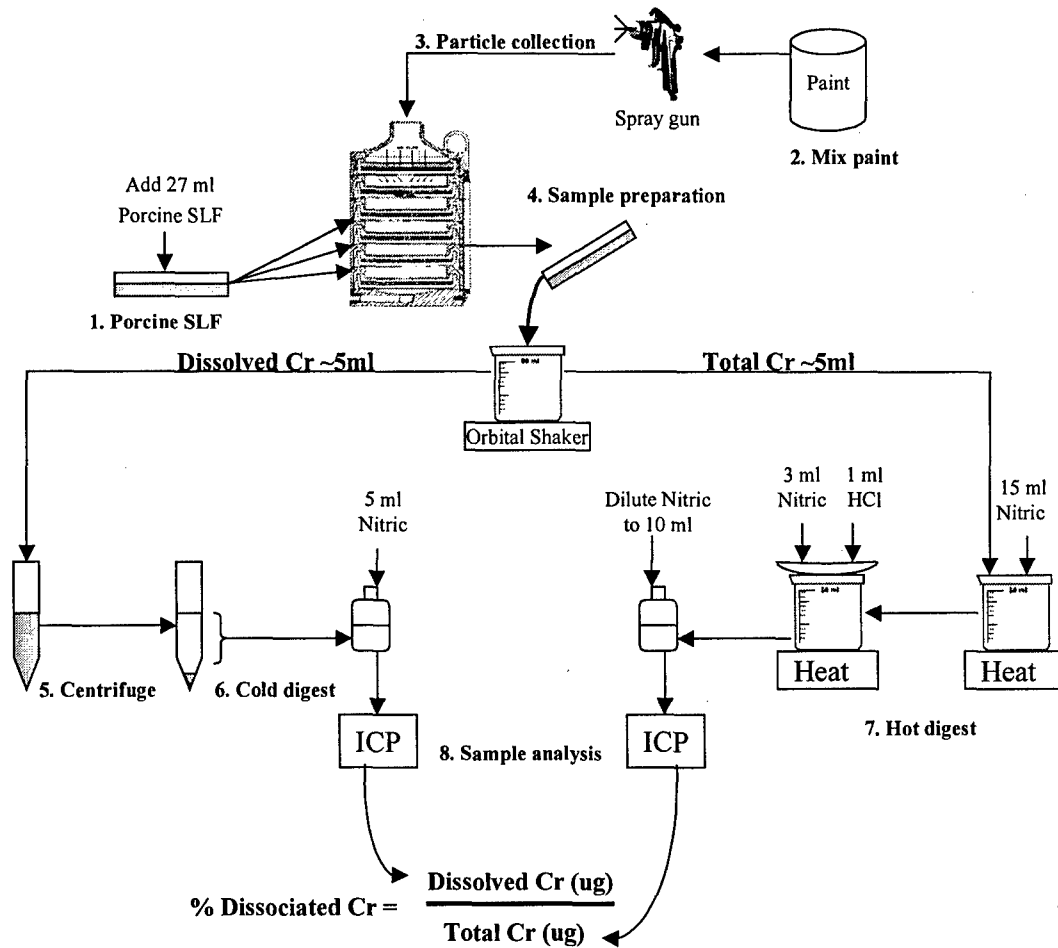


Figure 3-1 Method Overview

3.1 Porcine-SLF

To prepare the impactor for collection, 27 mL of Porcine-SLF was poured into each of the impactor's six petri dishes. Each petri dish was labeled to identify which stage of the impactor the petri dish was placed. The stage number identifies the size of particles deposited in the corresponding petri dish.

3.1.1 Porcine-SLF Preparation

All materials to prepare the Porcine-SLF were obtained from Sigma Aldrich (St Louis, MO). The materials for Porcine-SLF preparation are as follows: Type II mucin from porcine stomach (M2378), phosphate buffered saline (P3813), sodium azide (S2002) and dialysis tubing cellulose acetate (D9652).

The Porcine-SLF was prepared based on the method reported by List (1978). The Porcine-SLF was prepared in 4-liter batches. The isotonic buffer solution was prepared by adding 0.8 mg of sodium azide to 4 L of deionized water in a 4 L Pyrex flask. Four packets (10 g each) of P3813 phosphate buffered saline were added to the deionized water and the solution was gently shaken until all solids were dissolved. The resulting solution had a pH of 7.2. The pH of the solution was adjusted by titrating in hydrochloric acid (35%) to a pH of 6.6. The pH was measured using an Accumet AP61 pH meter. Next, 160 g of type II mucin was added to the 4 L of the isotonic phosphate buffer solution (40 mg mucin/ mL buffer solution). The resulting solution was stirred at 4 °C using a Fisher Thermix Heated Stir Plate and a 2-inch teflon stir bar for 24 hours.

The Porcine-SLF solution must be purified to contain only the large molecular weight (MW) mucin molecules (> 12,000 daltons). The purification process consists of two main steps: centrifugation and dialysis. The mucin solution is centrifuged to remove undesirable solid particles and impurities and dialysis removes small MW compounds dissolved in the mucin solution.

3.1.2 Centrifugation

The mucin solution was transferred into 85 mL Oakridge round bottom centrifuge tubes (75 mL/tube). Each centrifuge batch contained six tubes (450 mL mucin solution).

The mucin solution was centrifuged for 15 minutes at 11,000 rpm at 4 °C. The centrifuge used was a refrigerated centrifuge (Eppendorf 5810 R) with a fixed angle rotor (F-34-6-38). The supernatant was decanted off and centrifuged again under the same conditions.

3.1.3 Dialysis

The final supernatant was poured into the dialysis tubing made from cellulose acetate. The cellulose acetate tubing retains 90% of molecules with MW greater than 12,400 daltons. The dialysis tubing containing the Porcine-SLF solution was placed into an isotonic phosphate buffer solution (pH 6.6). The buffer solution, outside the dialysis tubing, was five times the volume of the mucus solution, i.e. 1 L of mucus solution was dialyzed in 5 L buffer solution. The Porcine-SLF solution was dialyzed for 24 hours at 4 °C. Small MW molecules are transferred to the buffer solution outside the dialysis tubing. After dialysis, the solution was poured into a flask and allowed to hydrate at 4 °C for 24 hours. The resulting Porcine-SLF solution contained 3 – 3.5 % solids by weight and should be translucent and slippery to the touch. The Porcine-SLF was stored at 4 °C for short-term storage (1-2 day) and at -70 °F for long-term storage (greater than 2 days).

3.2 Mix Paint

Four primer paints commonly used by the DoD for corrosion control were selected for this study (Table 3-1). All four paints are two component primers consisting of a base material and a catalyst. Each paint was prepared following the manufacturer's mixing instructions for optimal spraying (step 2 on Figure 3-1). After the paint was mixed, 1 L of paint was transferred to the 2 quart Devilbiss paint cup and allowed to cure for 30 minutes.

	Solvent	Polyurethane	Water-Sr	Water-Ba
Deft Product #	02-Y-040A	09-Y-002	44-GN-072	44-GN-007
Military Specs	MIL-P-23377G	TT-P-2760	MIL-PRF-85582D	MIL-PRF-85582C
Properties	Solvent based, good adhesion, chemical resistant	Polyurethane Low VOC, High flexibility	Water reducible, SrCrO ₄	Water reducible, BaCrO ₄
Mix Ratio	1 Part Catalyst to 3 Parts Base	1 Part Catalyst to 1 Part Base	1 gallon kit base/catalyst + water to fill can	1 Part Catalyst to 1 Part Base + 8 parts water

Table 3-1 Chromate Paint Specification

3.2.1 Solvent (02-Y-040A)

The solvent-based primer paint was prepared by adding one volume of catalyst to three volumes of the base paint. The base paint was stirred using an electric drill with metal paddle until all SrCrO₄ was fully suspended into solution prior to addition of the catalyst. The resulting mixture was stirred for 5 minutes using the electric drill and metal paddle and yielded a viscosity of 20 seconds in #2 Zahn cup.

3.2.2 Polyurethane (09-Y-002)

The polyurethane based primer paint was prepared by adding one volume of catalyst to one volume of the base paint. The base paint was stirred for 5 minutes prior to addition of the catalyst. The mixture was stirred until thoroughly mixed and yielded a viscosity of 20 seconds in #2 Zahn cup.

3.2.3 Water-Sr (44 GN-072)

Water-Sr primer paint was prepared by adding all of the catalyst to the base paint (gallon can). Deionized water was added until the solution reaches the chime (the lower

edge of the upper rim in a gallon can). The solution was stirred for 10 – 15 minutes and yielded a viscosity of 20 seconds in #2 Zahn cup.

3.2.4 Water-Ba (44-GN-007)

Water-Ba primer paint was prepared by adding one volume of the catalyst to three volumes of the base paint. Deionized water was then added in increments. Three volumes of deionized water were added to the mixture and the mixture was stirred thoroughly. Three more volumes of deionized water were added to the mixture and stirred thoroughly. Finally, two volumes of deionized water were added to the mixture and stirred thoroughly. The resulting mixture yielded a viscosity of 20 seconds in #2 Zahn cup.

3.3 Particle Collection

3.3.1 Paint Booth

A portable paint booth from Global Finishing Solutions (FPX-3-BT) was used to capture overspray from the spraying operation (Figure 3-2). The working area of the paint booth was 36 inches wide, 40 inches tall, and 24 inches deep. Because of the high airflow in the booth, the gun velocity and the shallow depth of the booth, a cardboard extension was placed at the front of the booth to slow particle trajectory from the paint gun and increase particle capture in the cascade impactors. An 18" flexible duct exhausted air from the paint booth into a dedicated canopy hood to eliminate solvent vapors from the spraying operation.

3.3.2 Cascade Impactors

Cascade impactors (8 inches tall) were assembled (petri dishes with Porcine-SLF inserted) on the lower edge of the paint booth and positioned near the center of the paint booth. Impactors were assembled in the booth to prevent spilling Porcine-SLF.

3.3.3 Particle Collection System

A sampling train (Figure 3-2) was set up to capture the overspray from a spray gun painting operation. Three viable cascade impactors were placed in a portable paint booth. The impactors were connected to a valve, then a reservoir, and then a vacuum pump using polyethylene tubing. The vacuum pumps were GAST 23 series Lubricated Laboratory Vacuum Pump and Compressor. A reservoir tank was placed between the vacuum pump and the cascade impactor to dampen oscillations in airflow from the vacuum pump. The valve placed between the impactor and reservoir was used to set the airflow rate through the impactor to 28.3 L/min. The collection system was calibrated using a BIOS Drycal DC-2 high flow calibrator. The Drycal DC-2 was placed between the valve and the cascade impactor. The pumps were turned on and allowed to run for 5 minutes to ensure a constant flow through the sampling train. The Drycal DC-2 was turned on and the valves were adjusted until 28.3 L/min (1 cfm) was flowing through each impactor. The flow rate was calibrated before and after each sampling run.

A Devilbiss HVLP pressure feed spray gun (EXL-520P-18) was used to spray the paint at a target. The spray gun was attached to a stand and positioned to shoot the cardboard target at approximately 20-degree angle as shown on Figure 3-2. The angle was adjusted to reduce bulk spray across the impactors and maximize the overspray (finer particles) to the impactors. The paint cup pressure was adjusted to 7 psi and the spray

nozzle inlet pressure was 25 psi (approximately 8.0 psi at the air cap) for all paints. These settings are consistent with typical aircraft painting operations that require the air cap pressure to be between 7–10 psi [78]. During spraying, the gun trigger was held open with lab clamps. Painting operations lasted until the paint cup was empty, usually 10–15 minutes.

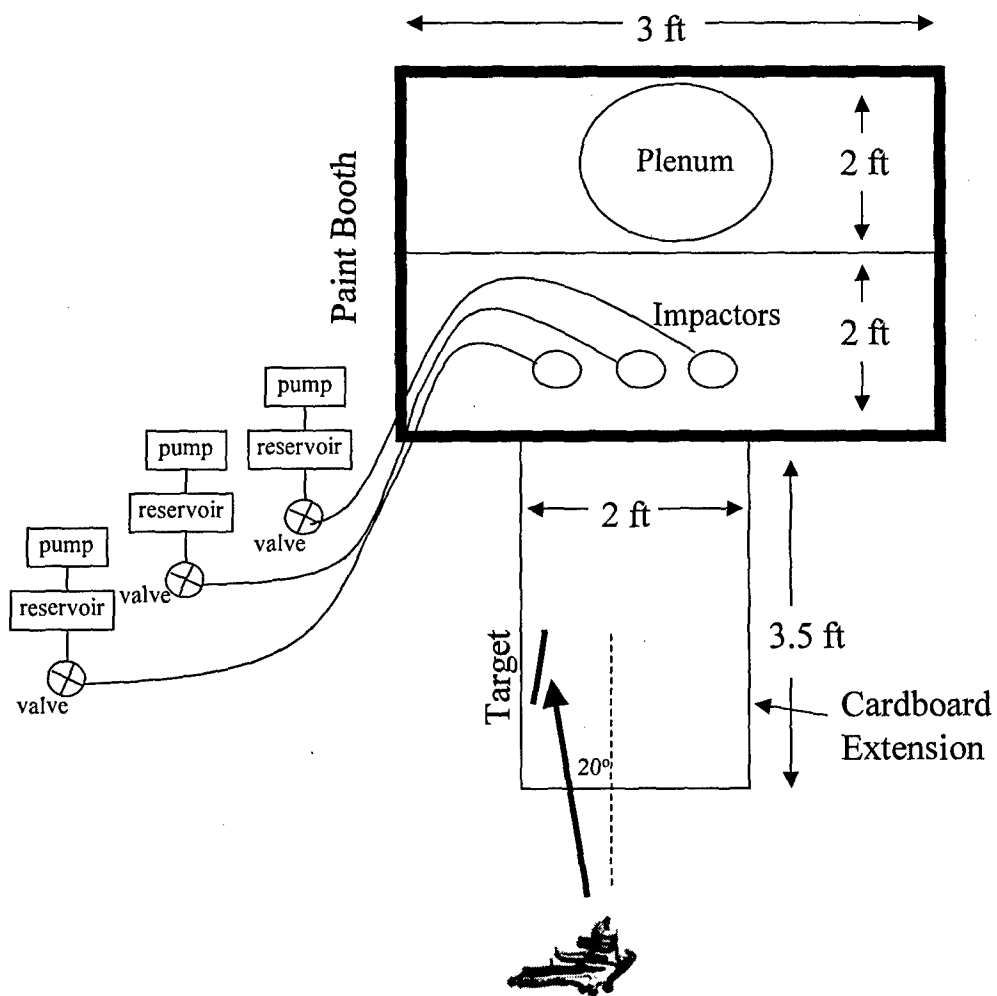


Figure 3-2 Particle Collection System

Upon completion of a spray painting session, the air pumps were turned off and the tubing was disconnected from the cascade impactors. The cascade impactors were disassembled and petri dishes were gently removed. Care was taken not to disturb the petri dishes to prevent paint particles from clumping or adhering to petri dish walls. Lids were placed on the petri dishes to prevent evaporation and contamination. For each of the four paint types, 12 sets of cascade impactors (6 petri dishes/impactor) were collected.

3.4 Sample Preparation

After particle collection, the petri dishes were incubated at 37 °C for 24 hours to allow dissociation of Cr⁺⁶ from the particles. Petri dishes were removed from the incubator and the Porcine-SLF containing particles were transferred to 50 mL glass beakers. The beakers were weighed while empty and then again with sample to obtain a more precise mass of the initial sample. Each beaker was then placed on an orbital shaker for 15 minutes at 100 rpm to evenly mix the particles and the dissolved Cr⁺⁶ in the Porcine-SLF. The samples were then split into two parts: Dissolved Cr and Total Cr as illustrated in Figure 3-1.

3.5 Centrifuge

In order to determine the mass of Cr⁺⁶ that dissociated from the paint particles into the Porcine-SLF (step 5 in Figure 3-1), approximately 5 mL of the initial sample was pipetted into a 15 mL Blue Max Jr. polypropylene conical centrifuge tube. The sample was centrifuged at 4000 rpm, 4 °C for 20 minutes [57] to remove the paint particles, leaving only dissociated Cr⁺⁶ in the Porcine-SLF. The supernatant from the centrifuged

sample was then transferred to a pre-weighed 30 mL Nalgene HDPE narrow-mouth sample bottle.

3.6 Cold Digest

After the supernatant was transferred, 5 mL of 70% nitric acid was added to the 30 mL sample bottle (step 6 of Figure 3-1). The addition of acid served two purposes: to partially digest mucin prior to analysis and to keep Cr^{+6} in solution (keeps all Cr^{+6} soluble). The sample bottle was weighed after the acid addition to calculate the final mass that would be analyzed by the ICP for dissolved Cr concentration. Dissolved Cr samples did not require aggressive digestion since the Cr^{+6} ions were already in solution. In addition to Cr, samples were also analyzed for barium (Ba) or Sr for quality control purposes. In a molecule of BaCrO_4 and SrCrO_4 , there is one atom of Ba, Sr or Cr so their concentration should be a ratio of their MWs.

3.7 Hot Digest

For accurate analytical results, ICP analysis requires metals to be dissolved in solution. The Total Cr samples contain solid paint particles that must be digested prior to analysis. EPA method 3010A was chosen to digest Total Cr samples. Method 3010A is an aggressive digestion method approved for metals analysis by ICP for paint particles in an aqueous matrix. The remaining 20 mL of the sample from the petri dish was digested using EPA Method 3010A to determine the total mass of Cr^{+6} in the initial samples.

Digestion (step 7 in Figure 3-1) was conducted by adding 15 mL of concentrated nitric acid (70%) to the 20 mL of the sample. The samples were placed on a hot plate and slowly evaporated to a volume of approximately 3 – 5 mL. Care was taken not to allow

the liquid to completely evaporate. The beaker was then removed and allowed to cool briefly. Next, 3 mL of concentrated nitric acid (70%) was added to the samples and the samples were returned to the hot plate. A watch glass was placed on the beaker and the samples were allowed to reflux until the sample was completely digested (i.e. digestate was light in color or there was no change in appearance after continued reflux). Nitric acid was added as needed during reflux to assure the samples did not dry out. After complete digestion, samples were removed and allowed to cool. Finally, 1 mL of 35% hydrochloric acid was added to the samples and they were returned to the hot plate. The hydrochloric acid dissolved any precipitates or residue resulting from sample volume reduction. Samples were refluxed for another 15 minutes and then removed and allowed to cool. Dilute nitric acid (2% w/w) was added to the samples to bring the total volume up to 10 mL. The dilute nitric acid was used to rinse the beaker walls to minimize transfer losses to the beaker. Samples were poured into 15 mL Blue Max Jr. polypropylene conical centrifuge tube. The digested samples were centrifuged at 4000 rpm, 4 °C for 20 minutes to remove any remaining non-digestible particles. The supernatant from the centrifuged samples were then transferred to pre-weighed 30 mL Nalgene HDPE narrow-mouth sample bottles. The samples and bottles were weighed to obtain the mass of the Total Cr samples analyzed by ICP.

3.8 Sample Analysis

After digestion, the mass of Ba, Cr, Sr, was quantified using a Varian Vista-MPX radial view ICP (step 8 in Figure 3-1). Samples were analyzed after collection of 12 impactors per paint with 6 petri dishes per impactor (72 petri dishes per paint). These samples were split into dissolved ions and total metal for 144 samples per paint. Total Cr

samples were analyzed first (run 1) followed by Dissolved Cr samples (run 2). A calibration curve, that will be discussed later, was performed prior to analysis of each run.

Digested samples were transferred from the 30 mL sample bottles to 15 mL polyethylene test tubes and loaded into the Varian SPS3 auto sampler. Blank samples were run for every 6 samples analyzed, which corresponds to the number of samples in each impactor. Blanks consisted of 5 mL of Porcine-SLF to 5 mL of nitric acid solution to closely resemble the Dissolved Cr sample's final matrix. Blanks for the Total Cr sample matrix consisted of 10 mL of 2% nitric acid. The blanks were used to ensure that there was not carry over between samples (i.e. mass from the previous sample remaining in the tubing and artificially inflating sample results). Samples were drawn into the ICP using its integrated peristaltic pump. A "Y" connector was used to simultaneously draw the sample and a 3-ppm rhodium internal standard into the ICP (described later).

ICP sample results were reported as micrograms of metal per gram of solute. The mass of a specific metal (Ba, Cr, Sr) present in the two sample fractions, Dissolved Cr and Total Cr, was determined by multiplying the ICP result by the mass of the sample being analyzed. The calibration standard matrix matched the mass density of the sample matrix being analyzed. The mass of each sample was taken so any differences in density or volume between the samples would be accounted for through this mass ratio. The dissolved mass is then divided by the total mass to get the fraction dissociated as illustrated in Figure 3.1. For more details on sample mass calculations see Appendix D.

3.8.1 Inductively Coupled Plasma (ICP) Device

ICP capitalizes on the optical emission of excited atoms to determine metal concentrations. Samples are passed through a plasma torch generated by flowing argon through a radio frequency (RF) coil. The plasma reaches temperatures of 6,000 to 10,000 K, sufficient to ionize and excite most atoms. Excited metal ions only release light energy in certain wavelengths. These unique wavelengths allow the instrument to identify metals in a sample. ICP technology allows for up to 70 metals to be analyzed at once and it has five orders of magnitude of linearity that allows for a wide range of concentrations to be analyzed.

Samples enter the ICP via a nebulizer. In this study, the cold digested samples were expected to have 3-5 % dissolved solids. Therefore, a "V-groove" nebulizer was chosen because of its ability to handle greater amounts of dissolved solids without clogging. In the "V-groove" nebulizer, the liquid sample falls under gravity across a high-pressure argon jet and is sheared into small droplets into a spray chamber. The spray chamber allows larger droplets to fall out and only a fine mist is allowed to proceed up into the plasma torch. A large amount of liquid will extinguish the plasma torch.

There are two torch configurations, radial view and axial view. For radial view, the light path is perpendicular to the direction of argon flow through the torch where as the light path for the axial view is parallel with the flow of argon through the torch. The radial view was chosen because it has less interference and has better detection limits in complex matrices like the Porcine-SLF.

The light intensity is measured using a combination of Eschelle grating and a prism. The light from the prism is detected using a solid-state array detector (charged coupled

device), which allows all pixels to be read in rapid succession. Quantitative analysis results are calculated from comparison to a linear regression curve generated by using standards of known amounts of a specific compound or element in solution. The ICP was optimized using the settings in Figure 3-4.

Condition	Setting	Condition	Setting
Power	1.2 kW	Replicate Read Time	10 sec
Plasma Flow	15.0 L/min	Instrument Stabilization Delay	15 sec
Auxiliary Flow	1.5 L/min	Sample Uptake Delay	25 sec
Nebulizer Pressure	190 kPa	Pump Rate	15 rpm
Viewing Height	10 mm	Rinse Time	90 sec
Replicates	3		

Figure 3-3 ICP Settings

3.8.2 Calibration Standards

Six standard solutions (50 ppb, 200 ppb, 500 ppb, 1 ppm, 10 ppm, 50 ppm) were prepared from High Purity (Charleston, SC) certified 1000 ug/mL solutions for Ba, Cr and Sr. Standards were prepared in a matrix that most closely matched the sample matrix. A calibration curve was performed prior to each run. For Total Cr samples, which ultimately consisted of digested metals in a dilute nitric acid solution, the standards were prepared in a 2% nitric acid solution. For the Dissolved Cr samples, which contain half Porcine-SLF and half 70% nitric acid, the standard matrix was also half Porcine-SLF and half 70% nitric acid and spiked with the appropriate amount of known standard to achieve the desired concentration. Calibration curves were generated prior to each run. Samples were analyzed after all samples were collected for a specific paint type. The software was set to fail if the R^2 was less than 0.995. A check blank and calibration check sample were measured after calibration was completed.

3.8.3 Internal Standard

A 3-ppm solution of rhodium was used as an internal standard. The ICP instrument automatically introduced an internal standard into the sample stream. This ensures that all samples are spiked with the same amount of internal standard. Slight differences in densities or the concentration of solids in the sample may affect the intensity of light emitted from the excited ions in the sample that may over or under estimate the true concentration. Since the internal standard concentration is held constant, it can be used to adjust any variations in intensity due to matrix effects.

3.9 Solubility in SLF

The *Water Solubility* test from the Organization for Economic Co-operation and Development Environmental Fate Guideline for Testing of Chemicals [79] was followed to determine the solubility of SrCrO_4 in Porcine-SLF. The rate of dissociation decreases and approaches zero as the concentration nears the solubility limit. The calculated percent Cr^{+6} dissociated will be influenced if concentrations were near the solubility limit.

Raw SrCrO_4 was added to 200 mL of SLF (3 samples) and incubated at 45 °C for 48 hours. The temperature was reduced to 37 °C for 72 hours and then the sample was analyzed for Cr concentration using ICP. Sample Cr concentrations were 42, 50 and 52 ppm with an average Cr concentration of 48 ppm. SrCrO_4 paint samples near or greater than 48-ppm total Cr may underestimate the percent of Cr^{+6} dissociation. The Dissolved Cr concentrations were all less than 10 ppm for all SrCrO_4 paint samples. Cr concentrations were well below the solubility limit. Raw BaCrO_4 was not available and its solubility in Porcine-SLF could not be determined although it is very likely less soluble in Porcine-SLF than in water.

3.10 Detection Limits

The method detection limit (MDL) was determined following procedures in 40 CFR Part 136, Appendix B "Definition and Procedures for the Determination of the Method Detection Limit". The MDL was determined for barium, Cr and Sr in 1:1 Porcine-SLF:nitric acid (Dissolved Cr samples) and 2% nitric acid (Total Cr samples). Ten replicates for each matrix were analyzed. An average of standard deviation multiplied by 3 was used to calculate the MDL for each metal. Table 3-3 lists the results.

	Barium (ppb)	Cr (ppb)	Sr (ppb)
Porcine-SLF	9	18	23
2% Nitric	1	15	28

Figure 3-4 Method Detection Limits

4 Results

Figure 4-1 summarizes the results from the four types of paint with 95% confidence intervals. The mean fraction of Cr^{+6} dissociation is shown for each particle size range within each type of paint. Tabular summaries of calculated percentages of Cr^{+6} dissociation for all four paint types can be found in Appendix A.

The data illustrates that the mean percentage of Cr^{+6} dissociation for BaCrO_4 (Water-Ba) into Porcine-SLF is much less than Cr^{+6} dissociation from the three SrCrO_4 paints (Solvent, Polyurethane and Water-Sr). Particle size also appears to influence the fraction of Cr^{+6} dissociated from paint particles that contain SrCrO_4 . Smaller particles release less Cr^{+6} than larger particles. The influence of particle size for the BaCrO_4 paint is not apparent. This may be due to the low fraction of Cr^{+6} dissociation in comparison to the SrCrO_4 paints.

Raw SrCrO_4 particles were added to 10 petri dishes containing Porcine-SLF. These samples were split, incubated and digested following the same method as the other paint samples. The raw SrCrO_4 samples contained particle sizes with much larger particles because these samples were not separated with a cascade impactor. The mean with 95% confidence interval is included in Figure 4-1 for comparison with the other paints. Concentrations of Cr^{+6} from raw SrCrO_4 in Dissolved Cr samples were well below the solubility limit of 48 ppm. The concentration of Cr in the dissolved samples ranged from 5 – 10 ppm. The Cr^{+6} dissociation of the raw SrCrO_4 was similar to Cr^{+6} dissociation in particles greater than 2.1 microns from the solvent and Water-Sr paints. The dissociation of Cr^{+6} was significantly less in the polyurethane and Water-Ba paints compared to the raw SrCrO_4 .

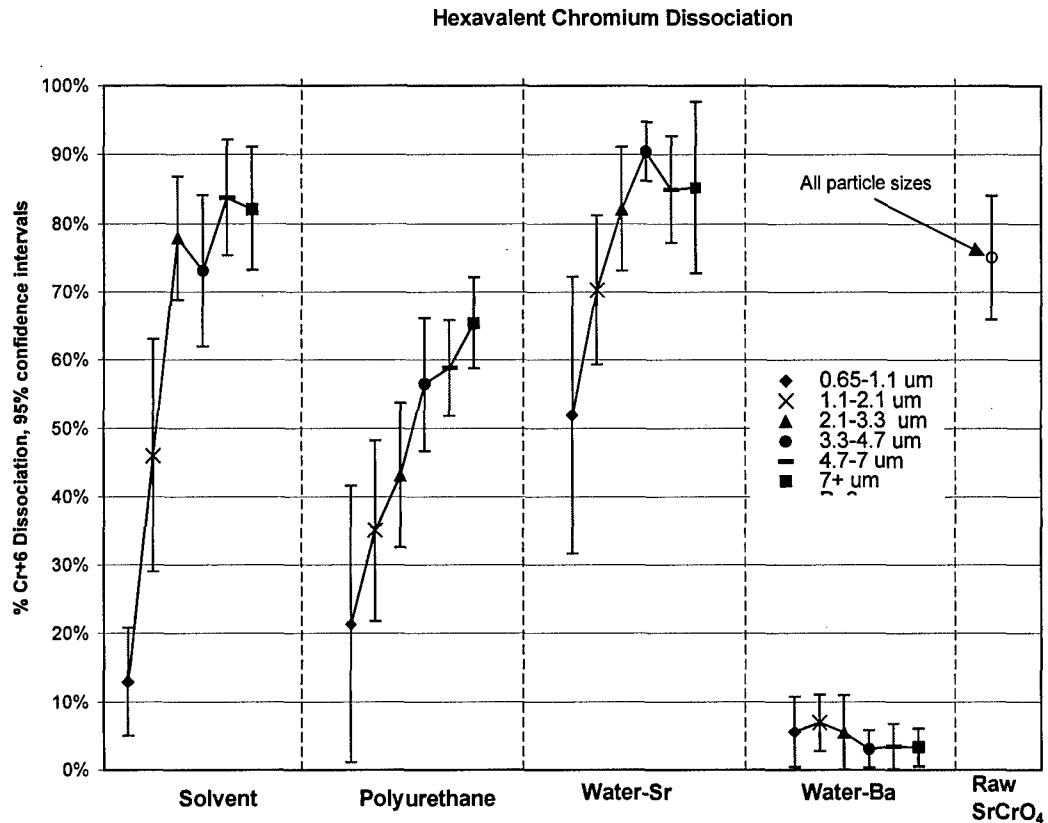


Figure 4-1 Mean and 95% Confidence Intervals for Cr⁺⁶ Dissociation (μg dissociated/ μg total)

4.1 Statistical Analysis

SPSS 12.0 statistical software was used to perform analysis of variance (ANOVA) tests to evaluate the data. ANOVA is a robust analytical technique and was used to determine if there were differences in or interaction between particle size and paint type. The assumptions made are the sample populations must be random and independent of each other. Also, the sample populations are assumed to be normally distributed and have the same variance. Due to the small number of samples, there was concern over the normality of the sample populations. Quantile-quantile (QQ) plots were used to assess the normality of each sample population. The QQ plot compares the percentile of sample

data (observed) to the percentile of a standard normal distribution (expected). Perfectly normal data will lie on the 45-degree line. Figure 4-2 is a representative QQ plot of data for the Water-Sr % dissociation. The remaining plots for the other paints are located in Appendix C. The data does not deviate significantly from the line; therefore the assumption of normality is not grossly violated.

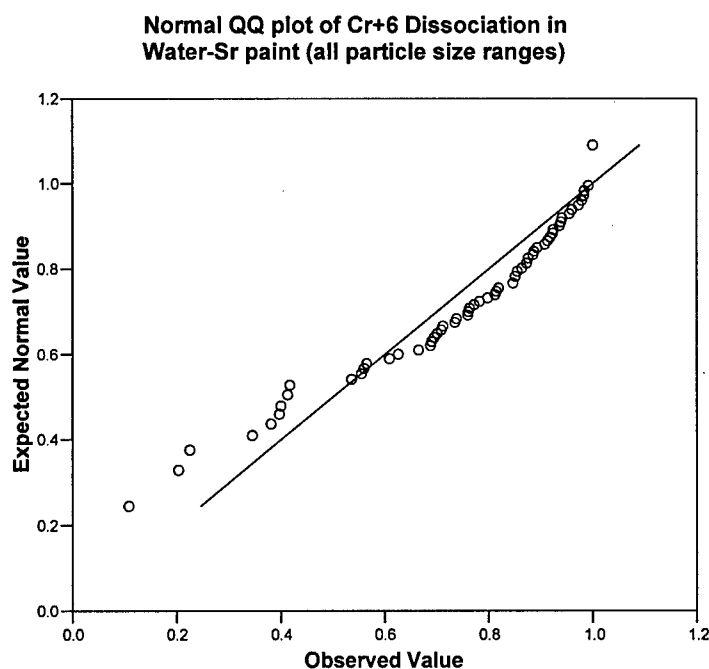


Figure 4-2 QQ Plot for Particle Sizes within Water-Sr Paint

A two way ANOVA test was run first to determine if there was any interaction between the two variables of interest: particle size and paint type. The test showed no interaction between the two variables ($p < 0.001$). Since there was no interaction, the one-way ANOVA test was used to compare the means of the different paint types and particle sizes.

4.1.1 Particle Size Comparison

Quantitative comparison of the means of Cr^{+6} dissociation between all six particle-size ranges within each paint type was done using SPSS one-way ANOVA. ANOVA is a simultaneous multiple comparison of the means and was performed at an overall significance level of $\alpha = 0.05$. Examining all of the particle sizes for each paint collectively revealed statistical differences between particle-size ranges in chromate dissociation for three of the paint types: solvent, polyurethane and water-Sr ($p < 0.001$). No statistical difference between particle sizes was noted in the Water-Ba paint ($p = 0.741$).

Figure 4-3 illustrates the simultaneous comparison of means between particle sizes in each paint type. Particle size ranges are grouped in subsets of means where no statistical difference was found (underlined groups). Although for the largest four particle size ranges there is no statistical difference, there is a clear trend indicating that smaller particles release less Cr^{+6} than larger particles. Overall, particle sizes greater than 4.7 microns released a significantly greater amount of Cr^{+6} than particles less than 2.1 microns for the polyurethane and solvent paint ($p < 0.001$) and particles less than 1.1 microns for water based paint ($p = 0.001$).

4.1.2 Paint – Paint Comparison

ANOVA was used to evaluate the effect of paint type on the dissociation rate of Cr^{+6} . Figure 4-4 illustrates the simultaneous comparison of means between paint types in each particle size range. Paint types are grouped in subsets of means (underlined groups) where no statistical difference was found. Each particle size range was compared across all four paint types and differences were noted among the paint types ($p < 0.001$). Overall,

the Water-Sr paint had the highest mean percentage of chromate dissociation for all particle size ranges, although the solvent paint was not statistically different for three

	0.65-1.1 micron	1.1-2.1 micron	2.1-3.3 micron	3.3-4.7 micron	4.7-7 micron	7+ micron
Solvent	0.13	0.46	0.78	0.73	0.84	0.82
Polyurethane	0.21	0.35	0.43	0.56	0.59	0.65
Water-Sr	0.52	0.70	0.82	0.90	0.85	0.85
Water-Ba	0.05	0.07	0.05	0.03	0.03	0.03

Figure 4-3 One way ANOVA Particle Size Comparison (Horizontal bar indicates “no significant difference” between underlined groups)

particle size ranges ($p > 0.89$), see Figure 4-4. The Water-Ba paint had the lowest mean chromate dissociation percentage ($p < 0.005$). The polyurethane paint had the lowest mean Cr^{+6} dissociation among the SrCrO_4 paints for particles greater than 2.1 microns ($p < 0.019$).

4.1.3 Base Paint Comparison

It was theorized that the chemical bonds formed during the reaction between the base paint and the catalyst sequester the Cr^{+6} particles and hinders its ability to dissociate into the Porcine-SLF. If this is true, then spraying the base component (no catalyst added)

alone, which contains all the chromate, should release more Cr^{+6} than the mixed paints. In order to determine if the paint mixture releases less Cr^{+6} over the base component, samples were collected spraying only the base paint. Three cascade impactors were used

	Solvent	Water-Sr	Polyurethane	Water-Ba
0.65-1.1 micron	0.13	0.52	0.21	0.05
1.1-2.1 micron	0.46	0.70	0.35	0.07
2.1-3.3 micron	0.78	0.82	0.43	0.05
3.3-4.7 micron	0.73	0.90	0.56	0.03
4.7-7 micron	0.84	0.85	0.59	0.03
>7 micron	0.82	0.85	0.65	0.03

Figure 4-4 One way ANOVA Paint Type Comparison (Horizontal bar indicates "no significant difference" between underlined groups)

for each base paint collection. With four paints, twelve impactors with all six-particle size ranges were collected. The base component samples were handled in the same way as all mixed paint samples. Figures 4-5 to 4-8 compare the mean Cr^{+6} dissociation for each two-part paint mixture and its corresponding base paint with 95% confidence intervals.

It was unexpected that the base paints released less Cr^{+6} than the paint mixtures. It is also interesting that the base appeared to release less Cr in the SrCrO_4 paints but not in

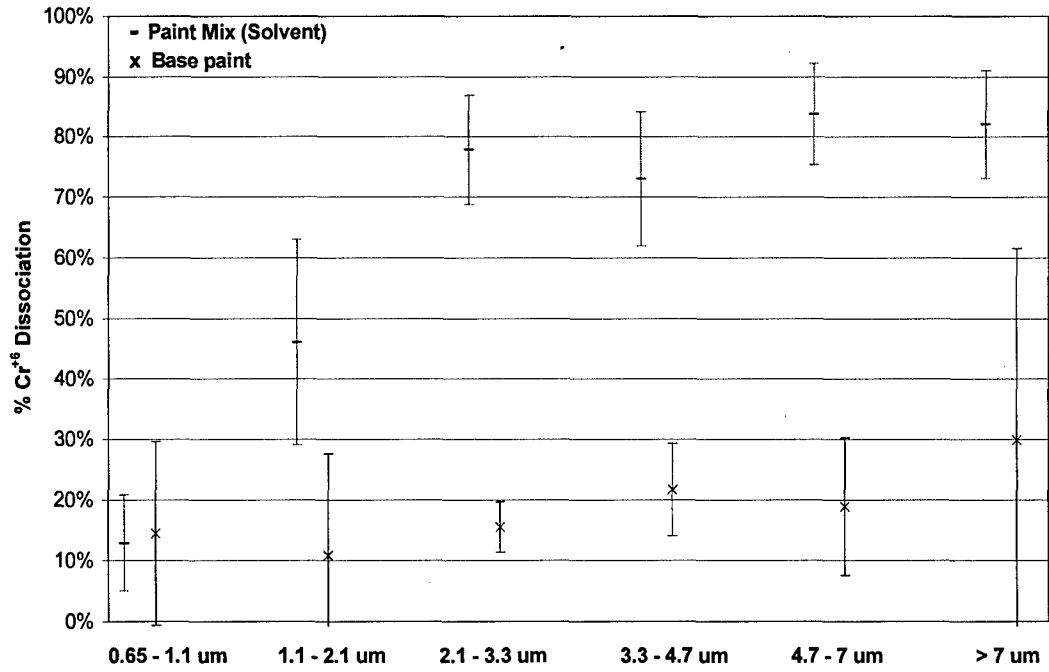


Figure 4-5 Cr⁺⁶ Dissociation: Paint Mix (solvent) vs. Base Paint (mean with 95% CI)

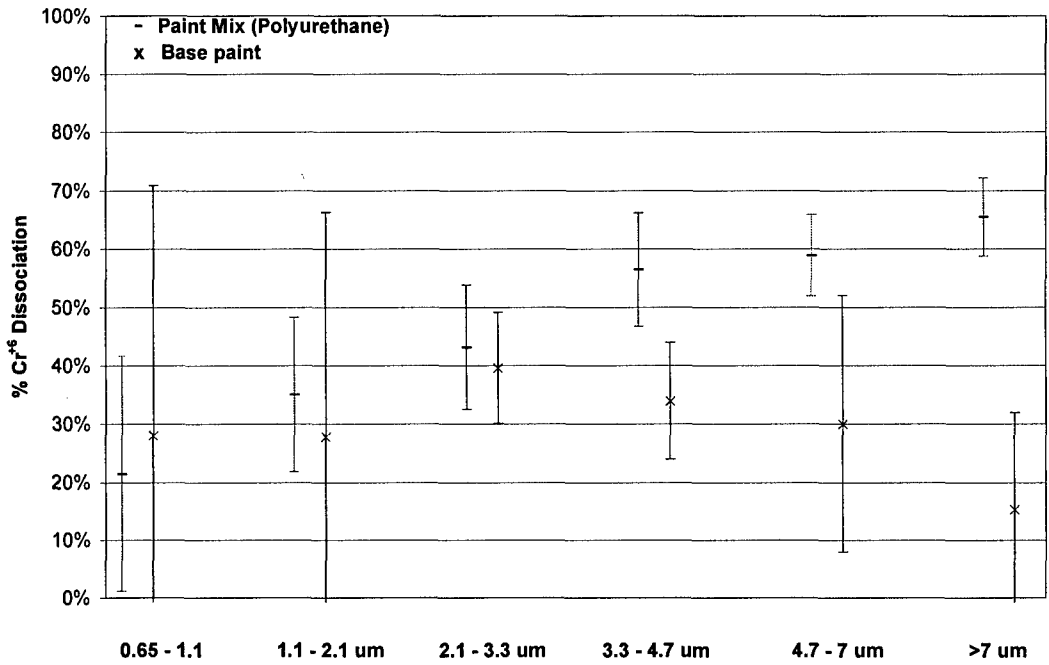


Figure 4-6 Cr⁺⁶ Dissociation: Paint Mix (polyurethane) vs. Base Paint (mean with 95% CI)

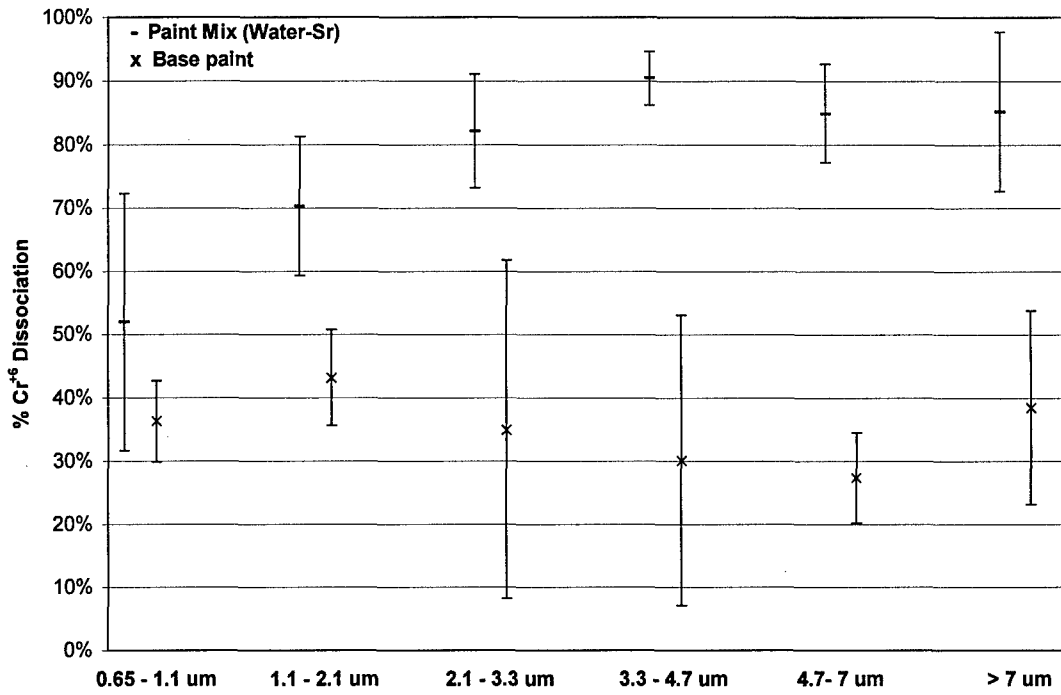


Figure 4-7 Cr⁺⁶ Dissociation: Paint Mix (Water-Sr) vs. Base Paint (mean with 95% CI)

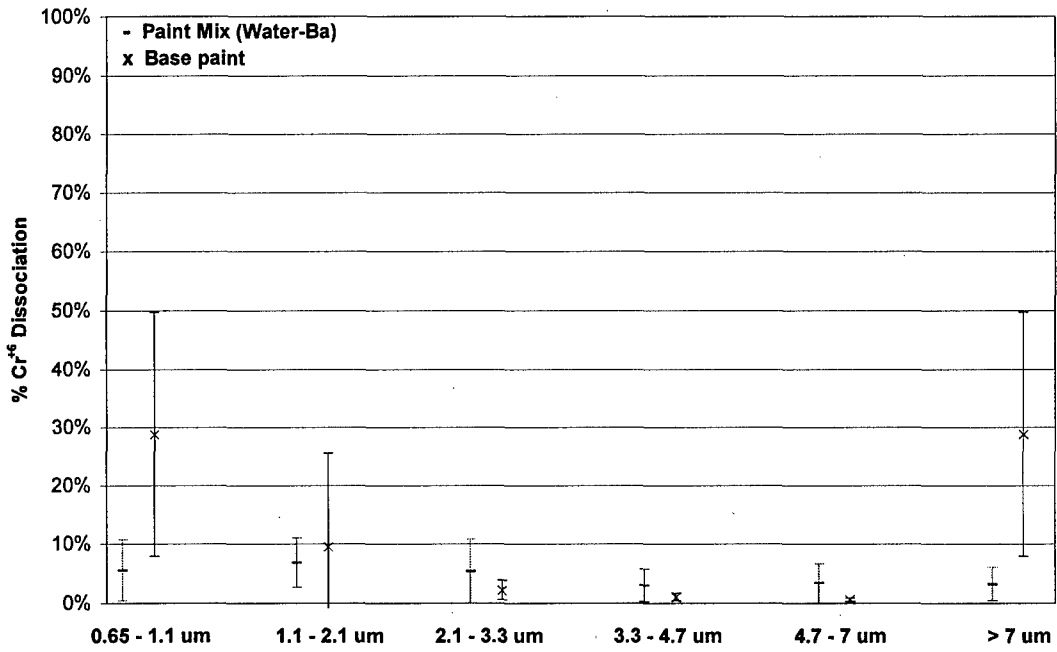


Figure 4-8 Cr⁺⁶ Dissociation: Paint Mix (Water-Ba) vs. Base Paint (mean with 95% CI)

the BaSrO₄. This implies that the release rate of BaCrO₄ may have more to do with BaCrO₄ interaction with the Porcine-SLF and little to do with the other constituents in the paint. The data does not support the theory that the chemical bonds in the base-catalyst reaction (cross linkages) sequester the Cr⁺⁶ ion from dissociating from the paint particles.

Due to the small sample size of base paints, normality could not be assumed so non-parametric methods were used to compare the base paints with the mixed paint samples. SPSS was used to compare the means of the base paint to the two-part mixture using the Mann-Whitney U two independent samples test. No statistical difference was found between the Water-Ba paint mixture and its base paint for all particle size ranges ($p > 0.05$). SrCrO₄ paint mixtures released more Cr⁺⁶ than the base paint in larger particle size ranges (particles $> 3.3 \mu\text{m}$, $p < 0.018$).

4.2 Particle Penetration in Porcine-SLF

The viable cascade impactor deposited particles captured from the paint overspray and deposited them into the Porcine-SLF. Particles clumping together on the surface of the Porcine-SLF could bias the results. A microscope was used to observe samples after they were removed from the cascade impactor prior to incubation. Observations found that the majority of the particles penetrated into the Porcine-SLF and were fully submerged. The force of the jets in the cascade impactor was sufficient to prevent surface accumulation of paint particle on the Porcine-SLF.

4.3 Quality Control

Sr and Ba were simultaneously analyzed with Cr to ensure all Cr detected was derived from the chromate compound. Sr and Ba are in a 1:1 mole ratio with the chromate ion. The number of moles of Sr and Ba were plotted against the number of moles of Cr for each paint type. A linear regression was performed using SPSS and the line of best fit was plotted on the graph with the corresponding R^2 for that line (see Figures 4-3 to 4-6). One paint (Water-Sr) was found to have the expected 1:1 ratio of Cr to Sr. The solvent and polyurethane paints deviated 34 – 40 percent, but the line of best fit had a R^2 of 0.98. This ruled out random error and likely can be attributed to a compound in the paint matrix interfering with the detection of either Cr or Sr. The fact that the error was repeatable suggests the comparison of dissolved Cr to total Cr will mediate the effect of the difference. The Water-Ba paint deviated significantly from unity and had a very low R^2 . The concentration of $BaCrO_4$ samples was close to the ICP detection limit in many samples and may have resulted in more variability than samples at greater concentrations.

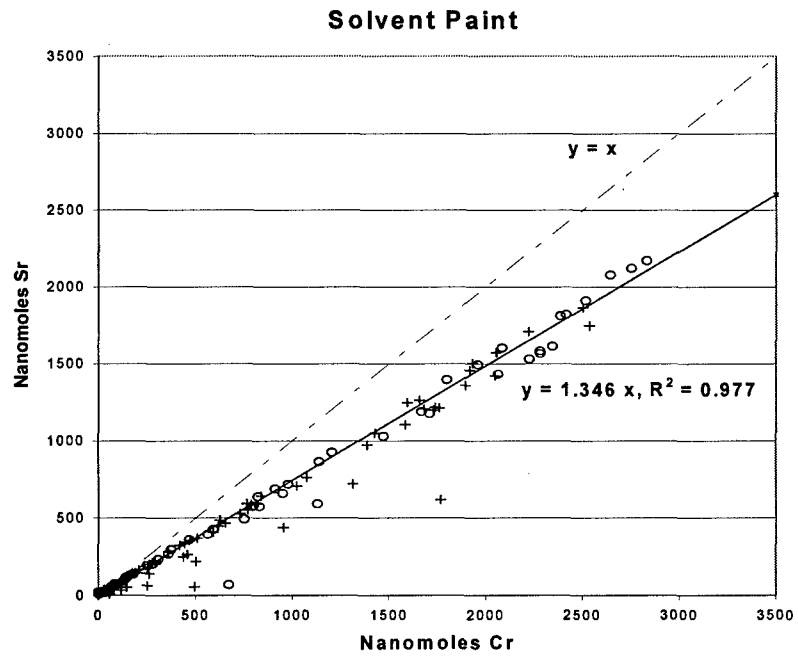


Figure 4-9 Solvent Cr:Sr Ratio

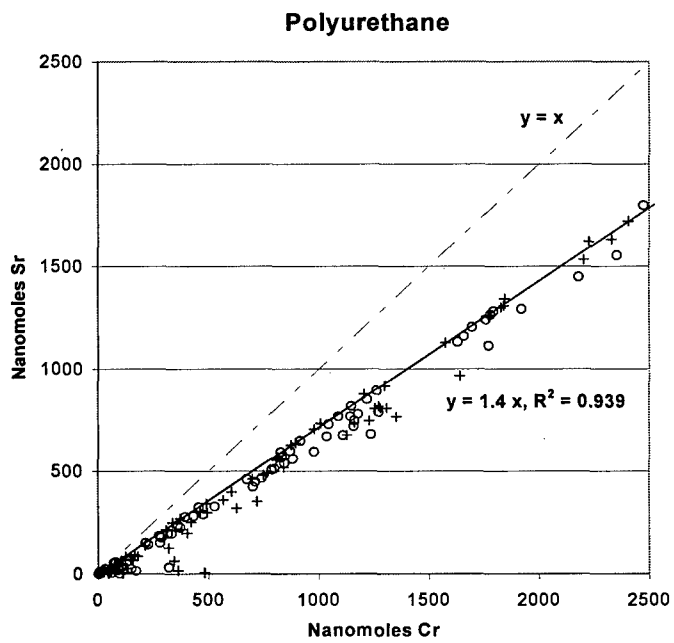


Figure 4-10 Polyurethane Cr:Sr Ratio

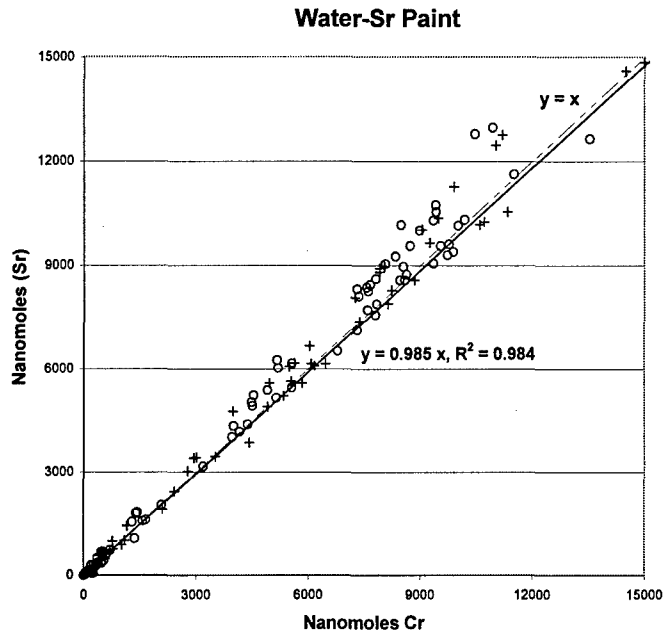


Figure 4-11 Water-Sr Cr:Sr Ratio

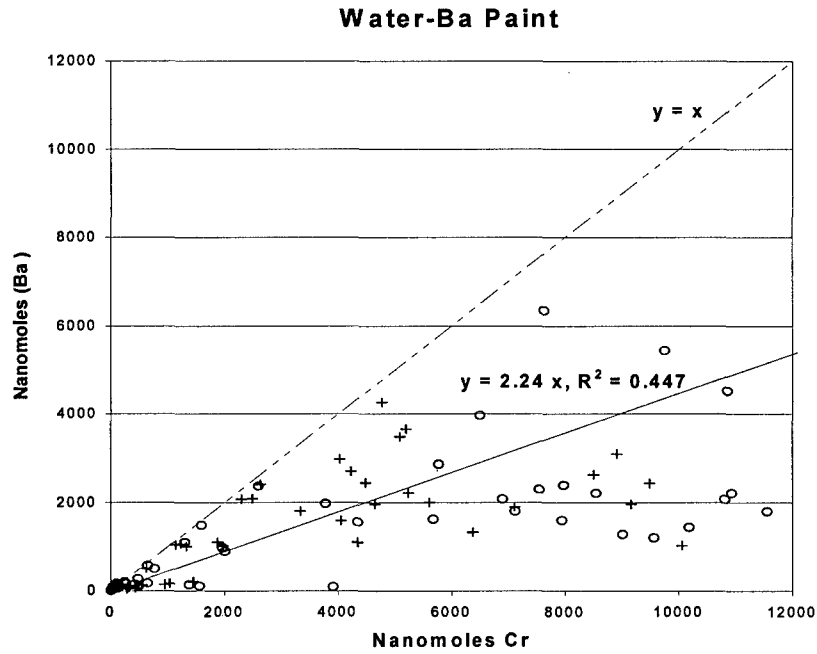


Figure 4-12 Water-Ba Cr:Ba Ratio

5 Discussion

The main objectives of this thesis were to:

1. Determine if particle size affects the amount of Cr^{+6} dissociation from primer paint particles into Porcine-SLF.
2. Determine if different paint types release the same fraction of Cr^{+6} into a Porcine-SLF.
3. Develop a method to separate particles based on aerodynamic diameter and deposit them in a fluid representative of human airway fluid.

There was a trend that indicates smaller particles release less Cr^{+6} than larger particles. Although statistical differences between all particle sizes were not consistent, statistical differences were found between particles above and below 2.1 microns. This trend is evident for the three SrCrO_4 paints where overall dissociation rates were highest. For the Water-Ba paint, no detectable difference between the particle sizes and Cr^{+6} dissociation was apparent. The first three paint types contain SrCrO_4 while the Water-Ba paint contains BaCrO_4 . The solubility of BaSrO_4 is likely less than SrCrO_4 based on their solubility in water (1200 ppm SrCrO_4 , 2.6 ppm BaSrO_4). It is possible that the dissolved Cr^{+6} concentration for the Water-Ba paint was near the solubility limit of BaSrO_4 , significantly reducing the dissociation rate.

The type of paint matrix was a significant factor that affects the amount of Cr^{+6} dissociation. The solvent and water based paints were found to have no significant difference in overall Cr^{+6} dissociation. The polyurethane paint had significantly less Cr^{+6} dissociation rates than the water based and solvent paints. The mean dissociation rates for

particles greater than 2.1 microns ranged from 21-65% for the Polyurethane paint while the Solvent and the Water-Sr were between 80-90%. The dissociation of Cr^{+6} for the Water-Ba was clearly the lowest, with the means for all particle sizes ranging from 3-7%. It is possible that the concentrations may have been near the solubility limit for BaCrO_4 . These factors are described more fully in the limitation section. These results suggest that the Water-Ba paint may be a safer paint from a health standpoint because the bioavailability and solubility of the Cr^{+6} is much less than the Sr based paints.

Raw SrCrO_4 was added directly to the Porcine-SLF and analyzed using the same method as other paint samples. The mean Cr^{+6} dissociation (75%) was lower than the expected 100% dissociation. This suggests that time may be a factor. It may take more than 24 hours for full dissociation.

Surprisingly, the two part paint mixtures (base plus catalysts) were found to release more chromate than the base paints alone. It was thought that the polymer cross-linking within the mixed paint would hinder Cr^{+6} dissociation. However, these results suggest otherwise. It appears that the base alone hinders the release of Cr^{+6} but the base catalyst reaction may act to release more Cr^{+6} . This experiment was designed to observe the release rate of Cr^{+6} from various mixtures. Further research is needed to better understand why the base paint releases less Cr^{+6} than the mixed paint.

This research also demonstrates a technique that can be used to test the bioavailability of other aerosols. The particles were successfully collected and separated based on particle size into a solution that closely resembles human lung fluid. Using centrifugation to then eliminate particles and testing the dissociated versus the total

analyte collected, is a useful tool in evaluating the bioavailability of most any constituent found within an aerosol.

5.1 Limitations

Several factors exist that may have biased the Cr^{+6} dissociation results. Concentrations of dissolved Cr^{+6} in the 0.65 – 1.1 micron range (0 to 50 ppb) was near or below the instruments detection limits for Cr (18 ppb), which introduces some variability. The separate handling of dissolved and total Cr samples may have introduced some systematic error. When the samples were split, the Porcine-SLF with captured paint particles may not have been a perfectly homogenous mixture (i.e. if a larger fraction of solid particles was removed with the dissolved fraction, the % dissociation would be over estimated). Because the solubility of BaCrO_4 is unknown, the percent Cr^{+6} dissociation may be underestimated if the dissolved Cr^{+6} concentration was near or reached the solubility limit.

5.2 Future Work

One of the aims of this study was to develop a method to assess what fraction of contaminants inhaled are available for uptake by the lung. The method developed for this study successfully captured the respirable fraction of a contaminant and deposited it into a Porcine-SLF. However, it was not possible at this time to validate the model. Human lung fluid is a complex mixture and difficult to reproduce, so future studies may pursue obtaining human lung fluid to evaluate how closely the Porcine-SLF compares.

Low concentrations and high variability made it difficult to evaluate Cr^{+6} dissociation at the lower range of particle sizes (<2 micron). Higher concentrations are

needed for all four paints for particles less than 2 microns. This may be accomplished by altering the sampling method to allow for higher concentrations of smaller particles to be collected. It is also unknown why the base paints and the raw SrCrO_4 dust did not reach 100% dissociation despite the fact that concentrations were below the solubility limit. More research is needed to understand if this is caused by a very slow dissolution rate or some other phenomenon.

The Porcine-SLF in this study was representative of the mucus layer in the respiratory tract. Results show that a large fraction of the SrCrO_4 escapes the paint particle into the Porcine-SLF. However, the Cr^{+6} must travel through the periciliary sol layer to reach the lung tissue and then through the cell membrane to reach the DNA. The next step would be to determine what portion of the Cr^{+6} in the mucus reaches the cell membrane and what fraction enters into lung cells.

Appendix A Cr⁺⁶ Dissociation Percentages

Solvent Cr ⁺⁶ Dissociation					
0.65 - 1.1 micron	1.1 - 2.1 micron	2.1 - 3.3 micron	3.3 - 4.7 micron	4.7 - 7 micron	7+ micron
0.0%	6.5%	52.0%	29.3%	58.7%	46.1%
0.0%	8.9%	64.3%	48.3%	68.4%	73.5%
0.0%	12.3%	66.1%	67.3%	77.1%	77.8%
3.8%	23.6%	71.0%	72.8%	79.9%	78.1%
6.4%	47.4%	74.4%	76.9%	82.8%	78.3%
7.1%	49.7%	75.2%	78.5%	86.9%	82.6%
13.6%	50.2%	77.6%	81.1%	87.3%	82.8%
13.9%	61.6%	81.0%	81.9%	88.5%	84.5%
21.5%	69.3%	81.2%	83.5%	92.3%	92.1%
21.7%	71.1%	94.5%	83.8%	100.0%	94.5%
29.2%	71.2%	98.0%	86.2%	100.0%	95.3%
37.8%	81.1%	99.3%	87.6%		100.0%
Polyurethane Cr ⁺⁶ Dissociation					
0.65 - 1.1 micron	1.1 - 2.1 micron	2.1 - 3.3 micron	3.3 - 4.7 micron	4.7 - 7 micron	7+ micron
0.0%	7.6%	12.5%	32.0%	44.3%	50.5%
0.0%	16.5%	33.5%	37.7%	45.7%	51.4%
0.0%	21.1%	33.6%	46.5%	50.9%	58.1%
0.0%	24.0%	34.2%	47.2%	51.1%	58.2%
2.2%	26.3%	36.6%	50.2%	52.2%	63.3%
5.1%	28.1%	38.0%	55.3%	53.1%	64.6%
7.3%	32.8%	41.4%	57.7%	57.9%	64.8%
17.0%	33.1%	45.4%	61.3%	63.7%	67.8%
18.5%	33.2%	49.2%	62.2%	66.9%	68.8%
40.6%	50.6%	51.8%	64.7%	70.4%	71.8%
65.6%	73.0%	62.5%	77.8%	74.4%	80.1%
100.0%	74.4%	79.0%	85.0%	75.8%	85.9%

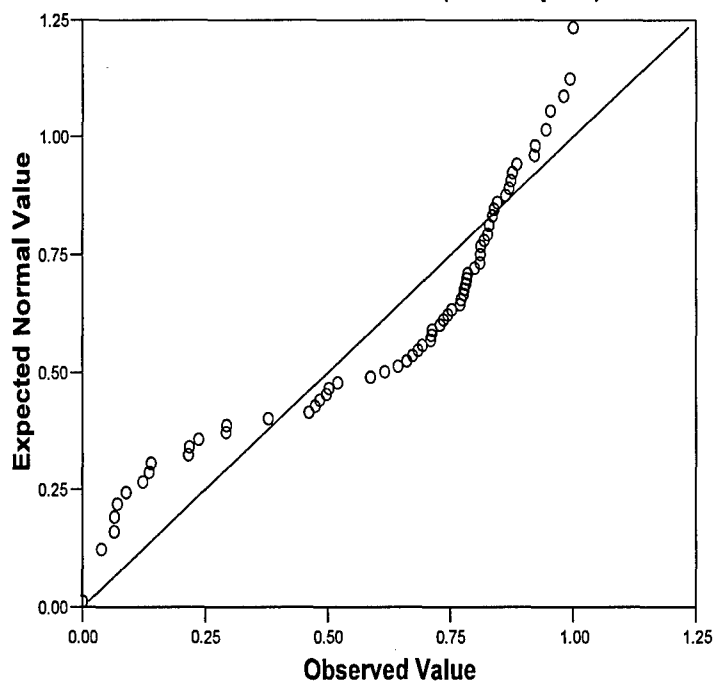
Water Cr⁺⁶ Dissociation					
0.65 - 1.1 micron	1.1 - 2.1 micron	2.1 - 3.3 micron	3.3 - 4.7 micron	4.7 - 7 micron	7+ micron
10.8%	39.7%	55.5%	76.0%	56.0%	38.1%
20.3%	53.6%	66.5%	84.7%	73.5%	60.9%
22.5%	56.5%	68.8%	85.1%	77.2%	69.5%
34.5%	62.6%	76.1%	87.3%	81.5%	79.8%
40.0%	69.0%	78.2%	88.5%	81.9%	92.4%
41.3%	70.1%	81.2%	89.3%	87.3%	93.9%
41.3%	70.9%	85.1%	91.3%	87.6%	94.1%
41.7%	71.2%	85.5%	93.6%	90.8%	95.5%
84.7%	73.8%	88.7%	96.0%	91.8%	98.3%
86.4%	76.3%	100.0%	97.3%	92.3%	100.0%
100.0%	100.0%	100.0%	97.9%	99.2%	100.0%
100.0%	100.0%	100.0%	98.4%	100.0%	100.0%
Water-Ba Cr⁺⁶ Dissociation					
0.65 - 1.1 micron	1.1 - 2.1 micron	2.1 - 3.3 micron	3.3 - 4.7 micron	4.7 - 7 micron	7+ micron
0.0%	1.5%	0.8%	0.4%	0.3%	0.3%
0.3%	1.6%	0.9%	0.7%	0.7%	0.6%
0.7%	2.2%	1.0%	1.0%	0.8%	0.7%
1.2%	2.2%	1.0%	1.1%	0.9%	0.9%
2.3%	2.9%	1.2%	1.1%	0.9%	1.0%
2.6%	3.0%	1.2%	1.4%	1.0%	1.1%
3.8%	5.1%	1.8%	1.6%	1.1%	1.2%
3.9%	7.1%	1.8%	1.8%	1.7%	1.4%
6.0%	8.9%	2.8%	3.2%	1.7%	1.7%
7.1%	9.8%	3.0%	3.4%	3.0%	8.2%
9.5%	16.9%	4.2%	4.2%	12.9%	8.9%
29.7%	21.9%	45.8%	16.2%	16.0%	13.5%

Appendix B Summary of Mean Dissociation (Figure 4-1)

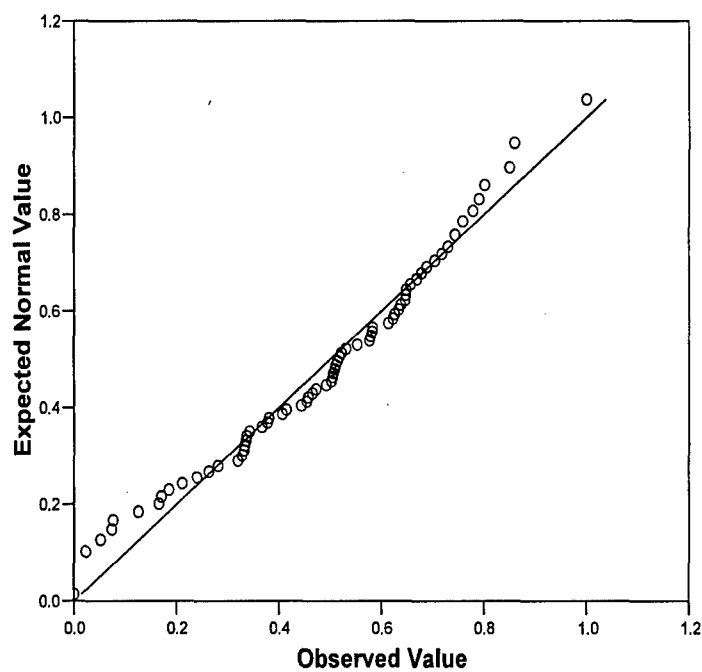
	Solvent		Polyurethane		Water-Sr		Water-Ba	
	Mean	St Dev	Mean	St Dev	Mean	St Dev	Mean	St Dev
0.65 - 1.1 micron	12.9%	12.4%	21.4%	21.1%	52.0%	31.9%	5.6%	8.1%
1.1 - 2.1 micron	46.1%	26.8%	35.1%	20.8%	70.3%	17.3%	6.9%	6.6%
2.1 - 3.3 micron	75.9%	13.1%	43.1%	16.7%	82.1%	14.2%	5.5%	12.7%
3.3 - 4.7 micron	73.1%	17.5%	56.5%	15.3%	90.5%	6.7%	3.0%	4.3%
4.7 - 7 micron	83.8%	12.5%	58.9%	11.0%	84.9%	12.2%	3.4%	5.2%
7+ micron	82.1%	14.0%	65.4%	10.6%	85.2%	19.6%	3.3%	4.4%

Appendix C Normal QQ Plots

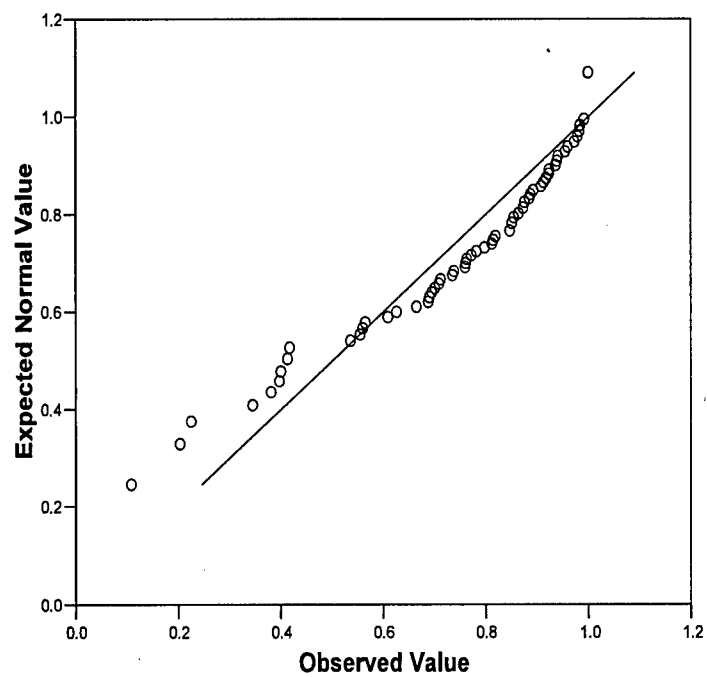
Normal Q-Q Plot of Solvent (all samples)



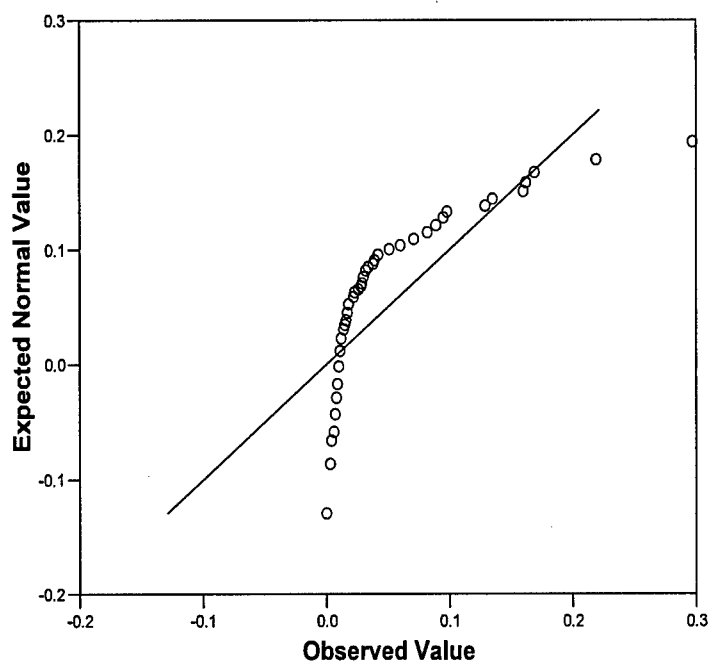
Normal Q-Q Plot of Polyurethane (all samples)



Normal Q-Q Plot of Water-Sr (all samples)



Normal Q-Q Plot of Water-Ba (all samples)



Appendix D Sample Data for % Cr⁺⁶ Calculation

This appendix contains raw sample data required to calculate the % Cr⁺⁶ dissociation. As described previously (Chapter 3), all initial samples (each petri dish) were split into two fractions (dissolved and total) and analyzed by ICP to determine the mass of Cr⁺⁶. Two steps are required to calculate the mass of dissolved and total Cr⁺⁶ in the initial sample. First, the mass of Cr⁺⁶ of each fraction of the split sample must be determined. The ICP result was multiplied by the mass of each sample fraction analyzed: M_{TD} or $[M_D + M_A]$. Next, the mass of dissolved (Cr_{OD}) and total (Cr_{OT}) Cr⁺⁶ in the initial sample was calculated. The mass of Cr⁺⁶ in each split fraction was multiplied by its corresponding mass fraction: mass of the initial sample (M_O) divided by the mass of the split fraction (M_D or M_T). These two steps were combined to form the equations below. The % Cr⁺⁶ dissociation was calculated by dividing Cr_{OD} by Cr_{OT} .

$$Cr_{OD} = ICP_D * [M_D + M_A] * \frac{M_O}{M_D}$$

Cr_{OD} mass dissolved Cr in initial sample (ug)
 ICP_D ICP result ug Cr /g solute ($M_D + M_A$)
 M_D mass of Dissolved Cr fraction (g)
 M_A mass of acid (g)
 M_O mass of initial sample (g)

$$Cr_{OT} = ICP_T * M_{TD} * \frac{M_O}{M_T}$$

Cr_{OT} mass total Cr in initial sample (ug)
 ICP_T ICP result ug Cr /g solute (M_{TD})
 M_{TD} mass of digested Total Cr sample (g)
 M_T mass of Total Cr fraction (g)
 M_O mass of initial sample (g)

Appendix D-1 Solvent Paint (Deft 02-Y-040A)

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 0.65 - 1.1 microns	1	total	21.661	10.416		16.091	0.213	2.991	22%
		diss.*		12.57	5.57		0.013	0.648	
	2	total	22.581	11.305		16.513	0.079	1.214	14%
		diss.*		13.068	6.068		0.003	0.168	
	3	total	22.616	10.223		16.824	0.163	2.239	22%
		diss.*		12.792	5.792		0.01	0.481	
	4	total	23.113	10.164		17.566	0.172	2.302	4%
		diss.*		12.547	5.547		0.002	0.087	
	5	total	23.077	12.039		17.265	0.058	0.941	7%
		diss.*		12.812	5.812		0.001	0.067	
	6	total	22.503	10.702		17.791	0.142	1.929	6%
		diss.*		11.712	4.712		0.002	0.124	
	7	total	23.676	10.817		18.752	0.557	7.601	14%
		diss.*		11.924	4.924		0.018	1.037	
	8	total	23.643	10.803		16.227	0.059	0.932	0%
		diss.*		14.416	7.416		0	0	
	9	total	21.84	10.382		15.848	0.148	2.119	0%
		diss.*		12.992	5.992		0	0	
	10	total	23.051	10.704		18.721	0.107	1.404	29%
		diss.*		11.33	4.33		0.007	0.409	
	11	total	22.3	10.72		18.17	0.198	2.603	115%
		diss.*		11.13	4.13		0.05	2.997	
	12	total	23.902	11.939		18.929	0.098	1.482	0%
		diss.*		11.973	4.973		0	0	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 1.1 - 2.1 microns	1	total	21.895	11.315		16.5	0.41	6.155	71%
		diss.*		12.395	5.395		0.087	4.376	
	2	total	22.325	10.918		17.566	0.483	6.705	50%
		diss.*		11.759	4.759		0.061	3.366	
	3	total	21.592	12.433		15.965	0.27	4.548	69%
		diss.*		12.627	5.627		0.065	3.152	
	4	total	21.554	11.538		16.059	0.519	8.035	62%
		diss.*		12.495	5.495		0.101	4.946	
	5	total	22.743	11.613		17.452	1.711	25.897	24%
		diss.*		12.291	5.291		0.116	6.11	
	6	total	21.919	10.851		17.361	2.554	34.992	9%
		diss.*		11.558	4.558		0.056	3.112	
	7	total	22.165	11.847		17.048	0.852	13.122	12%
		diss.*		12.117	5.117		0.031	1.617	
	8	total	23.235	10.581		14.815	0.134	2.23	7%
		diss.*		15.42	8.42		0.003	0.146	
	9	total	23.383	12.646		18.715	0.689	10.883	71%
		diss.*		11.668	4.668		0.133	7.753	
	10	total	21.578	11.06		16.808	0.628	8.919	50%
		diss.*		11.77	4.77		0.083	4.434	
	11	total	22.072	10.291		17.327	0.618	8.105	81%
		diss.*		11.745	4.745		0.12	6.569	
	12	total	22.498	10.359		17.546	0.702	9.328	47%
		diss.*		11.952	4.952		0.081	4.419	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 2.1 - 3.3 microns	1	total	21.198	11.978		15.97	2.053	32.634	81%
		diss.*		12.228	5.228		0.533	26.426	
	2	total	21.857	10.552		16.524	1.151	16.059	75%
		diss.*		12.333	5.333		0.239	12.073	
	3	total	21.196	15.426		16.196	1.15	23.211	66%
		diss.*		12	5		0.302	15.346	
	4	total	22.695	10.137		17.278	1.47	19.574	74%
		diss.*		12.417	5.417		0.28	14.567	
	5	total	22.941	11.28		16.843	1.709	26.258	52%
		diss.*		13.098	6.098		0.277	13.652	
	6	total	23.779	12.641		18.709	0.456	7.333	99%
		diss.*		12.07	5.07		0.129	7.286	
	7	total	21.236	12.531		16.264	0.608	9.952	81%
		diss.*		11.972	4.972		0.158	8.083	
	8	total	23.955	11.935		18.403	0.884	13.736	64%
		diss.*		12.552	5.552		0.163	8.832	
	9	total	22.607	11.73		17.709	1.641	24.573	95%
		diss.*		11.898	4.898		0.423	23.21	
	10	total	22.313	12.289		17.622	1.56	24.273	78%
		diss.*		11.691	4.691		0.339	18.841	
	11	total	22.799	10.47		18.785	1.723	21.89	1090%
		diss.*		11.014	4.014		3.813	238.503	
	12	total	22.606	11.606		18.311	0.915	13.11	71%
		diss.*		11.295	4.295		0.157	9.312	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 3.3 - 4.7 microns	1	total	22.714	11.217		17.605	0.304	4.394	73%
		diss.*		12.109	5.109		0.059	3.197	
	2	total	21.464	11.949		16.301	3.766	59.245	84%
		diss.*		12.163	5.163		0.978	49.471	
	3	total	22.475	12.192		16.882	0.238	3.855	29%
		diss.*		12.593	5.593		0.022	1.128	
	4	total	23.645	11.443		17.782	4.121	62.711	81%
		diss.*		12.863	5.863		0.981	50.886	
	5	total	21.363	13.299		16.325	2.851	49.623	48%
		diss.*		12.038	5.038		0.469	23.952	
	6	total	23.442	10.688		18.421	2.876	39.122	79%
		diss.*		12.021	5.021		0.547	30.695	
	7	total	23.821	11.988		19.233	1.273	18.9	77%
		diss.*		11.588	4.588		0.241	14.524	
	8	total	23.506	12.244		18.308	1.454	22.85	67%
		diss.*		12.198	5.198		0.279	15.372	
	9	total	22.893	11.289		18.038	6.018	86.219	84%
		diss.*		11.855	4.855		1.293	72.292	
	10	total	23.36	10.019		18.676	7.47	93.608	82%
		diss.*		11.684	4.684		1.315	76.644	
	11	total	23.453	11.353		19.191	6.596	91.508	213%
		diss.*		11.262	4.262		3.151	195.292	
	12	total	23.91	11.886		19.565	3.267	47.459	88%
		diss.*		11.345	4.345		0.666	41.551	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated	
Particle size range 4.7 - 7 microns	1	total	22.224	14.258		17.06	7.008	130.174	101%	
		diss.*		12.164	5.164		2.52	131.937		
	2	total	22.924	12.703		17.436	6.102	101.913	87%	
		diss.*		12.488	5.488		1.705	88.924		
	3	total	22.384	12.085		17.519	6.515	100.593	87%	
		diss.*		11.865	4.865		1.602	87.446		
	4	total	21.699	11.635		16.465	7.076	108.495	80%	
		diss.*		12.234	5.234		1.71	86.729		
	5	total	22.54	10.934		17.226	4.775	68.314	59%	
		diss.*		12.314	5.314		0.767	40.076		
	6	total	23.159	10.861		18.43	3.137	42.81	68%	
		diss.*		11.729	4.729		0.51	29.278		
	7	total	Lost							
		diss.*		12.886	5.886		0.779	38.066		
	8	total	21.676	10.871		16.68	2.824	39.894	77%	
		diss.*		11.996	4.996		0.591	30.765		
	9	total	21.305	11.07		16.78	5.285	74.285	121%	
		diss.*		11.525	4.525		1.658	89.965		
	10	total	23.167	10.952		18.78	10.906	147.343	83%	
		diss.*		11.387	4.387		2.03	122.066		
	11	total	23.829	10.439		18.841	8.75	115.519	92%	
		diss.*		11.988	4.988		1.861	106.573		
	12	total	22.917	11.276		18.269	9.253	130.886	89%	
		diss.*		11.648	4.648		2.016	115.804		

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 7+ microns	1	total	22.022	9.935		16.953	6.429	82.971	119%
		diss.*		12.069	5.069		1.881	98.652	
	2	total	23.816	11.714		18.6	8.374	125.595	95%
		diss.*		12.216	5.216		2.128	118.69	
	3	total	21.256	10.846		15.742	2.984	43.701	78%
		diss.*		12.514	5.514		0.705	34.004	
	4	total	22.28	11.366		16.86	8.26	124.057	92%
		diss.*		12.42	5.42		2.238	114.274	
	5	total	22.293	11.531		17.211	3.741	55.879	95%
		diss.*		12.082	5.082		1.005	53.25	
	6	total	23.434	11.706		18.453	3.954	58.779	74%
		diss.*		11.981	4.981		0.767	43.222	
	7	total	22.255	12.35		17.833	2.662	41.026	78%
		diss.*		11.422	4.422		0.559	32.12	
	8	total	23.99	10.36		18.735	6.936	92.006	46%
		diss.*		12.255	5.255		0.759	42.448	
	9	total	23.969	12.215		18.767	6.861	107.03	85%
		diss.*		12.202	5.202		1.609	90.481	
	10	total	23.566	10.09		18.984	11.439	143.272	83%
		diss.*		11.582	4.582		1.992	118.673	
	11	total	21.748	10.336		17.017	7.555	99.796	83%
		diss.*		11.731	4.731		1.528	82.41	
	12	total	23.367	10.214		18.895	10.891	137.564	78%
		diss.*		11.472	4.472		1.791	107.388	

Appendix D-2 Polyurethane Paint (Deft 09-Y-002)

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 0.65 - 1.1 microns	1	total	22.98	11.803		18.264	0.183	2.711	41%
		diss.*		11.68	4.716		0.019	1.1	
	2	total	23.538	12.42		18.699	0.297	4.65	66%
		diss.*		11.467	4.839		0.055	3.048	
	3	total	22.659	11.374		18.032	0.214	3.059	191%
		diss.*		11.419	4.627		0.104	5.834	
	4	total	21.486	11.196		16.67	0.615	8.878	0%
		diss.*		11.688	4.816		0	0	
	5	total	23.565	10.843		18.63	0.078	1.071	0%
		diss.*		15.229	4.935		0	0	
	6	total	23.751	11.098		19.006	0.115	1.597	19%
		diss.*		12.218	4.745		0.005	0.295	
	7	total	23.823	11.188		18.814	0.11	1.557	524%
		diss.*		12.242	5.009		0.14	8.167	
	8	total	22.782	12.607		18.159	0.253	4.007	126%
		diss.*		11.828	4.623		0.086	5.037	
	9	total	23.764	10.237		18.925	0.367	4.718	7%
		diss.*		11.818	4.839		0.006	0.347	
	10	total	23.22	10.994		18.253	0.215	3.007	17%
		diss.*		12.12	4.967		0.009	0.512	
	11	total	23.204	10.235		17.475	0.093	1.263	0%
		diss.*		12.623	5.729		0	0	
	12	total	23.991	10.192		19.127	0.605	7.73	2%
		diss.*		11.818	4.864		0.003	0.171	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 1.1 - 2.1 microns	1	total	23.885	10.575		18.899	1.2	16.034	33%
		diss.*		12.037	4.986		0.092	5.323	
	2	total	24.031	10.408		19.367	1.125	14.53	28%
		diss.*		11.767	4.664		0.067	4.082	
	3	total	22.678	10.755		17.998	0.565	7.662	327%
		diss.*		11.621	4.68		0.445	25.071	
	4	total	23.447	10.911		18.638	1.493	20.489	26%
		diss.*		11.699	4.809		0.094	5.386	
	5	total	22.782	10.136		17.769	1.377	17.897	17%
		diss.*		11.976	5.013		0.054	2.96	
	6	total	23.909	10.93		19.174	1.642	22.379	74%
		diss.*		12.053	4.735		0.274	16.651	
	7	total	23.442	13.876		18.668	0.464	8.092	233%
		diss.*		11.658	4.774		0.329	18.825	
	8	total	23.755	10.683		19.073	0.838	11.149	33%
		diss.*		11.698	4.682		0.062	3.653	
	9	total	22.982	10.194		17.907	0.712	9.315	73%
		diss.*		12.066	5.075		0.124	6.8	
	10	total	23.091	9.159		18.469	1.022	11.707	51%
		diss.*		11.731	4.622		0.101	5.927	
	11	total	23.909	10.743		19.153	0.82	11	21%
		diss.*		11.517	4.756		0.04	2.326	
	12	total	22.525	10.39		17.737	1.088	14.353	33%
		diss.*		11.727	4.788		0.086	4.748	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 2.1 - 3.3 microns	1	total	23.298	10.213		18.602	3.306	42.294	52%
		diss.*		11.741	4.696		0.376	21.91	
	2	total	22.82	10.964		18.231	3.955	54.273	45%
		diss.*		11.775	4.589		0.421	24.658	
	3	total	23.976	11.881		19.184	1.179	17.51	37%
		diss.*		12.094	4.792		0.106	6.414	
	4	total	22.943	10.479		18.224	3.275	43.206	38%
		diss.*		12.04	4.719		0.28	16.403	
	5	total	23.046	10.815		18.044	1.396	19.281	34%
		diss.*		12.078	5.002		0.116	6.466	
	6	total	22.871	11.503		18.256	3.924	56.553	34%
		diss.*		11.44	4.615		0.342	19.367	
	7	total	24.063	11.717		19.379	1.352	19.673	13%
		diss.*		11.448	4.684		0.042	2.46	
	8	total	23.674	12.823		18.941	2.186	35.042	49%
		diss.*		11.587	4.733		0.297	17.241	
	9	total	23.098	10.138		18.114	1.626	21.02	79%
		diss.*		11.737	4.984		0.305	16.609	
	10	total	22.708	13.372		17.985	2.675	45.164	41%
		diss.*		11.662	4.723		0.333	18.69	
	11	total	22.049	11.127		17.268	1.796	25.51	34%
		diss.*		11.645	4.781		0.159	8.562	
	12	total	23.189	10.194		18.439	1.848	23.694	63%
		diss.*		11.746	4.75		0.258	14.8	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 3.3 - 4.7 microns	1	total	22.452	10.179		17.888	7.488	95.669	61%
		diss.*		11.398	4.564		1.046	58.636	
	2	total	22.772	11.211		17.975	4.199	59.644	65%
		diss.*		11.734	4.797		0.692	38.566	
	3	total	23.146	11.942		18.456	4.515	67.614	55%
		diss.*		11.824	4.69		0.641	37.404	
	4	total	22.671	11.709		17.862	6.148	91.364	50%
		diss.*		12.217	4.809		0.797	45.881	
	5	total	21.68	10.983		16.913	4.833	68.037	38%
		diss.*		11.71	4.767		0.482	25.678	
	6	total	21.455	12.835		16.892	5.405	88.12	47%
		diss.*		11.341	4.563		0.769	40.981	
	7	total	23.498	11.478		18.271	3.447	50.882	47%
		diss.*		12.047	5.227		0.444	24.041	
	8	total	24.098	11.98		19.192	2.852	42.904	85%
		diss.*		11.961	4.906		0.62	36.447	
	9	total	23.564	11.758		18.676	2.829	41.963	78%
		diss.*		12.079	4.888		0.561	32.646	
	10	total	23.366	11.163		18.518	4.218	59.417	62%
		diss.*		11.841	4.848		0.648	36.959	
	11	total	22.899	12.184		18.077	5.967	92.101	32%
		diss.*		11.73	4.822		0.53	29.5	
	12	total	22.623	11.328		17.813	3.305	47.545	58%
		diss.*		11.387	4.81		0.512	27.436	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 4.7 - 7 microns	1	total	21.908	12.079		17.121	7.834	121.081	70%
		diss.*		11.609	4.787		1.605	85.252	
	2	total	24.247	10.515		19.616	6.632	86.201	67%
		diss.*		11.508	4.631		0.957	57.636	
	3	total	23.917	10.707		19.048	9.304	125.088	51%
		diss.*		12.012	4.869		1.083	63.916	
	4	total	22.947	10.985		18.206	8.842	122.42	140%
		diss.*		11.562	4.741		3.061	171.319	
	5	total	22.624	11.205		17.938	6.786	95.896	46%
		diss.*		11.285	4.686		0.804	43.796	
	6	total	22.309	10.103		17.714	16.32	207.65	44%
		diss.*		11.419	4.595		1.66	92.048	
	7	total	22.472	7.567		16.637	6.143	62.782	64%
		diss.*		12.719	5.835		0.816	39.98	
	8	total	22.479	10.955		17.77	6.114	84.733	76%
		diss.*		11.612	4.709		1.159	64.245	
	9	total	23.011	11.063		18.331	3.776	52.433	74%
		diss.*		11.625	4.68		0.682	38.998	
	10	total	22.686	11.262		18.058	7.057	99.84	51%
		diss.*		11.888	4.628		0.872	50.786	
	11	total	21.941	10.21		17.076	8.824	115.762	52%
		diss.*		12.062	4.865		1.11	60.384	
	12	total	22.907	11.342		18.181	7.934	113.372	53%
		diss.*		11.777	4.726		1.054	60.183	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 7+ microns	1	total	23.604	10.583		18.822	7.161	95.042	69%
		diss.*		12.168	4.782		1.088	65.352	
	2	total	22.957	11.581		18.199	4.192	61.24	72%
		diss.*		11.862	4.758		0.768	43.941	
	3	total	20.696	11.319		16.124	9.026	131.139	51%
		diss.*		11.525	4.572		1.269	66.181	
	4	total	21.654	10.617		17.041	6.91	93.217	65%
		diss.*		11.41	4.613		1.127	60.381	
	5	total	22.387	11.012		17.753	5.899	81.914	86%
		diss.*		11.685	4.634		1.247	70.367	
	6	total	21.893	11.107		17.171	9.083	128.633	51%
		diss.*		11.559	4.722		1.233	66.065	
	7	total	23.299	12.689		18.491	2.908	46.5	68%
		diss.*		11.744	4.808		0.554	31.512	
	8	total	23.711	13.22		18.953	3.973	65.702	63%
		diss.*		11.792	4.758		0.708	41.584	
	9	total	23.167	10.986		18.462	3.293	45.401	80%
		diss.*		11.799	4.705		0.626	36.369	
	10	total	22.697	12.62		17.831	3.945	63.37	65%
		diss.*		11.588	4.866		0.757	40.907	
	11	total	22.911	11.221		18.151	8.092	114.606	58%
		diss.*		12.125	4.76		1.14	66.538	
	12	total	23.096	10.561		18.153	6.883	92.491	58%
		diss.*		12.093	4.943		0.952	53.803	

Appendix D-3 Water-Sr Paint (Deft 44-GN-072)

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 0.65 - 1.1 microns	1	total	22.751	11.004		17.953	0.88	12.268	11%
		diss.*		11.639	4.798		0.024	1.328	
	2	total	21.636	10.283		16.585	0.536	7.187	35%
		diss.*		11.675	5.051		0.05	2.478	
	3	total	24.677	10.279		19.686	0.616	7.941	171%
		diss.*		12.175	4.991		0.226	13.602	
	4	total	23.465	10.452		18.601	0.291	3.84	40%
		diss.*		11.66	4.864		0.027	1.537	
	5	total	24.247	10.458		19.713	0.845	10.874	20%
		diss.*		11.419	4.534		0.036	2.206	
	6	total	22.951	11.371		17.915	0.361	5.253	41%
		diss.*		11.905	5.036		0.04	2.172	
	7	total	22.71	13.568		18.118	0.694	11.796	85%
		diss.*		11.724	4.592		0.172	9.99	
	8	total	23.959	11.029		19.155	0.326	4.49	41%
		diss.*		11.995	4.804		0.031	1.855	
	9	total	23.881	10.771		19.296	0.351	4.682	42%
		diss.*		11.443	4.585		0.033	1.953	
	10	total	23.43	10.291		18.756	0.708	9.1	23%
		diss.*		11.806	4.674		0.035	2.05	
	11	total	22.919	11.437		17.644	0.257	3.816	240%
		diss.*		12.687	5.275		0.166	9.17	
	12	total	22.651	12.901		17.795	0.27	4.442	86%
		diss.*		11.777	4.856		0.07	3.838	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 1.1 - 2.1 microns	1	total	22.499	12.3		17.868	0.907	14.044	63%
		diss.*		11.535	4.631		0.157	8.785	
	2	total	23.827	11.237		18.376	2.516	36.661	74%
		diss.*		12.068	5.451		0.513	27.057	
	3	total	24.489	11.676		19.322	4.795	70.961	40%
		diss.*		11.905	5.167		0.499	28.165	
	4	total	24.349	11.27		19.425	1.425	20.134	123%
		diss.*		11.877	4.924		0.421	24.738	
	5	total	22.752	12.349		17.912	3.652	57.278	70%
		diss.*		11.773	4.84		0.725	40.126	
	6	total	22.629	14.125		17.838	1.496	26.798	71%
		diss.*		11.333	4.791		0.355	18.987	
	7	total	22.631	8.287		17.819	2.888	30.399	71%
		diss.*		11.842	4.812		0.388	21.633	
	8	total	23.792	11.327		19.072	1.2	16.955	57%
		diss.*		11.65	4.72		0.163	9.585	
	9	total	22.395	11.222		17.715	2.611	37.045	69%
		diss.*		11.542	4.68		0.463	25.547	
	10	total	22.733	10.527		17.941	1.448	19.318	54%
		diss.*		11.683	4.792		0.187	10.356	
	11	total	21.991	10.2		17.145	3.137	41.037	130%
		diss.*		11.66	4.846		1.008	53.325	
	12	total	23.356	11.183		18.429	2.254	31.948	76%
		diss.*		11.335	4.927		0.454	24.375	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 2.1 - 3.3 microns	1	total	23.401	11.785		18.622	7.418	109.856	56%
		diss.*		11.659	4.779		1.068	60.982	
	2	total	22.149	11.743		17.207	13.622	205.912	114%
		diss.*		11.425	4.942		4.575	234.267	
	3	total	24.077	12.351		19.364	14.086	216.316	108%
		diss.*		11.462	4.713		3.982	233.159	
	4	total	22.575	13.162		17.83	5.18	86.318	78%
		diss.*		11.564	4.745		1.227	67.524	
	5	total	21.643	12.367		16.89	11.537	182.824	86%
		diss.*		11.628	4.753		2.951	156.249	
	6	total	23.547	10.807		18.761	16.785	227.674	104%
		diss.*		11.601	4.786		4.135	236.019	
	7	total	24.373	11.744		19.576	17.483	255.626	81%
		diss.*		11.857	4.797		3.446	207.62	
	8	total	23.991	9.789		19.289	6.74	82.066	89%
		diss.*		11.337	4.702		1.259	72.813	
	9	total	24.211	12.166		19.462	15.204	230.109	67%
		diss.*		11.734	4.749		2.557	152.974	
	10	total	23.196	12.199		18.495	7.082	108.354	69%
		diss.*		11.674	4.701		1.295	74.599	
	11	total	23.264	12.927		18.133	18.312	303.706	85%
		diss.*		12.011	5.131		4.744	258.341	
	12	total	22.518	11.131		17.713	24.947	353.013	76%
		diss.*		11.806	4.805		4.857	268.713	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 3.3 - 4.7 microns	1	total	23.632	11.551		18.55	29.104	428.285	96%
		diss.*		12.092	5.082		7.314	411.267	
	2	total	22.612	10.533		17.999	37.49	496.087	87%
		diss.*		11.052	4.613		7.994	433.092	
	3	total	24.017	11.999		18.124	30.574	486.133	91%
		diss.*		12.599	5.893		8.645	443.923	
	4	total	22.156	10.65		17.354	32.804	446.029	85%
		diss.*		11.818	4.802		6.964	379.719	
	5	total	24.445	10.088		19.344	30.08	383.47	98%
		diss.*		11.903	5.101		6.617	377.422	
	6	total	23.326	11.274		18.634	26.965	380.549	76%
		diss.*		11.506	4.692		5.057	289.267	
	7	total	24.304	12.052		19.407	21.275	321.112	98%
		diss.*		12.642	4.897		5.01	314.367	
	8	total	23.314	11.787		18.591	19.538	288.803	94%
		diss.*		11.382	4.723		4.81	270.22	
	9	total	23.732	13.456		19.04	25.213	422.874	97%
		diss.*		12.018	4.692		6.77	411.508	
	10	total	23.475	10.123		18.697	40.957	520.563	85%
		diss.*		11.819	4.778		7.595	441.048	
	11	total	23.102	11.551		18.722	39.095	557.235	89%
		diss.*		10.954	4.38		8.535	493.109	
	12	total	22.458	10.241		17.667	39.003	507.748	89%
		diss.*		11.932	4.791		8.109	453.554	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 4.7 - 7 microns	1	total	23.418	11.183		18.615	53.602	754.101	77%
		diss.*		11.67	4.803		10.237	582.463	
	2	total	23.028	12.696		18.253	24.617	394.299	100%
		diss.*		11.659	4.775		7.026	395.074	
	3	total	22.622	11.439		17.705	36.23	529.524	92%
		diss.*		11.514	4.917		9.173	485.948	
	4	total	22.455	10.161		17.457	45.766	598.166	82%
		diss.*		11.936	4.998		9.137	490.001	
	5	total	23.803	10.321		18.878	22.154	288.309	99%
		diss.*		11.759	4.925		5.03	285.891	
	6	total	24.316	10.881		19.453	32.987	448.656	88%
		diss.*		11.731	4.863		6.702	393.107	
	7	total	23.147	11.522		18.461	38.137	550.954	87%
		diss.*		12.075	4.686		8.066	481.1	
	8	total	22.845	12.509		18.338	32.986	514.032	82%
		diss.*		11.16	4.507		7.408	419.03	
	9	total	21.784	12.023		17.072	30.013	460.444	91%
		diss.*		11.703	4.712		7.729	418.145	
	10	total	22.571	13.471		17.873	59.682	1015.31	56%
		diss.*		11.64	4.698		10.169	568.698	
	11	total	23.646	9.976		18.936	62.597	779.794	74%
		diss.*		11.385	4.71		10.026	573.074	
	12	total	22.457	11.751		17.732	33.98	505.701	92%
		diss.*		11.483	4.725		8.552	466.727	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 7+ microns	1	total	22.856	10.795		18.045	61.819	845.257	61%
		diss.*		11.64	4.811		9.314	515.078	
	2	total	22.214	10.848		17.421	11.976	165.654	125%
		diss.*		11.075	4.793		4.048	207.771	
	3	total	22.238	11.387		17.351	30.096	439.233	92%
		diss.*		11.871	4.887		7.513	405.853	
	4	total	21.832	11.95		16.305	25.438	407.032	94%
		diss.*		12.436	5.527		7.777	382.009	
	5	total	21.86	15.459		17.351	6.504	126.668	114%
		diss.*		10.709	4.509		2.781	144.396	
	6	total	22.621	10.28		17.588	20.223	267.383	96%
		diss.*		11.94	5.033		4.759	255.365	
	7	total	22.501	12.301		17.709	21.528	336.468	94%
		diss.*		11.767	4.792		5.729	316.518	
	8	total	22.83	15.402		18.153	36.335	703.807	70%
		diss.*		11.576	4.677		8.661	489.419	
	9	total	22.277	12.862		17.667	17.136	277.907	106%
		diss.*		11.223	4.61		5.412	293.489	
	10	total	21.679	10.981		17.291	103.568	1425.89	38%
		diss.*		11.309	4.388		9.735	543.935	
	11	total	21.96	12.696		17.113	36.189	589.583	80%
		diss.*		11.95	4.847		8.688	470.379	
	12	total	21.636	10.89		16.859	28.971	404.89	98%
		diss.*		11.616	4.777		7.561	397.808	

Appendix D-4 Water-Ba Paint (Deft 44-GN-007)

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 0.65 - 1.1 microns	1	total	22.51	12.181		17.232	0.515	8.191	6%
		diss.*		12.242	5.278		0.009	0.493	
	2	total	22.963	14.261		17.868	0.23	4.222	2%
		diss.*		11.852	5.095		0.002	0.095	
	3	total	24.622	11.088		19.627	3.549	49.366	30%
		diss.*		11.475	4.995		0.259	14.643	
	4	total	22.788	10.783		17.812	2.444	33.716	4%
		diss.*		12.066	4.976		0.023	1.288	
	5	total	16.36	10.931		11.23	0.101	1.616	1%
		diss.*		12.129	5.13		0.001	0.02	
	6	total	23.391	11.379		18.675	0.398	5.673	4%
		diss.*		12.021	4.716		0.004	0.222	
	7	total	23.355	11.086		18.616	0.311	4.328	7%
		diss.*		11.729	4.739		0.005	0.306	
	8	total	23.369	12.884		18.728	1.576	25.333	0%
		diss.*		11.686	4.641		0.001	0.088	
	9	total	23.743	11.187		19.093	5.428	75.505	1%
		diss.*		11.402	4.65		0.009	0.535	
	10	total	23.527	11.884		18.942	1.484	21.898	3%
		diss.*		11.472	4.585		0.01	0.573	
	11	total	24.432	10.8		19.614	1.201	16.151	0%
		diss.*		12.112	4.818		0	0	
	12	total	23.881	11.198		18.205	0.845	12.412	10%
		diss.*		12.612	5.676		0.022	1.175	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 1.1 - 2.1 microns	1	total	23.221	12.794		18.295	6.318	102.602	22%
		diss.*		11.63	4.926		0.409	22.42	
	2	total	22.71	11.411		17.683	2.289	33.548	5%
		diss.*		11.854	5.027		0.032	1.698	
	3	total	22.477	11.821		17.466	6.422	97.687	17%
		diss.*		12.069	5.011		0.304	16.464	
	4	total	22.958	12.183		16.971	5.035	82.98	7%
		diss.*		13.289	5.987		0.116	5.899	
	5	total	22.585	10.803		17.312	4.198	59.165	10%
		diss.*		12.147	5.273		0.112	5.809	
	6	total	23.492	11.831		18.336	2.633	39.908	9%
		diss.*		11.718	5.156		0.067	3.566	
	7	total	22.956	10.85		18.255	4.707	64.216	2%
		diss.*		11.571	4.701		0.025	1.385	
	8	total	22.721	11.897		18.058	1.652	24.728	3%
		diss.*		11.518	4.663		0.013	0.734	
	9	total	22.851	11.293		18.113	4.845	69.02	3%
		diss.*		11.608	4.738		0.035	1.979	
	10	total	23.777	11.198		18.983	7.256	101.767	2%
		diss.*		11.634	4.794		0.026	1.487	
	11	total	23.161	11.741		18.4	2.213	32.707	2%
		diss.*		11.739	4.761		0.013	0.718	
	12	total	23.787	10.796		19.25	7.807	104.151	2%
		diss.*		11.279	4.537		0.029	1.69	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 2.1 - 3.3 microns	1	total	24.18	10.886		19.046	12.553	173.482	2%
		diss.*		12.321	5.134		0.055	3.207	
	2	total	21.217	10.301		16.246	10.051	135.21	1%
		diss.*		11.796	4.971		0.032	1.622	
	3	total	22.273	11.353		17.645	16.873	241.803	4%
		diss.*		11.496	4.628		0.185	10.223	
	4	total	22.621	12.93		17.661	26.824	444.241	46%
		diss.*		11.901	4.96		3.745	203.271	
	5	total	23.15	10.926		18.14	9.294	129.588	3%
		diss.*		11.725	5.01		0.073	3.946	
	6	total	23.871	12.609		18.809	12.273	196.394	1%
		diss.*		12.699	5.062		0.033	1.991	
	7	total	22.661	13.342		17.891	8.11	137.054	2%
		diss.*		11.879	4.77		0.043	2.434	
	8	total	22.914	10.13		18.135	5.279	67.57	3%
		diss.*		11.944	4.779		0.033	1.876	
	9	total	23.762	11.282		19.077	17.65	248.031	1%
		diss.*		11.824	4.685		0.051	3.037	
	10	total	22.417	12.471		17.901	26.551	414.648	1%
		diss.*		11.71	4.516		0.068	3.938	
	11	total	23.309	10.742		18.822	8.996	119.667	1%
		diss.*		11.574	4.487		0.021	1.25	
	12	total	23.365	10.891		18.675	30.307	412.961	1%
		diss.*		11.566	4.69		0.056	3.246	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 3.3 - 4.7 microns	1	total	23.538	10.61		18.456	27.336	369.901	2%
		diss.*		12.244	5.082		0.105	5.945	
	2	total	22.567	11.194		17.605	20.57	295.16	1%
		diss.*		12.068	4.962		0.062	3.388	
	3	total	22.818	11.929		17.726	15.202	233.433	4%
		diss.*		11.838	5.092		0.187	9.915	
	4	total	24.052	11.243		19.27	27.961	392.379	3%
		diss.*		11.731	4.782		0.216	12.718	
	5	total	22.856	11.131		17.847	23.267	331.677	16%
		diss.*		11.66	5.009		1.012	53.824	
	6	total	23.571	11.419		18.513	38.645	561.854	3%
		diss.*		12	5.058		0.341	19.062	
	7	total	23.475	11.134		18.751	15.12	210.762	2%
		diss.*		11.831	4.724		0.066	3.896	
	8	total	23.124	9.804		18.375	24.342	300.33	1%
		diss.*		11.752	4.749		0.05	2.855	
	9	total	23.616	10.758		19	20.245	270.713	1%
		diss.*		11.636	4.616		0.064	3.834	
	10	total	23.474	10.976		18.942	44.171	600.813	1%
		diss.*		11.517	4.532		0.074	4.414	
	11	total	24.033	12.28		19.478	34.515	522.965	0%
		diss.*		11.307	4.555		0.038	2.282	
	12	total	23.186	11.503		18.491	27.512	396.819	1%
		diss.*		11.432	4.695		0.075	4.211	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 4.7 - 7 microns	1	total	24.751	13.782		19.556	12.622	220.159	13%
		diss.*		12.107	5.195		0.493	28.46	
	2	total	21.861	12.689		16.366	29.914	507.018	16%
		diss.*		12.426	5.495		1.639	81.028	
	3	total	22	10.973		17.177	19.4	272.644	3%
		diss.*		11.532	4.823		0.154	8.096	
	4	total	22.473	11.799		17.617	23.829	358.658	2%
		diss.*		11.656	4.856		0.112	6.033	
	5	total	22.458	11.396		17.601	20.067	291.795	2%
		diss.*		11.818	4.857		0.089	4.841	
	6	total	23.4	10.021		18.148	52.46	677.835	1%
		diss.*		11.954	5.252		0.106	5.67	
	7	total	23.463	11.817		18.773	17.937	264.912	1%
		diss.*		11.909	4.69		0.051	3.043	
	8	total	23.447	12.386		18.722	21.771	337.706	1%
		diss.*		12.005	4.725		0.059	3.527	
	9	total	23.723	13.504		18.92	26.115	442.185	1%
		diss.*		12.002	4.803		0.07	4.168	
	10	total	22.582	11.409		18.042	49.229	702.985	1%
		diss.*		11.912	4.54		0.086	5.092	
	11	total	22.57	10.045		17.902	77.567	982.323	0%
		diss.*		11.454	4.668		0.052	2.874	
	12	total	23.096	12.274		18.387	36.596	564.213	1%
		diss.*		11.651	4.709		0.087	4.972	

	Impact. #	Sample type	M _O (grams)	M _{TD} or [M _D +M _A]* (grams)	M _D * (grams)	M _T (grams)	ICP _T or ICP _D *	Cr _{OT} or Cr _{OD} * (ug)	% Cr dissociated
Particle size range 7+ microns	1	total	24.027	10.806		18.863	34.62	476.514	1%
		diss.*		11.871	5.164		0.106	5.827	
	2	total	22.887	14.186		18.247	29.745	529.256	14%
		diss.*		11.686	4.64		1.243	71.635	
	3	total	21.319	12.879		16.384	12.512	209.684	8%
		diss.*		11.881	4.935		0.334	17.135	
	4	total	22.445	11.073		17.559	15.959	225.88	9%
		diss.*		12.037	4.886		0.363	20.079	
	5	total	23.071	12.336		18.155	14.414	225.963	2%
		diss.*		12.031	4.916		0.068	3.855	
	6	total	22.728	12.622		17.667	28.858	468.596	1%
		diss.*		11.794	5.061		0.121	6.403	
	7	total	22.947	14.032		18.452	26.571	463.676	1%
		diss.*		11.409	4.495		0.074	4.288	
	8	total	23.024	11.365		18.307	39.76	568.307	1%
		diss.*		12.102	4.717		0.071	4.181	
	9	total	23.591	11.482		18.883	34.41	493.601	1%
		diss.*		12.143	4.708		0.047	2.859	
	10	total	21.988	9.914		17.362	39.591	497.087	1%
		diss.*		11.856	4.626		0.089	4.993	
	11	total	21.953	12.281		17.333	74.64	1160.99	0%
		diss.*		11.61	4.62		0.073	4.05	
	12	total	23.353	10.135		18.697	29.242	370.165	1%
		diss.*		11.477	4.656		0.072	4.118	

Appendix E MSDS for Solvent Paint part A & B

Page: 1 MATERIAL SAFETY DATA SHEET Printed: 07/22/04
 For Coatings, Resins and Related Materials Revised: 10/27/03

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEFT, INC. (CAGE CODE 33461) Information Phone: (949) 474-0400
 17451 VON KARMAN AVENUE Emergency Phone: (800) 424-9300
 CHEMTREC Phone: 800-424-9300
 IRVINE CA
 92614

Product Class: TYPE I, CLASS C Hazard Ratings: Health - 4
 Trade Name: MIL-PRF-23377H, COMPONENT A none -> extreme Fire - 3
 Product Code: 02Y040A 0 -> 4 Reactivity - 1
 C.A.S. Number: NONE Personal Protection - I

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	Exposure Limits				VP mm HG
			TLV	ACGIH STEL	OSHA PEL	OSHA STEL	
METHYL n-AMYL KETONE	110-43-0	5.740	50 ppm	N.E.	100 ppm	N.E.	2.8 @ 68F
BENZENE, 1-CHLORO-4 TRIFLUOROMETHYL	98-56-8	1.680	N.E.	N.E.	N.E.	N.E.	5.3 @ 68F
STRONTIUM CHROMATE	7789-06-2	19.130	.5		.1 mg/M3	N.E.	
The ACGIH TWA for Strontium Chromate (CAS 7789-06-2) as Cr is 0.0005 mg/m3 or 0.5 micrograms/m3.							
TITANIUM DIOXIDE	13463-67-7	2.930	10 mg/M3	N.E.	15 mg/M3	N.E.	
ACGIH/TLV & OSHA/PEL Exposure limits are for total dust.							
AMORPHOUS SILICA	7631-86-9	0.000	10 mg/M3	10 mg/M3	80 mg/M3	80 mg/M3	
n-BUTYL ACETATE	123-86-4	1.230	150 ppm	200 ppm	150 ppm	200 ppm	13 @ 68F
METHYL n-PROPYL KETONE	107-87-9	14.660	200 ppm	250 ppm	200 ppm	250 ppm	27.8 @ 68F
ISOBUTYL ALCOHOL	78-93-1	0.030	50 ppm	N.E.	.50 ppm	N.E.	8.8 @ 68F

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST.
 ALSO ANY UNLISTED INGREDIENTS.

N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 213 - 306 Deg. F Vapor Density: Heavier than Air.
 Evap. Rate: 1.37 X n-Butyl Acetate Liquid Density: Heavier than Water.
 Volatiles vol % 44.3 Wgt% 24.3 Wgt per gallon: 12.68 Pounds.
 Spec. Gravity: 1.52221

Appearance: YELLOW LIQUID WITH SOLVENT ODOR
 V.O.C.: 352 G/L
 SOLUBILITY IN WATER: Insoluble PH: Not applicable
 AUTOIGNITION TEMPERATURE: No information found
 DECOMPOSITION TEMPERATURE: No information found
 CORROSION RATE: No information found
 VISCOSITY: Thin liquid to heavy viscous material
 MIXED VOC: 340 G/L OR LESS WHEN MIXED WITH 02Y040ACAT
 PER INSTRUCTIONS.

Page: 1 MATERIAL SAFETY DATA SHEET Printed: 07/22/04
For Coatings, Resins and Related Materials Revised: 10/27/03

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEPT, INC. (CAGE CODE 33461) Information Phone: (949) 474-0400
17451 VON KARMAN AVENUE Emergency Phone: (800) 424-9300
CHEMTEC Phone: 800-424-9300
IRVINE CA
92614

Product Class: TYPE I, CLASS C Hazard Ratings: Health - 3
Trade Name: MIL-PRF-23377H, COMPONENT B none -> extreme Fire - 3
Product Code: 02Y040ACAT 0 ---> 4 Reactivity - 1
C.A.S. Number: NONE Personal Protection - G

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	Exposure Limits		OSHA		VP mm HG
			TLV ACGIH	STEL	PEL	STEL	
n-BUTYL ALCOHOL	71-36-3	9.660	50 ppm	N.E.	50 ppm	N.E.	4.4 @ 68F
PETROLEUM NAPHTHA LT, AROMATIC	64742-95-6	6.640	100 ppm	N.E.	N.E.	N.E.	3 @ 68F
1,2,4 TRIMETHYLBENZENE	95-63-6	6.870	25 ppm	35 ppm	N.E.	N.E.	
CUMENE	98-82-8	0.340	50 ppm	N.E.	50 ppm	N.E.	
1,3,5 TRIMETHYLBENZENE	108-67-8	1.890	123 mg/M3	N.E.	N.E.	N.E.	
AMINO SILANE ESTER	1760-24-3	1.450	200 ppm	250 ppm	200 ppm	250 ppm	

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST.
ALSO ANY UNLISTED INGREDIENTS.

N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 244 - 401 Deg. F Vapor Density: Heavier than Air.
Evap. Rate: 0.36 x n-Butyl Acetate Liquid Density: Lighter than Water.
Volatiles vol % 41.4 Wgt% 38.6 Wgt per gallon: 8.04 Pounds.
Spec. Gravity: 0.96519
Appearance: AMBER LIQUID WITH SOLVENT ODOR
V.O.C.: 259 G/L
SOLUBILITY IN WATER: Insoluble PH: Not applicable
AUTOIGNITION TEMPERATURE: No information found
DECOMPOSITION TEMPERATURE: No information found
CORROSION RATE: No information found
VISCOSITY: Thin liquid to heavy viscous material
MIXED VOC: 340 G/L OR LESS WHEN MIXED WITH 02Y040A
PER INSTRUCTIONS.

Appendix F MSDS for Polyurethane Paint part A & B

Page: 1 MATERIAL SAFETY DATA SHEET Printed: 07/22/04
 For Coatings, Resins and Related Materials Revised: 12/06/01

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEPT, INC. (CAGE CODE 33461) Information Phone: (949) 474-0400
 17451 VON KARMAN AVENUE Emergency Phone: (800) 424-9300
 IRVINE CA CHEMTEC Phone: 800-424-9300
 92614

Product Class: POLYURETHANE
 Trade Name: TT-P-2760A TYP 1 CLASS C
 Product Code: 09Y002
 C.A.S. Number: NONE

Hazard Ratings: Health - 4
 none -> extreme Fire - 3
 0 -> 4 Reactivity - 1
 Personal Protection - I

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	Exposure Limits				VP mm HG
			TLV	ACGIH STEL	OSHA PEL	OSHA STEL	
n-BUTYL ACETATE	123-86-4	3.970	150 ppm	200 ppm	150 ppm	200 ppm	13 @ 68F
ETHYL 3-ETHOXYPROPIONATE	763-69-9	10.280	N.E.	N.E.	N.E.	N.E.	7 @ 68F
Manufacturer recommends a workplace exposure limit of 50 PPM-TWA; 100 PPM-STEL.							
DISPERSION AID	PROPRIETARY	0.250	N.E.	N.E.	N.E.	N.E.	
New Jersey Trade Secret Registry Number: 800963-5040							
ISOBUTYL ALCOHOL	78-83-1	0.030	50 ppm	N.E.	50 ppm	N.E.	8.8 @ 68F
STROMTIUM CHROMATE	7789-06-2	18.750	5	5	.1 mg/M3	N.E.	
The ACGIH TWA for Strontium Chromate (CAS 7789-06-2) as Cr is 0.0005 mg/m3 or 0.5 micrograms/m3.							
TITANIUM DIOXIDE	13463-67-7	3.110	10 mg/M3	N.E.	15 mg/M3	N.E.	
ACGIH/TLV & OSHA/PEL Exposure limits are for total dust.							
METHYL ETHYL KETONE	78-93-3	1.010	200 ppm	300 ppm	200 ppm	300ppm	70 @ 68F
2-4 PENTANEDIONE	123-54-6	3.530	N.E.	N.E.	N.E.	N.E.	6.9 @ 68F
Union Carbide recommends a TLV of 20 ppm-TWA.							
DIBUTYL TIN DILAURATE	77-58-7	0.050	N.E.	N.E.	.1 mg/M3	.1 mg/M3	2.0320F
Causes skin and eye irritation. Harmful if swallowed or absorbed through skin. May cause liver and kidney damage.							

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST.

N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 175 - 401 Deg. F Vapor Density: Heavier than Air.
 Evap. Rate: 0.66 x n-Butyl Acetate. Liquid Density: Heavier than Water.
 Volatiles vol % 28.4 Wgt% 19.0 Wgt per gallon: 11.53 Pounds.
 Spec. Gravity: 1.38415

Appearance: BROWN LIQUID WITH SOLVENT ODOR
 V.O.C.: 262 G/L
 SOLUBILITY IN WATER: Insoluble PH: Not applicable
 AUTOIGNITION TEMPERATURE: No information found
 DECOMPOSITION TEMPERATURE: No information found
 CORROSION RATE: No information found
 VISCOSITY: Thin liquid to heavy viscous material

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEPT, INC. (CAGE CODE 33461) Information Phone: (949) 474-0400
 17451 VON KARMAN AVENUE Emergency Phone: (800) 424-9300
 IRVINE CA CHEMPREC Phone: 800-424-9300
 92614

Product Class: ALIPHATIC ISOCYANATE Hazard Ratings: Health - 4
 Trade Name: CAT, TT-P-2760A, TYP 1, CL C none -> extreme Fire - 3
 Product Code: 09Y002CAT 0 -> 4 Reactivity - 1
 C.A.S. Number: NONE

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	Exposure Limits				NFPA
			ACGIH TLV	OSHA STEL	OSHA PEL	OSHA STEL	
POLYMERIC HEXAMETHYLENE DIISOCYANAT	28182-81-2	55.530	N.E.	N.E.	N.E.	N.E.	
E 822-06-0 HEXAMETHYLENE DIISOCYANATE (HDI) CAS NO. 822-06-0, free monomer content averages 0.10% based on resin solids at the time of manufacture. However, after 12 months storage, the free monomer content may rise to a maximum of 0.14%. The ACGIH has a TLV of 0.005 ppm TWA.							
METHYL ISOBUTYL KETONE	108-10-1	17.980	50 ppm	75 ppm	50 ppm	75 ppm	15 # 68F
n-BUTYL ACETATE	123-86-4	3.650	150 ppm	200 ppm	150 ppm	200 ppm	13 # 68F
METHYL ETHYL KETONE	78-93-3	21.870	300 ppm	300 ppm	200 ppm	300ppm	70 # 68F
ORGANOSILANE ESTER	24801-88-5	0.970	N.E.		N.E.		1 # 68F

*** ALL Ingredients in this product are listed in the T.S.C.A. Inventory.

THE ABOVE LISTED INGREDIENTS ARE ON THE TSCA INVENTORY LIST, ALSO ANY UNLISTED INGREDIENTS.

N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 175 - 460 Deg. F Vapor Density: Heavier than Air.
 Evap. Rate: 2.92 x n-Butyl Acetate Liquid Density: Lighter than Water.
 Volatiles vol % 52.6 Wgt% 43.5 Wgt per gallon: 8.14 Pounds.
 Spec. Gravity: 0.97719
 Appearance: AMBER LIQUID WITH SOLVENT ODOR
 V.O.C.: 420 G/L
 SOLUBILITY IN WATER: Insoluble PH: Not applicable
 AUTOIGNITION TEMPERATURE: No information found
 DECOMPOSITION TEMPERATURE: No information found
 CORROSION RATE: No information found
 VISCOSITY: Thin liquid to heavy viscous material

Appendix G MSDS for Water-Sr Paint part A & B

Page: 1 MATERIAL SAFETY DATA SHEET Printed: 07/22/04
 For Coatings, Resins and Related Materials Revised: 10/22/03

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEFT, INC. (CAGE CODE 33461) Information Phone: (949) 474-0400
 17451 VON KARMAN AVENUE Emergency Phone: (800) 424-9300
 IRVINE CA CHEMTREC Phone: 800-424-9300
 92614

Product Class: Hazard Ratings: Health - 3
 Trade Name: MIL-PRF-85582D, TY I, CL C2 none -> extreme Fire - 3
 Product Code: 44GN072 0 ---> 4 Reactivity - 1
 C.A.S. Number: NONE

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	Exposure Limits				VP mm HG
			TLV ACGIH	STEL	PEL	OSHA STEL	
sec-BUTYL ALCOHOL	78-92-2	26.520	100 ppm	N.E.	100 ppm	N.E.	12.5 @ 68F
CUMENE	98-82-8	0.010	50 ppm	N.E.	50 ppm	N.E.	
STRONTIUM CHROMATE	7789-06-2	26.910	.001mg/M3	N.E.	.1 mg/M3	N.E.	
BARIUM CHROMATE	10294-40-3	0.830	.01 mg/M3	N.E.	.1 mg/M3	N.E.	
TITANIUM DIOXIDE	13463-67-7	4.600	10 mg/M3	N.E.	15 mg/M3	N.E.	

ACGIH/TLV & OSHA/PEL Exposure limits are for total dust.

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST.
 ALSO ANY UNLISTED INGREDIENTS.

N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 211 - 306 Deg. F Vapor Density: Heavier than Air.
 Evap. Rate: 0.65 x n-Butyl Acetate Liquid Density: Heavier than Water.
 Volatiles vol % 43.0 Wgt% 26.8 Wgt per gallon: 10.80 Pounds.
 Spec. Gravity: 1.29652

Appearance: GREEN LIQUID WITH SOLVENT ODOR
 V.O.C.: 334
 SOLUBILITY IN WATER: Insoluble PH: Not applicable
 AUTOIGNITION TEMPERATURE: No information found
 DECOMPOSITION TEMPERATURE: No information found
 CORROSION RATE: No information found
 VISCOSITY: Thin liquid to heavy viscous material
 MIXED VOC: 340 g/L OR LESS WHEN MIXED PER INSTRUCTIONS
 WITH 44GN072CAT.

Page: 1 MATERIAL SAFETY DATA SHEET Printed : 07/22/04
 For Coatings, Resins and Related Materials Revised : 10/22/03

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEFT, INC. (CAGE CODE 33461) Information Phone: (949) 474-0400
 17451 VON KARMAN AVENUE Emergency Phone: (800) 424-9300
 IRVINE CA CHEMTREC Phone: 800-424-9300
 92614

Product Class: | Hazard Ratings: Health - 3
 Trade Name : MIL-PRF-85582D, TY I, CL C2 | none -> extreme Fire - 3
 Product Code : 44GN072CAT | 0 ---> 4 Reactivity - 1
 C.A.S. Number: NONE |

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	Exposure Limits		OSHA		VP mm Hg
			ACGIH TLV	STEL	PEL	STEL	
NITROETHANE	79-24-3	30.040	100 ppm	N.E.	100 ppm	N.E.	16 @ 68F
ORGANOSILOXANE	2530-83-8	0.910	N.E.	N.E.	N.E.	N.E.	1 @ 68F

1 PPM TLV Suggested by DOW CHEMICAL.

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST.
 ALSO ANY UNLISTED INGREDIENTS.

N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 237 - 554 Deg. F Vapor Density: Heavier than Air.
 Evap. Rate: 1.27 x n-Butyl Acetate Liquid Density: Heavier than Water.
 Volatiles vol % 32.2 Wgt% 30.1 Wgt per gallon: 9.38 Pounds.
 Spec. Gravity: 1.12605

Appearance: AMBER LIQUID WITH SOLVENT ODOR
 V.O.C.: 345 G/L
 SOLUBILITY IN WATER: Insoluble PH: Not applicable
 AUTOIGNITION TEMPERATURE: No information found
 DECOMPOSITION TEMPERATURE: No information found
 CORROSION RATE: No information found
 VISCOSITY: Thin liquid to heavy viscous material
 MIXED VOC: 340 G/L OR LESS WHEN MIXED WITH 44GN072 PER INSTRUCTIONS.

Appendix H MSDS for Water-Ba Paint part A & B

Page: 1

MATERIAL SAFETY DATA SHEET Printed: 07/22/04
For Coatings, Resins and Related Materials Revised: 10/27/03

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEPT. INC. (CAGE CODE 33461) Information Phone: (949) 474-0400
17451 VON KARMAN AVENUE Emergency Phone: (800) 424-9300
CHENTREC Phone: 800-424-9300
IRVINE CA
92614

Product Class: TYPE I, CLASS C1, POLYAMIDE
Trade Name: MIL-PRF-85582C (MIL-P85582B)
Product Code: 44GN007
C.A.S. Number: NONE
Hazard Ratings: Health - 4
none -> extreme Fire - 3
0 -> 4 Reactivity - 1
Personal Protection - G

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	Exposure Limits		OSHA	UP
			TLV	STEL		
2-BUTOXYETHANOL	111-76-2	13.230	25 ppm	N.E.	25 ppm	N.E.
PETROLEUM NAPHTHA LT. AROMATIC	64742-95-6	4.790	100 ppm	N.E.	N.E.	N.E.
1,2,4 TRIMETHYLBENZENE	95-63-6	4.950	25 ppm	35 ppm	N.E.	N.E.
CUMENE	98-82-8	0.250	50 ppm	N.E.	50 ppm	N.E.
1,3,5 TRIMETHYLBENZENE	108-67-8	1.360	123 mg/M3	N.E.	N.E.	N.E.
BARIUM CHROMATE	10294-40-3	23.090	.01 mg/M3	N.E.	.1 mg/M3	N.E.
ZINC CHROMATE	11103-86-9	0.020	.001mg/M3	N.E.	.10 mg/M3	N.E.

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST.
ALSO ANY UNLISTED INGREDIENTS.

N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 306 - 343 Deg. F Vapor Density: Heavier than Air.
Evap. Rate: 0.46 x n-Butyl Acetate Liquid Density: Heavier than Water.
Volatiles vol % 44.0 Wgt% 25.6 Wgt per gallon: 12.68 Pounds.
Spec. Gravity: 1.52221

Appearance: GREEN LIQUID WITH SOLVENT ODOR
V.O.C.: 389 G/L
SOLUBILITY IN WATER: Insoluble PH: Not applicable
AUTOIGNITION TEMPERATURE: No information found
DECOMPOSITION TEMPERATURE: No information found
CORROSION RATE: No information found
VISCOSITY: Thin liquid to heavy viscous material
MIXED VOC: 340 G/L OR LESS WHEN MIXED WITH 44GN007CAT
PER INSTRUCTIONS.

Page: 1 MATERIAL SAFETY DATA SHEET Printed: 07/22/04
 For Coatings, Resins and Related Materials Revised: 10/27/03

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEFT, INC. (CAGE CODE 33461) Information Phone: (949) 474-0400
 17451 VON KARMAN AVENUE Emergency Phone: (800) 424-9300
 IRVINE CA CHEMTREC Phone: 800-424-9300
 92614

Product Class: TYPE I, CLASS C1, EPOXY Hazard Ratings: Health - 3
 Trade Name: MIL-PRF-85582C (MIL-P-85582B) none -> extreme Fire - 3
 Product Code: 44GN007CAT 0 ---> 4 Reactivity - 1
 C.A.S. Number: NONE

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	Exposure		Limits		VP mm HG
			TLV	ACGIH STEL	PEL	OSHA STEL	
NITROETHANE	79-24-3	16.280	100 ppm	N.E.	100 ppm	N.E.	16 @ 68F
ORGANOSILOXANE	2530-83-8	0.610	N.E.	N.E.	N.E.	N.E.	1 @ 68F
1 PPM TLV Suggested by DOW CHEMICAL.							

THE ABOVE LISTED PRODUCTS ARE ON THE TSCA INVENTORY LIST.
 ALSO ANY UNLISTED INGREDIENTS.

N.E. = Not Established

SECTION III - PHYSICAL DATA

Boiling Range: 237 - 554 Deg. F Vapor Density: Heavier than Air.
 Evap. Rate: 1.27 x n-Butyl Acetate. Liquid Density: Heavier than Water.
 Volatiles vol % 17.8 Wgt% 16.3 Wgt per gallon: 9.53 Pounds.
 Spec. Gravity: 1.14406

Appearance: AMBER LIQUID WITH SOLVENT ODOR
 V.O.C.: 187 G/L

SOLUBILITY IN WATER: Insoluble PH: Not applicable

AUTOIGNITION TEMPERATURE: No information found

DECOMPOSITION TEMPERATURE: No information found

CORROSION RATE: No information found

VISCOSITY: Thin liquid to heavy viscous material

MIXED VOC: 340 G/L OR LESS WHEN MIXED WITH 44GN007

PER INSTRUCTIONS.

Bibliography

1. LaPuma, P.T., J.M. Fox, and E.C. Kimmel, *Chromate Concentration Bias in Primer Paint Particles*. Regulatory Toxicology and Pharmacology, 2001. **33**: p. 1-7.
2. Occupational Safety and Health Administration (OSHA), *Occupational Exposure to Hexavalent Chromium; Proposed Rule*. Federal Register, 2004. **69**(191): p. 59305-59474.
3. NIOSH, *Testimony of the National Institute for Occupational Safety and Health on the Occupational Safety and Health Administration's Proposed Rule on Air Contaminants*. 1988.
4. IARC, *Chromium, Nickel and Welding*. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 1990. **49**: p. 213.
5. Technical Order (TO) 1-1-8, *Application and Removal of Organic Coatings, Aerospace and Non-Aerospace Equipment*. 2004, U.S. Air Force.
6. Fox, J.M., *Chromium Concentration Bias in the Particle Size Distribution of Primer Overspray*, in *Systems and Engineering Management*. 2000, Air Force Institute of Technology (AU): Wright-Patterson AFB, OH.
7. JGPP (Joint Group on Pollution Prevention), *Nonchromate Primers for Aircraft Exteriors*. 1998, http://www.jgpp.com/projects/projects_index.html.
8. Occupational Safety and Health Administration (OSHA), *Unified Agenda No. 61: 62748-62788. Occupational Exposure to Hexavalent Chromium (Preventing Occupational Illness: Chromium)*. http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FEDERAL_REGISTER&p_id=13593&p_text_version=FALSE, 1996.
9. Environmental Protection Agency (EPA), *Aerospace Manufacturing and Rework National Emission Standards for Hazardous Air Pollutants (NESHAP)*. 40 Code of Federal Regulation 63 Subpart GG, 1998.
10. National Defense Center for Environmental Excellence (NDCEE), *Engineering and Technical Services for Joint Group on Acquisition Pollution Prevention (JG-APP) Pilot Projects for Laboratory Alternatives to Chromate-Containing Primers for Aircraft Exterior Mold Line Skins*. Contract No. DAAA21-93-C-0046, 1998.
11. LaPuma, P.T. and W.E. Bolch, *The Impact of Recirculating Industrial Air on Aircraft Painting Operations*. Applied Occupational and Environmental Hygiene, 1999. **14**: p. 10.
12. LaPuma, P.T., *Validation of a Recirculation Model*. Applied Occupational and Environmental Hygiene, 2001. **16**: p. 4.
13. Carlton, G.N., *The Impact of a Change to Inhalable Occupational Exposure Limits: Strontium Chromate Exposure in the U.S. Air Force*. AIHA Journal, 2003. **64**: p. 306-311.
14. Proctor, D.M., et al., *Is Hexavalent Chromium Carcinogenic Via Ingestion? A Weight-of-Evidence Review*. Journal of Toxicology and Environmental Health, 2002. **65**: p. 10.

15. Albert, R.E., et al., *Bronchial Deposition and Clearance of Aerosols*. Archives of Internal Medicine, 1973. **131**: p. 115-127.
16. Brain, J.D., J. Godleski, and W. Kreyling, *In Vivo Evaluation of Chemical Biopersistence of Nonfibrous Inorganic Particles*. Environmental Health Perspectives, 1994. **102**: p. 119-125.
17. DeFlora, S., et al., *Circadian Reduction of Chromium in the Gastric Environment*. Mutation Research, 1987. **192**: p. 169-174.
18. Felter, S.P. and M.L. Dourson, *Hexavalent Chromium-Containing Soils: Options for Risk-Assessment and Risk-Management*. Regulatory Toxicology and Pharmacology, 1997. **25**: p. 43-59.
19. Lippmann, M. and R.B. Schlesinger, *Interspecies Comparisons of particle Deposition and Mucociliary Clearance in Tracheobronchial Airways*. Journal of Toxicology and Environmental Health, 1984. **13**: p. 441-469.
20. Stahlhofen, W., J. Gebhart, and J. Heyder, *Experimental Determination of the Regional Deposition of Aerosol Particles in the Human Respiratory Tract*. American Industrial Hygiene Association Journal, 1980. **41**: p. 385-398.
21. Chiazze, L., Jr., L.D. Ference, and P.H. Wolf, *Mortality among Automobile Assembly Workers*. Journal of Occupational Medicine, 1980. **22**(8): p. 520-526.
22. Alexander, B.H., et al., *Lung Cancer in Chromate-Exposed Aerospace Workers*. Journal of Occupational and Environmental Medicine, 1996. **38**(12): p. 1253-1258.
23. Dalager, N.A., et al., *Cancer Mortality among Workers Exposed to Zinc Chromate Paints*. Journal of Occupational Medicine, 1980. **22**(1): p. 25-29.
24. Wager, G., et al., *Airway Surface Liquid (ASL) Composition in Normal Humans*. The American Review of Respiratory Disease, 1990. **141**: p. A106.
25. Mentz, W.M., et al., *Measurement of Airway Surface Liquid (ASL) Composition of Normal Human Subjects*. The American Review of Respiratory Disease, 1984. **129**: p. A315.
26. Widdicombe, J.H., *Regulation of the Depth and Composition of Airway Surface Liquid*. Journal of Anatomy, 2002. **201**: p. 313-318.
27. Kim, S., M.X.G. Shao, and J.A. Nadel, *Murray and Nadel's Textbook of Respiratory Medicine e-dition, Chapter 13*. 4th edition ed. Vol. 1. 2005.
28. Takizawa, H., M. Tanaka, and K. Takami, *Increased Expression of Inflammatory Mediators in Small-Airway Epithelium from Tobacco Smokers*. American Journal of Physiology. Lung Cellular and Molecular Physiology, 2000. **278**: p. L906-L913.
29. Borchers, M.T., M.P. Carty, and G.D. Leikauf, *Regulation of Human Airway Mucins by Acrolein and Inflammatory Mediators*. American Journal of Physiology, 1999. **276**: p. L549-L555.
30. Borchers, M.T., S.E. Wert, and G.D. Leikauf, *Acrolein-Induced MUC5ac Expression in Rat Airways*. American Journal of Physiology, 1998. **274**: p. L573-L581.
31. Repine, J.E., A. Bast, and I. Lankhorst, *Oxidative Stress in Chronic Obstructive Pulmonary Disease*. American Journal of Respiratory and Critical Care Medicine, 1997. **156**: p. 341-357.

32. Harkema, J.R., J.A. Hotchkiss, and E.B. Barr, *Long-Lasting Effects of Chronic Ozone Exposure on Rat Nasal Epithelium*. American Journal of Respiratory Cell and Molecular Biology, 1999. **20**: p. 517-529.
33. Harkema, J.R., J.A. Hotchkiss, and W.C. Griffith, *Mucous Cell Metaplasia in Rat Nasal Epithelium after a 20-month Exposure to Ozone: A Morphometric Study of Epithelial Differentiation*. American Journal of Respiratory and Cell and Molecular Biology, 1997. **16**: p. 521-530.
34. Wanner, A., M. Salathe, and T.G. O'Riordan, *Mucociliary Clearance in the Airways*. American Journal of Respiratory and Critical Care Medicine, 1996. **154**: p. 1868-1902.
35. Hill, H.D., J.A. Reynolds, and R.L. Hill, *Purification, Composition, Molecular Weight and subunit structure of ovine submaxillary Mucin*. Journal of Biological Chemistry, 1977. **252**: p. 3791-3798.
36. Sachdev, G.P., et al., *Isolation, Chemical Composition, and Properties of the Major Mucin Component of Normal Human Tracheobronchial Secretions*. Biochemical Medicine, 1980. **24**: p. 82-94.
37. Boat, T.F. and P.W. Cheng, *Biochemistry of Airway Mucus Secretions*. Federation Proceedings, 1980. **39**(13): p. 3067-3074.
38. King, M. and J.G. Zayas, *Mucomodulator Therapy in Cystic Fibrosis: Balancing Mucus Clearability Against the Spread of Airborne Pathogens*. Pediatric Pulmonology, 2004. **26**: p. 77-79.
39. Nadel, J.A., B. Davis, and R.J. Phipps, *Control of Mucus Secretion and Ion Transport in Airways*. Annual Review of Physiology, 1979. **41**: p. 369-381.
40. Baskerville, A., *Ultrastructure of the Bronchial Epithelium of the Pig*. Zentralblatt fur Veterinarmedizin. Reihe A., 1970. **17**: p. 796-802.
41. Baker, A.P., et al., *Effect of Kallidin, Substance P, and Other Basic Polypeptides on the Production of Respiratory Macromolecules*. The American Review of Respiratory Disease, 1977. **115**: p. 811-817.
42. Carlstedt, I. and J.K. Sheehan, *Macromolecular properties and polymeric structure of mucus glycoproteins*. Ciba Foundation Symposium, 1984. **109**: p. 157-172.
43. List, S.J., et al., *Enhancement of the Viscosity of Mucin by Serum Albumin*. Biochemical Journal, 1978. **175**(2): p. 565-571.
44. University of Iowa, *Gastric pig mucin formulation*, M.D. Donovan, Editor. 2004. p. Interview.
45. Yeates, D.B., et al., *Mucociliary Tracheal Transport Rates in Man*. Journal of Applied Physiology, 1975. **39**: p. 487-495.
46. Servera, E., J. Sancho, and M.J. Zafraa, *Cough and Neuromuscular Diseases. Noninvasive Airway Secretion Management*. Archivos de Bronconeumologia, 2003. **39**(9): p. 418-427.
47. Davidson, T.M., *Handbook of Nasal Disease*, <http://www-surgery.ucsd.edu/ent/DAVIDSON/NASHAND/nasal.htm>, Editor. 2003.
48. Smaldone, G.C., et al., *Interpretation of "24 Hour Lung Retention" in Studies of Mucociliary Clearance*. Journal of Aerosol Medicine, 1988. **1**: p. 11-20.
49. Agnew, J.E., *Characterizing Lung Aerosol Penetration*. Journal of Aerosol Medicine, 1991. **4**: p. 237-250.

50. Ilowite, J.S., et al., *Relationship between Tracheobronchial Particle Clearance Rates and Sites of Initial Deposition in Man*. Archives of Environmental Health, 1989. **44**: p. 267-273.
51. Jones, J.G., *Clearance of Inhaled Particles from the Alveoli*, in *Aerosols and the Lung: Clinical and Experimental Aspects*, S. Clarke and D. Pavia, Editors. 1984, Butterworths: London. p. 290.
52. Bayvel, L. and Z. Orzechowski, *Liquid Atomization*. 1993, Washington DC: Taylor and Francis.
53. Novy, D.B., *Chromate Content Bias as a Function of Particle Size in Aircraft Primer Paint Overspray*, in *School of Engineering and Management*. 2001, Air Force Institute of Technology (AU): Wright-Patterson AFB, OH.
54. Schilke, R.A., *Hexavalent Chromium Dissociation from Overspray Particles into Fluid for Three Aircraft Primers*, in *Systems and Engineering Management*. 2002, Air Force Institute of Technology (AU): Wright-Patterson AFB, OH.
55. Weast, R.C., M.J. Astle, and W.H. Beyer, *CRC Handbook of Chemistry and Physics*. 65th ed. 1985.
56. Morgan, T.J.R., *Chromate Dissociation from Primer Paint in Simulated Lung Fluid*, in *Systems and Engineering Management*. 2000, Air Force Institute of Technology (AU): Wright-Patterson AFB, OH.
57. Kauth, D.A., *Dissolution of Chromium from Inhalable Primer Paint Particles into a Simulated Lung Fluid*, in *Systems and Engineering Management*. 2001, Air Force Institute of Technology (AU): Wright-Patterson AFB, OH.
58. Gibb, H.J., et al., *Lung Cancer Among Workers in Chromium Chemical Production*. American Journal of Industrial Medicine, 2000. **38**: p. 115-126.
59. Hayes, R.B., A.M. Lilienfeld, and L.M. Snell, *Mortality in Chromium Chemical Production; A Prospective Study*. International Journal of Epidemiology, 1979. **8**(4): p. 365-374.
60. Mancuso, T.F., *Chromium as an Industrial Carcinogen: Part I*. American Journal of Industrial Medicine, 1997. **31**: p. 129-139.
61. Luippold, R.S., et al., *Lung Cancer Mortality among Chromate Production Workers*. Occupational and Environmental Medicine, 2003. **60**: p. 451-457.
62. Davies, J.M., D.F. Easton, and P.I. Bidstrup, *Mortality from Respiratory Cancer and Other Causes in United Kingdom Chromate Production Workers*. British Journal of Industrial Medicine, 1991. **48**: p. 299-313.
63. Langard, S. and T. Vigander, *Occurrence of Lung Cancer in Workers Producing Chromium Pigments*. British Journal of Industrial Medicine, 1983. **40**(1): p. 71-74.
64. Deschamps, F., et al., *Mortality Study among Workers Producing Chromate Pigments in France*. International Archives of Occupational and Environmental Health, 1995. **67**(3): p. 147-152.
65. Boice, J.D., Jr., et al., *Mortality among Aircraft Manufacturing Workers*. Occupational and Environmental Medicine, 1999. **56**: p. 581-597.
66. Wells, W.F., *Airborne Contagion and Air Hygiene*. 1955, Cambridge, MA: Harvard University Press.
67. LaPuma, P.T., et al., *Chromate Dissociation from Three Types of Paint Particles*. Regulatory Toxicology and Pharmacology, 2002. **36**: p. 1-6.

68. Sawyer, K.F. and W.H. Walton, *The Conifuge-a Size-Separating Sampling Device for Airborne Particles*. Journal of Scientific Instruments, 1950. 27: p. 272-276.
69. May, K.R., *The Cascade Impactor*. Journal of Scientific Instruments, 1945. 22: p. 187-195.
70. Wilcox, J.D., *Design of a New Five-Stage Cascade Impactor*. Archives of Industrial Hygiene and Occupational Medicine, 1953. 7: p. 376-382.
71. Armour Research Foundation, *Automatic Counting and Sizing of Aerosol Particles*. 1953.
72. Ranz, W.E. and J.B. Wong, *Jet Impactors for Determining the Particle Size Distribution of Aerosols*. Archives of Industrial Hygiene and Occupational Medicine, 1952. 5: p. 464-477.
73. Andersen, A.A., *New Sampler for the Collection, Sizing, and Enumeration of Viable Airborne Particles*. Journal of Bacteriology, 1958. 76(5): p. 471-484.
74. Marple, V.A. and et al, *Inertial, Gravitational, Centrifugal, and Thermal Collection Techniques*, in *Aerosol Measurement*, K. Willeke, Editor. 1993, Ban Nostrand Reinhold: New York NY.
75. EPA, *National Primary and Secondary Ambient Air Quality Standards*. 2004.
76. Mitchell, J.P., et al., *Aerodynamic Particle Size Analysis of Aerosols from Pressurized Metered-Dose Inhalers: Comparison of Andersen 8-Stage Cascade Impactor, Next Generation Pharmaceutical Impactor, and Model 3321 Aerodynamic Particle Sizer Aerosol Spectrometer*. AAPS PharnSciTech, 2003. 4(4): p. article 54.
77. NIOSH, *NIOSH Manual of Analytical Methods*. 1998, <http://www.cdc.gov/niosh/nmam/>.
78. Rhodes, B.S., *Chromate Content Bias Versus Overspray Particle Size in Three Aircraft Primer Paints*, in *Systems and Engineering Management*. 2002, Air Force Institute of Technology (AU): Wright-Patterson AFB, OH.
79. (OECD), O.f.E.C.a.D., *OECD Guideline for Testing of Chemicals, No. 105: Water Solubility*. 1987.

Vita

Captain Michael Moran was born in New London, Connecticut. [REDACTED]

He graduated from Wheeler High School in June 1988. He entered undergraduate studies at the University of Connecticut where he graduated with a Bachelors of Science degree in Chemical Engineering in 1995. He received a direct commission into the Air Force and entered active duty on Nov 2 1997.

His first assignment was at Nellis AFB, NV where he served as a Bioenvironmental Engineer from 1997 until 2000. He served as the Environmental Protection Element Chief from 2000 to 2003 at RAF Lakenheath. In July 2003, he entered the Master of Science in Public Health graduate program at Uniformed Services University. Upon graduation in June 2005, he will be assigned to the Air Force Institute for Operational Health, Brooks City Base, San Antonio Texas.

JUL 18 2005

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 13.Jul.05	3. REPORT TYPE AND DATES COVERED THESIS	
4. TITLE AND SUBTITLE DISSOCIATION OF HEXAVALENT CHROMIUM FROM PRIMER PAINT PARTICLES INTO SIMULATED MUCUS FLUID			5. FUNDING NUMBERS	
6. AUTHOR(S) CAPT MORAN MICHAEL P				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIFORMED SERVICES UNIV OF HEALTH SCIENC			8. PERFORMING ORGANIZATION REPORT NUMBER CI04-1136	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) THE DEPARTMENT OF THE AIR FORCE AFIT/CIA, BLDG 125 2950 P STREET WPAFB OH 45433			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION AVAILABILITY STATEMENT Unlimited distribution In Accordance With AFI 35-205/AFIT Sup			12b. DISTRIBUTION CODE	
<p>DISTRIBUTION STATEMENT A Approved for Public Release Distribution Unlimited</p>				
13. ABSTRACT (Maximum 200 words)				
14. SUBJECT TERMS			15. NUMBER OF PAGES 107	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	