3-2002

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Recommended Citation

Schilke, Richard A., "Hexavalent Chromium Dissociation from Overspray Particles into Fluid for Three Aircraft Primers" (2002). *Theses and Dissertations*. 4434.
https://scholar.afit.edu/etd/4434

HEXAVALENT CHROMIUM DISSOCIATION FROM OVERSPRAY PARTICLES INTO FLUID FOR THREE AIRCRAFT PRIMERS

THESIS

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AFIT/GEE/ENV/02M-12

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY
AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

AFIT/GEE/ENV/02M-12

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THESIS

Presented to the Faculty

Department of Systems and Engineering Management

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Engineering and Environmental Management

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March 2002

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Acknowledgements

I must first thank my wife who made more than her fair share of sacrifices during the past year. Likewise, thanks to my son and daughter for always demonstrating exquisite patience when Dad was working. Thank you all for your understanding and support, I love you, forever.

Many thanks to my thesis advisor, Major Peter LaPuma, USAF, who first captured my interest with this project and continually renewed my motivation and focus. To my committee members, Dr. Michael Shelley and Dr. Glen Perram, I say thank you for your time, patience, and insight into this research. Thank you also to Dr. Dan Reynolds for your enthusiastic willingness to share time and statistical expertise. Next, a thank you to all the professionals at the Air Force Coatings Technology Integration Office, especially to Ken Chitwood and Scott Lanter for consistently going out of your way to coordinate, teach, and provide support. A big thank you also goes to Air Force Institute of Technology research librarians Kathi French and Robin Hayes. You provided tremendous service and were true force-multipliers in my research efforts.

Thank you to my colleague, Captain Brian Rhodes, USAF, for keeping me honest and sharing in the struggle to better understand the research questions in this study.

Finally, thank you to the U. S. Air Force Materiel Command Pollution Prevention Branch and the Air Force Research Laboratory Pollution Prevention Research & Development Program Office for funding this research.

Richard A. Schilke

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Abstract

The Department of Defense and industry use chromate-containing primer paints extensively to inhibit corrosion on metal assets. Chromate, a primer pigment, provides excellent corrosion inhibition, but contains hexavalent chromium (Cr^{6+}), a human carcinogen. There is no reliable epidemiological evidence of increased lung cancer incidence among painters potentially exposed to primer overspray particles. Using bio-aerosol impingers, overspray particles from three different primers (solvent-borne epoxy, water-borne epoxy, and solvent-borne polyurethane) were collected into water to test the hypothesis that the paint matrix influences Cr^{6+} release into water. This collection method is intended to simulate Cr^{6+} release from paint particles into lung fluid. Collected particles were allowed to reside in the water for 1 and 24 hours after which the particles were separated from the water by centrifugation. Supernatant water was then tested for dissolved $[Cr^{6+}]$. The mean fractions of Cr^{6+} released into the water after 1 and 24 hours for each primer (95% confidence) were: 70 ± 5% and 85 ± 5% (solvent epoxy), 74 ± 4% and 84 ± 4% (water epoxy), and 94 ± 3% and 95 ± 2% (polyurethane). The epoxy primers demonstrated a range of 24-hour Cr^{6+} release from complete (100%) dissociation to as low as 33% for the solvent epoxy, and 48% for the water epoxy. Correlations between the distribution of Cr^{6+} with particle size and % Cr^{6+} dissociated from each sample indicate that particles $< 5\ \mu m$ release a larger fraction of their Cr^{6+} during the first 24 hours versus particles $> 5\ \mu m$.

HEXAVALENT CHROMIUM DISSOCIATION FROM OVERSPRAY PARTICLES INTO FLUID FOR THREE AIRCRAFT PRIMERS

I. Introduction

Primer Paint Applications

Chromate-containing primer paints are widely used throughout the Department of Defense (DOD) and industry to inhibit corrosion on metal assets that are regularly exposed to corrosive environmental effects. The United States Navy (USN), Marine Corps (USMC), Army (USA), and Air Force (USAF) are large consumers of these chromate-containing primers for ship, aircraft, vehicle, and weapons coating systems. Primers coat the metal skin of an asset providing an adhesive coating for topcoat paints and long-term corrosion protection. Some benefits of corrosion protection include: reduced maintenance, improved structural integrity, and longer service-life. Chromate salts, such as strontium chromate ($SrCrO_4$), barium chromate ($BaCrO_4$) , or zinc chromate ($ZnCrO_4$) , serve as the primary ingredient in primers to protect metal surfaces from corrosion. Chromate-containing primer paints provide superior corrosion protection over any other primer paints (NDCEE, 1998b). However, chromate contains hexavalent chromium (Cr^{6+}), a heavily regulated human carcinogen.

Primer paint performance requirements are dictated by military (MIL-P) and federal (TT-P) specifications. Frequently used DOD chromate-containing primer specifications for ship and aerospace applications are shown in Table 1. $SrCrO_4$ is the most common form of chromate in these specifications.

Table 1. Prominent Chromate-containing Military Primers

Specification #	Primer Type
MIL-P-23377G	Solvent-borne epoxy polyamide
MIL-P-85582B	Water-borne epoxy polyamide
TT-P-2760A	Solvent-borne elastomeric polyurethane

Chromium Carcinogenicity

Chromium in the trivalent form (Cr^{3+}) is an essential mineral for human health. Hexavalent chromium (Cr^{6+}), however, has been shown to be carcinogenic to both animals and humans. Based on evidence from animal toxicology and human epidemiology studies, several agencies have declared Cr^{6+} a known human carcinogen due to its potential to cause DNA damage. These agencies include: the Agency for Toxic Substances and Disease Registry (ATSDR, 1990), the International Agency for Research on Cancer (IARC, 1990), the Occupational Safety and Health Administration (OSHA, 1996), the National Institute for Occupational Safety and Health (NIOSH, 1997), and the American Conference of Governmental Industrial Hygienists (ACGIH, 2001). While the intracellular mechanism of DNA damage is not well understood, the idea that Cr^{6+} facilitates the DNA damage is well accepted (Sugden & Stearns, 2000; Jones, 1990).

Occupational Chromium Exposure

Prolonged inhalation exposure to high doses of Cr^{6+} is a significant risk factor for lung cancer and can cause other non-carcinogenic respiratory effects such as nasal ulceration (IARC, 1990; Jones, 1990). Epidemiology and animal studies have shown the genotoxic potential of Cr^{6+} when it is readily available for absorption into cells in amounts that exceed the body's capacity to reduce Cr^{6+} to the less hazardous Cr^{3+} [see Jones (1990) for a review]. Cr^{6+} carcinogenic effects due to chronic inhalation exposure are well documented by case studies of workers in such industries as chromium manufacturing, chromium plating, leather tanning, stainless steel welding, and chromate pigment production where exposure to Cr^{6+} is from acid mists, fumes, or dusts (IARC, 1990; Langard, 1990; O'Flaherty and Radike, 1991). However, current epidemiology studies do not include credible evidence of similar effects from chromate exposure during painting operations. Also, previous animal studies do not accurately represent exposure pathways seen in painting operations. Painters are exposed to airborne paint particles containing $SrCrO_4$ that is predominantly in solid form (LaPuma et al., 2001). The $SrCrO_4$ is contained in the paint matrix, which primarily consists of resin and organic solvents or, for water-borne primers, a combination of resin, water, and solvents. This paint matrix may inhibit Cr^{6+} availability even if paint particles are deposited into the lung fluid. Differences in composition between paint particles and other chromate-bearing particulates may explain the lack of a clear connection between chromate-containing primer painting and lung cancer incidence. These factors suggest that the bioavailability of Cr^{6+} from inhaled paint overspray particles differs from that due to inhalation of particles found in other occupations.

Exposure Standards

In the United States, OSHA is charged with setting workplace exposure limits, known as permissible exposure limits (PEL), for hazardous substances. OSHA considers both worker health and feasibility when setting limits for industry (OSHA, 1996). The agency sometimes limits inhalation hazards using ceiling PELs that limit the maximum substance concentration in the air. The current OSHA ceiling for chromate (as CrO_3) is 0.1 mg/m^3 (29 Code of Federal Regulations 1910.1000, Table Z-2). In 1993, OSHA received a petition from the Oil, Chemical, and Atomic Workers International Union (OCAW) and the Public Citizen's Health Research Group (HRG) to issue an emergency temporary standard (ETS) for Cr^{6+} compounds of 0.0005 mg/m^3 as an 8-hour time-weighted average (TWA) [OSHA, 1996]. This standard is the ACGIH recommended Threshold Limit Value (TLV) for $SrCrO_4$ (ACGIH, 2001). The petition, while denied, provided the impetus for a proposed rule pending further OSHA investigation (OSHA, 1996; 2000). If adopted, the limit would virtually ban military and industrial use of chromate-containing primer paints due to the difficulty in meeting such a low standard, even with respirator protection. Furthermore, if Cr^{6+} bioavailability from primer overspray particles is much lower than from particles in other industrial exposures, the proposed standard may be unnecessarily low for painting operations.

Thesis Objective

Previous research investigating Cr^{6+} bioavailability in painting operations suggests that the paint matrix hinders Cr^{6+} dissociation from primer particles into a simulated lung fluid (SLF) [Kauth, 2001]. The research focused on the solvent-borne epoxy polyamide (MIL-P-23377G) specification only. This study, which is a follow-up to the Kauth study, has three primary objectives:

1) Observe the influence of particle residence time in fluid on the quantity of Cr^{6+} dissociated from chromate-containing primer overspray particles
2) Compare the solvent-borne epoxy (MIL-P-23377G), water-borne epoxy (MIL-P-85582B), and solvent-borne polyurethane (TT-P-2760) primers to observe differences in Cr^{6+} dissociation
3) Quantitatively relate particle size to Cr^{6+} dissociation from primer particles into fluid

II. Literature Review

Overview

Aircraft painters are potentially exposed to paint particles via inhalation of overspray. Actual exposure can vary greatly over time due to many environmental, physiological, and chemical influences. In addition to examining existing epidemiology and animal studies, assessing a painter's risk due to Cr^{6+} exposure from primer paints requires an understanding of the fundamental mechanisms that determine Cr^{6+} bioavailability. Cr^{6+} bioavailability to painters depends on complex interactions related to such factors as: paint composition, lung particle deposition and clearance mechanisms, physiological Cr^{6+} reduction, particle inhalation dynamics, the size and composition of inhaled overspray particles, and Cr^{6+} dissociation from inhaled paint particles once in the lung fluid. After establishing a historical perspective regarding Cr^{6+} bioavailability and carcinogenicity, this chapter discusses the significance and interaction of these six factors as they apply to better understanding a painter's risk of Cr^{6+} exposure from chromate-containing primer overspray particles.

Epidemiology/Pathology/Animal Studies

Epidemiology, human pathology, and animal studies provide abundant evidence of the inherent carcinogenicity of Cr^{6+} (IARC, 1990). In order to damage DNA, Cr^{6+} must first be made available to the target (lung) cell. Studies indicate the importance of the chemical and physical form of a Cr^{6+} compound in determining bioavailability. Evidence suggests that only certain Cr^{6+}-containing compounds have demonstrated the ability to cause lung cancer and that there is an exposure threshold below which carcinogenic effects are not seen. (Ishikawa, et al., 1994; Jones, 1990; Mancuso, 1975)

Since Newman (1890) reported the first known association of cancer with a worker's exposure to chromium pigments, numerous cohort studies report increased cancer risks due to chronic exposure to certain Cr^{6+}-containing compounds (IARC, 1990). Elevated lung cancer rates are observed primarily in the production of chromium compounds from chromite ore, chromate pigment production, chromium electroplating, and stainless steel welding (OSHA, 1996; IARC, 1990). These processes generate Cr^{6+}-containing compounds in the form of a dust, fume, or acid mist. Chromium electroplating, for example, generates acid mist containing chromium trioxide (IARC, 1990). Based on a review of epidemiological studies conducted on workers in these industries, Langard (1990) concluded that exposure to Cr^{6+} as chromates, dichromates, or chromic trioxide is responsible for increased lung cancer risk. Langard et al. (1990) found only weak evidence of lung cancer risk in chromium ferroalloy workers. Chromium ferroalloy production exposes workers to chromium compounds consisting primarily of Cr^{3+} and very limited Cr^{6+}. Only one author (Mancuso, 1975; 1997) claims a carcinogenic potential for Cr^{3+}. Thus, evidence strongly implicates inhalation of Cr^{6+}-containing compounds, such as chromate, as the primary Cr-related lung cancer hazard.

Multiple studies indicate the importance of chromate dosage and bioavailability in assessing lung cancer risk from Cr^{6+} exposure. A change in processes, around 1960, to eliminate high levels of exposure to slightly water-soluble calcium chromate led to a significant reduction, if not elimination, of excess lung cancer risk in such industries as chromite ore processing and chromate pigment production (Aw, 1997; Jones, 1990). Steinhoff et al. (1986) found evidence of a Cr^{6+} carcinogenic threshold in rats after intratracheal installation of various doses of sodium dichromate. 14 of 80 rats receiving a single dose of 1.25 mg/kg presented with one or more lung tumors, but no tumors were seen in 80 rats dosed with the same concentration spread over five days (0.25 mg/kg/day). One pathology study based on autopsies of 13 chromate compound production workers found the lung tissue Cr burden was generally much higher in subjects with lung tumors (40 – 15,800 µg/g) than in those without (8-28 µg/g) [Ishikawa, et al., 1994]. These studies, among others (Mancuso, 1975; Axelsson et al., 1980; Korallus et al., Bidstrup and Davies, 1986), suggest that a threshold dose exists for Cr^{6+} lung carcinogenicity, and imply the importance of Cr^{6+} concentration in the lung fluid. Finally, a cohort study of male chromate pigment workers producing several Cr^{6+}-containing compounds, including $SrCrO_4$, found no excess risk of lung cancer (Kano et al., 1993). The study proposed several possible explanations for the results, including: improved industrial hygiene practices, lower carcinogenicity of some Cr^{6+} compounds, work environment concentrations below a dose-response threshold, or a dependence of carcinogenicity on the chemical form of the compound.

Epidemiological evidence of carcinogenic risk from chromate-containing paint operations is weak. One study (Dalager et al., 1980) of 977 male aircraft painters using zinc chromate-containing paint found an excess of respiratory cancer (21 observed, 11.4 expected). Unfortunately, this study did not account for smoking and, according to the authors, smoking among painters is more prevalent than in the general population. Another study (Alexander et al., 1996) of 2,429 chromate-exposed aerospace workers found no excess of lung cancer in 1,064 spray painters (6 observed, 11.1 expected). The authors suggest “incorporation of the chromate into the paint matrix may render it less biologically active.” Further support for this statement is offered by the fact that sanders in this study who were exposed to the same compounds, but in potentially less encapsulated dust particles, showed an excess of lung cancer.

Documented animal studies demonstrate that the solubility of Cr^{6+}-containing compounds is a key factor in determining carcinogenic potential. Animal studies indicate that the moderately soluble zinc, calcium, and strontium chromate salts have much greater carcinogenic potential than the highly soluble sodium, potassium, and ammonium chromates (Hathaway, 1989; Gibb and Chen, 1989). Sodium dichromate, installed in rat trachea in the Steinhoff et al. (1986) study, is highly soluble. These authors conclude that "easily soluble chromates signify a relatively small risk of a carcinogenic effect and then only when high doses are absorbed over a very long period", and also that the chronic irritant effect associated with repeated high doses probably served to promote pulmonary tumors in the rats. It seems that while highly soluble Cr^{6+} compounds might temporarily produce higher available Cr^{6+} concentrations in the lung, their Cr^{6+} is chemically reduced and cleared more rapidly (Gad, 1989; O'Flaherty and Radike, 1991). To the contrary, insoluble Cr^{6+} compounds, such as lead chromate, fail to produce high concentrations of Cr^{6+} in the lung. Thus, the carcinogenic potential appears greatest for moderately soluble Cr^{6+} compounds, which possess the ability to release sufficient Cr^{6+} *and* to reside in the lung fluid for a sufficient time.

Animal studies demonstrate that some Cr^{6+}-containing compounds are genotoxic, but do not provide information about the relationship between exposure and carcinogenic effects. The majority of existing animal studies used implantation of solid chromate compounds directly into target tissues (e.g. intrabronchial, intratracheal) [IARC, 1990]. While implantation studies demonstrate a carcinogenic potential for Cr^{6+}-containing compounds, inhalation exposure of animals to these compounds has not shown a clear link to pulmonary tumors (IARC, 1990; Langard, 1988). IARC reports only one animal inhalation study (Nettesheim et al., 1971) that shows a significant incidence of lung tumors. That study exposed mice to calcium chromate dust.

ACGIH set its lower TLV based primarily on a study by Levy et al. (1986) in which rats were dosed through intrabronchial implantation of cholesterol pellets containing various chromate compounds (ACGIH, 2001). After two years of observation, the study found that groups exposed to strontium chromate and zinc chromate showed a statistically significant increase in bronchial tumors. While the study effectively demonstrates the carcinogenicity of these compounds, the implantation exaggerates exposure concentration, negates the effects of respiratory filtering and clearance mechanisms, and does not present the compound in a matrix similar to paint.

Primer Paint Composition

Primer paints are complex mixtures that are tailored to meet the coating needs of various types of metal and anticipated exposure environments. The primary paint constituents are the pigment, the vehicle, and the solvents (USAF, 2001). Pigments are mostly insoluble and provide several benefits including color and corrosion-inhibition. The three primers used in this study (Table 1) all use Cr^{6+}-containing $SrCrO_4$ pigment as the corrosion inhibitor (USAF, 2001; USN, 2001). The vehicle, or liquid portion of the coating, enables paint delivery, adhesion, flexibility, durability, and chemical resistance. The vehicle contains both volatile and non-volatile components. Volatiles consist primarily of a solvent mixture that thins the paint for delivery to a metal surface, and enables smoothing and binding of the paint coating. Resins comprise the majority of non-volatiles and act as binding agents to link together pigment granules and a potential host of secondary components depending on the intended application. Epoxy and polyurethane primers cure by chemical cross-linking rather than dry by evaporation (USAF, 2001). Cross-links form during curing of the paint matrix to establish the paint film and bind the chromate (Munger, 1984). If the paint subsequently cracks or is scratched, chromate ions are electrochemically attracted to the exposed metal (anode) and prevent oxidation of the metal by reforming the protective barrier (Miller, 1979).

Deft® Incorporated supplies the military with large amounts of chromate-containing solvent-borne epoxy, water-borne epoxy, and solvent-borne polyurethane primers. For this reason, and the desire to maintain manufacturer consistency between paints, Deft® primers were selected exclusively for this study. Deft® Material Safety Data Sheet (MSDS) excerpts for the three specifications used in this study are included in Appendices A, B, and C. All of these primers are two-component mixtures consisting of a pigment- and resin-containing base (Component A) and a curing agent catalyst (Component B). The water-borne primer requires addition of water as a reducing component. Table 2 summarizes the primer mix ratios and Table 3 summarizes the MSDS-listed contents of the Deft® primers.

Table 2. Primer Component Mix Ratios.
Shown as a % volume in the final mixture.

Primer	Base	Catalyst	H_2O
Solvent-borne epoxy	75.0 %	25.0 %	N/A
Water-borne epoxy	28.6 %	14.3 %	57.1 %
Solvent-borne polyurethane	50.0 %	50.0 %	N/A

Table 3. Comparison of Deft® Mixed Primer Contents (adapted from MSDSs).

Solvent-Borne Epoxy		Water-Borne Epoxy		Polyurethane	
Constituent	% Wt	Constituent	% Wt	Constituent	% Wt
Benzene, 1-Chloro-4 Trifluoromethyl	< 4.1	sec-Butyl Alcohol	8.4	Isobutyl Alcohol	< 0.1
Benzene, 1-Chloro-4 Trifluoromethyl	< 0.1	C8 & 10 Aromatic Hydrocarbon	< 0.3	Ethyl 3-Ethoxypropionate	5.9
n-Butyl Acetate	< 4.1			n-Butyl Acetate	< 3.0
Methyl n-Propyl Ketone	20.3			Methyl Ethyl Ketone	< 3.0
Strontium Chromate	20.3	Strontium Chromate	9.9	Strontium Chromate	11.9
Aromatic Hydrocarbon	< 0.8			2,4-Pentanedione	< 3.0
Xylene	< 0.08			Xylene	< 0.6
1, 2, 4 Trimethylbenzene	< 0.8			Dibutyltin Dilaurate	< 0.1
Cumene	< 0.1			Dispersion Aid	< 0.6
1, 3, 5 Trimethylbenzene	< 0.8			Anti-float Agent	< 0.6
Diethylbenzene	< 0.8			Ethyl Benzene	< 0.1
Ethyl Benzene	< 0.1				
n-Methylpyrrolidone	< 0.8				
Polyamide Resin	≥ 36.3	Polyamide Resin	≥ 25.3	Oil-free Polyester	≥ 30.7
Aliphatic Amine	< 3.0	Nitroethane	4.4	Polymeric Hexamethylene Diisocyanate	22.4
sec-Butyl Alcohol	5.6			Methyl Isobutyl	8.1
Aromatic Hydrocarbon	< 0.2			n-Butyl Acetate	< 2.0
Xylene	< 0.02			Methyl Ethyl Ketone	8.1
1, 2, 4 Trimethylbenzene	< 0.2	De-ionized Water	51.7		
Cumene	< 0.02				
1, 3, 5 Trimethylbenzene	< 0.2				
Diethylbenzene	< 0.02				
Ethyl Benzene	< 0.02				
Amino Silane Ester	< 0.2				
Epoxy Resin Hardener	< 1.0				

Double lines separate components (base||catalyst||water, top to bottom). % Wt represents the constituent post-mixing percent weight in the mixture.

Though some portion of chromate pigment dissolves into each primer's volatiles, consisting of solvents or water and solvents, the majority of the chromate remains in solid form. The total mass of $SrCrO_4$ per volume of paint in this study's three primers is approximately: 251,900 mg/L (solvent-borne epoxy), 111,200 mg/L (water-borne epoxy), and 139,200 mg/L (solvent-borne polyurethane). The solubility limit of $SrCrO_4$ in methyl ethyl ketone (MEK), a solvent representative of the volatiles in the solvent-borne primers, is 45 mg/L (LaPuma et al., 2001), but in water at 15° C it's 1200 mg/L. Therefore, while a very small portion of chromate actually dissolves into the volatiles, the water-borne epoxy volatiles (77% water by volume) contain nearly 21 times as much $SrCrO_4$ (940 mg/L) as the solvent-borne epoxy and polyurethane volatiles at saturation. Finally, the water-borne primer contains a much larger fraction of volatiles (74% by volume vs. 41% for the solvent epoxy and polyurethane), which are mostly water.

Solvent-borne vs. Waterborne Primers

Solvent-borne paints are preferred for their longer shelf life, shorter dry times, ease of application, and performance for a wide range of metal surfaces and environmental conditions (NDCEE, 1998a), but they release volatile organic compounds (VOCs) to the atmosphere. VOCs accelerate the production of tropospheric ozone, a major contributor to photochemical smog and a human health concern, especially for individuals suffering from respiratory disorders (Godish, 1997). Water-borne primers, such as MIL-P-85582B, have become increasingly available in recent years due to the benefits of their low VOC formulation in complying with more stringent regional tropospheric ozone standards (USEPA, 2000). Although water-borne primer use reduces VOC emissions, and presumably tropospheric ozone, it may increase the carcinogenic risks to painters by delivering Cr^{6+} in a more bioavailable form.

If the primer matrix limits Cr^{6+} dissociation from primer particles such that Cr^{6+} is only available from the chromate dissolved in the volatiles, then increasing the amount of chromate in the volatiles or the ability of the volatiles to transfer Cr^{6+} to the fluid may increase Cr^{6+} bioavailability. This may occur through an increase in: chromate solubility in the volatile fraction, volatile fraction solubility in lung fluid, or the volatile % volume in the paint mixture. If chromate dissolved in the paint volatiles is the primary source of Cr^{6+} to the lung fluid, the volatile fraction saturation limit and % volume comparisons made in the previous section predict that more Cr^{6+} mass may be released from the water-borne epoxy primer than from either solvent-borne primer. Additionally, the increased solubility of the mostly-water volatile fraction in an aqueous lung fluid compared to that of non-polar solvent volatiles predicts greater Cr^{6+} release from the water-borne primer.

Primer Painting Operations

Primers containing zinc, barium, or strontium chromate are applied to aluminum, magnesium, and their alloys to provide corrosion protection and an adherent layer between the metal and the topcoat (USAF, 2001; USN, 2001). Large-scale spray painting operations typically take place in ventilated painting areas or booths that have a minimum airstream velocity of 100 feet per minute (ACGIH, 1995). To reduce VOC emissions and the amount of coating material lost to overspray, the use of high-volume low-pressure (HVLP) spray guns at nozzle pressure settings between 1 and 10 pounds per square inch (psi) is becoming the standard for aircraft painters (USAF, 2001). HVLP spray is used to apply very thin coats of primer to the target surface. Air Force and Naval technical manuals (USAF, 2001; USN, 2001) specify desired primer dry coat thickness ranges of:

- 0.6 to 1.8 mils (.0006 to .0018 inches) for the solvent-borne epoxy and water-borne epoxy primers
- 1.0 to 2.0 mils (.0010 to .0020 inches) for the polyurethane primer

Since paint transfer efficiency may be as low as 65% for HVLP and even lower (35-50%) when conventional high-pressure spray guns are used, a portion of the paint becomes inhalable overspray (USN, 2001; US AF, 2001). Variables such as painting technique, object size, and number and location of individuals painting simultaneously contribute to varying inhalation exposure potential. Since ventilation systems and personal respirators can be improperly used or overwhelmed, the opportunity for chronic worker exposure to chromate-containing overspray particles remains an important concern.

Particle Deposition and Clearance Mechanisms in the Lung

Inhalation is the primary route of painter exposure to aerosolized paint particles. When particles are inhaled, they deposit throughout the respiratory system with a distribution that depends on many factors but is strongly related to particle aerodynamic diameter. Some other important parameters are: airway shape, structure, and diameter; air flow rate; air velocity; route of entry (nasal or oral); particle size, solubility, and hygroscopicity (Seinfeld, 1986; Phalen, 1984). These factors combine to force particle deposition via interception, impaction, sedimentation, or diffusion.

Aerodynamic diameter (d_{ae}) is defined as the diameter of a unit density (1 g/cm^3) sphere having the same terminal settling velocity as the particle under study (Seinfeld, 1986). Assuming spherical particles, terminal settling velocity (v_t) for an aerosol particle is defined by Stokes' Law as (Clark, 1996):

$$v_t = \frac{C_c ?_p d_p^2}{18 \cdot \mu} \cdot g \tag{1}$$

where: C_c = Cunningham Slip Correction factor (unitless) [diameter-dependent]
ρ_p = particle density (g/cm^3)
d_p = particle diameter (cm)
μ = dynamic viscosity of air (g/cm·s) [temperature-dependent]
g = acceleration due to gravity (cm/s^2)

d_{ae} is determined by substituting this v_t and solving equation 1 for d_p when $\rho_p = 1$ g/cm^3:

$$d_{ae} = \sqrt{\frac{v_t \cdot (18 \cdot \mu)}{C_c \cdot \left(1\frac{g}{cm^3}\right) \cdot g}} \qquad (2)$$

The relationship between particle diameter (d_p), particle density (ρ_p), and d_{ae} is easily seen if the right-hand side of equation 1 is substituted into equation 2 for v_t and constants are cancelled:

$$\mathrm{d}_{\mathrm{ae}} = \sqrt{\frac{?_{\mathrm{p}} \cdot \mathrm{d}_{\mathrm{p}}^2}{\left(1\frac{\mathrm{g}}{\mathrm{cm}^3}\right)}} \qquad (3)$$

Thus, d_p and ρ_p directly influence d_{ae}, which affects how a particle is inhaled and deposited in the respiratory tract.

The respiratory system contains two main regions called the conducting zone and the respiratory zone (Figures 1 & 2). The conducting zone consists of the oral and nasal airways, pharynx, larynx, trachea, bronchi, and bronchioles, and can be subdivided into the head and conductive airway regions. During inhalation, the upper conducting zone filters large particles, and pre-warms and humidifies air prior to passage through the trachea and bronchi. The respiratory zone, also called the pulmonary region, includes the respiratory bronchioles and alveoli (Fox, 1999; Seinfeld, 1986) and is the area of oxygen and carbon dioxide gas exchange with the blood. Gas is primarily exchanged in the alveoli, which provide about 60 to 80 m^2 of gas exchange surface area in the lung (Fox, 1999). The respiratory system (except the alveoli) is lined with a layer of mucus atop hair-like cilia that project from the walls of the airways. Cilia protrude from lung cells and exist in a watery serous fluid that is covered by the mucus layer. Cilia transport the mucus layer upward at a rate of 1 to 2 cm per minute (Fox, 1999) by beating in a coordinated stroking motion. This process is known as mucociliary escalation.

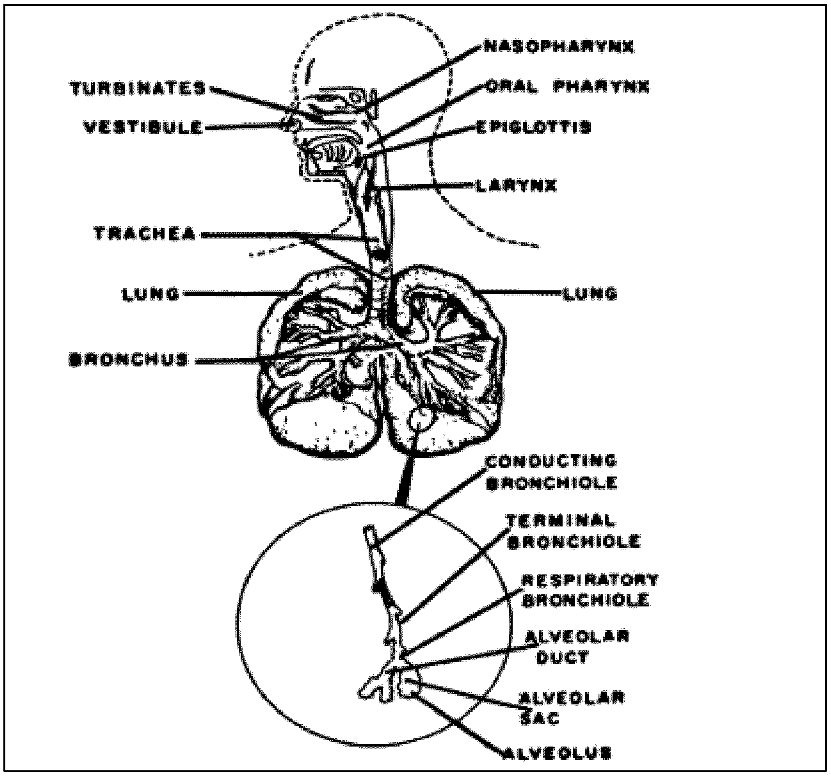


Figure 1. Human Respiratory Tract Schematic Diagram (Hinds, 1982:17)

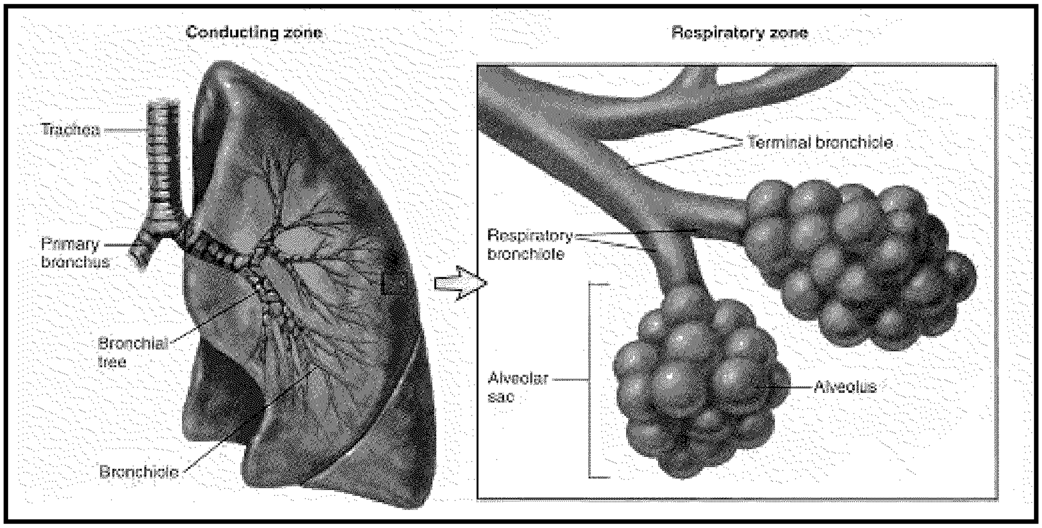


Figure 2. Conducting and Respiratory Zones (Fox, 1999:484)

Mucociliary escalation of deposited particles is the primary means of particle removal in the conducting zone. Inertial impaction is most prevalent in the conducting zone and accounts for the greatest deposition by mass (Miller et al., 1979). Air velocity, greatest after entering the nostril, gradually slows as the bronchi bifurcate (divide) 19 to 21 times prior to reaching the terminal bronchioles. Due to inertia, most particles with d_{ae} larger than 5 μm tend to maintain their trajectories when the airway changes direction causing them to impact the mucus lining of the nasal cavity or bronchi walls (Miller et al., 1979). Impaction, interception, sedimentation, and diffusion continue to filter smaller and smaller particles as air descends toward the terminal bronchioles. Particles captured by the mucus lining in the bronchi are transported up the bronchial tree to the pharynx by mucociliary escalation. Mucus and trapped particles are then swallowed or expectorated (Fox, 1999). Mucociliary escalation clears the conducting zone rapidly, removing most trapped particles within 24 hours of inhalation (Lippmann and Albert, 1969; Stahlhofen et al., 1980).

Some particles with d_{ae} less than 5 μm can navigate past the conducting zone to the respiratory zone (Chan and Lippmann, 1980). The lack of mucus lining and cilia in the alveoli prevents mucociliary escalation, which increases clearance time and, thus, the potential for health effects (Phalen, 1984). Particles that reach the alveoli are predominantly removed by phagocytosis, where cells called pulmonary alveolar macrophage (PAM) engulf particles and enzymatically break them down.

At inhalation rates of approximately 30 L/min (moderate exercise), inertial impaction in the upper respiratory system removes almost all particles with d_{ae} greater than 10 μm during nasal inhalation and 15 μm during oral inhalation (Seinfeld, 1986). At this flow rate, studies have found that about 20 percent of 1 µm, 30 percent of 2 µm, 40 to 50 percent of 3 to 4 µm, and less than 10 percent of 5 to 10 µm particles are deposited in the respiratory zone (Chan and Lippmann, 1980; Stahlhofen et al., 1980; Lippman, 1977; Lippman and Altschuler, 1976; Lippmann and Albert, 1969). Figure 3 shows a typical adult male lung particle deposition distribution by region.

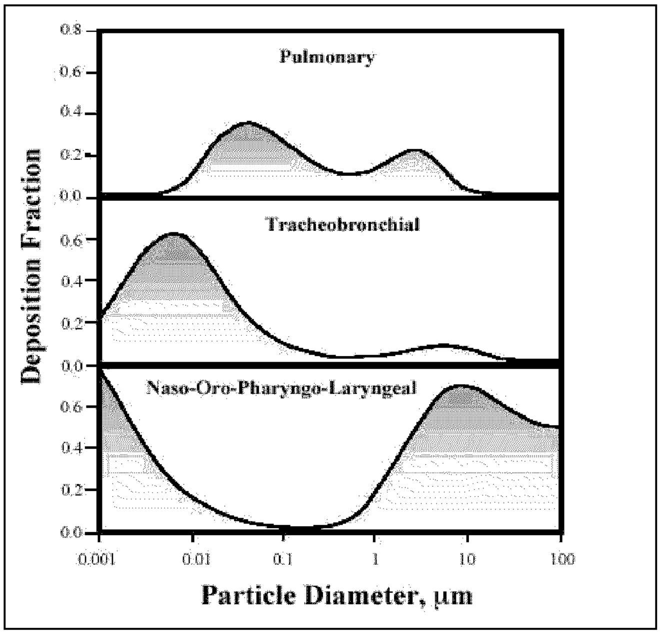


Figure 3. Respiratory Particle Deposition Distributions by Region (Health Effects Institute, 1998:2)

Cr^{6+} Reduction Mechanisms

In addition to lung clearance mechanisms, the human body has a robust capacity for reducing Cr^{6+} to non-carcinogenic Cr^{3+}. Stomach enzymes and acids are able to break down particles that are directly ingested or swallowed after mucociliary escalation, and efficiently reduce Cr^{6+} to Cr^{3+} prior to excretion (DeFlora et al., 1987). Also, enzymes and acids in the lung are capable of reducing Cr^{6+} both inside and outside the epithelial cells. For example, glutathione, cysteine, and ascorbic acid can reduce Cr^{6+} in the extracelluar environment, and are readily available throughout the lung (Connett and Wetterhahn, 1985). It is known that Cr in the 6+ oxidation state is highly diffusible and able to penetrate into cells (Jones, 1990). Cells are much less permeable to Cr^{3+}, Cr^{4+} (tetravalent), and Cr^{5+} (pentavalent), and resist absorption of these species following extracellular reduction of Cr^{6+}. Reduced species are escalated in the mucous, swallowed, and excreted. If C^{6+}-containing particles reach the respiratory zone, PAM have the ability to enzymatically reduce Cr^{6+} to Cr^{3+} (Petrilli and DeFlora, 1998). In fact, most lung cancers related to Cr^{6+} exposure originate in the nasopharynx and upper airways (conducting zone) [Casarett, 1986].

In order for Cr^{6+} to be absorbed by lung cells it must first saturate the reducing capacity of the lung fluid and concentrate near cell membranes (Jones, 1990). Cr^{6+} may then be actively transported into cells by mimicking the structure of sulfate and phosphate (Connett and Wetterhahn, 1983). If Cr^{6+} *is* taken into a cell and then reduced by the cytoplasm, enzymes, or organelles (Connett and Wetterhahn, 1985; Steinhoff et al., 1986; Sugden and Stearns, 2000), the less diffusible reduced species are retained in the cell. It is suspected that these “trapped” reactive intermediates (Cr^{4+} and Cr^{5+}), particularly Cr^{5+}, are responsible for producing oxidative DNA damage (Sugden and Stearns, 2000). Nevertheless, the capacity of respiratory clearance and reduction make it likely that a carcinogenic concentration threshold does exist for inhaled Cr^{6+}. One animal study found that only about 5% of the Cr^{6+} from an inhaled dose was actually absorbed by lung tissue and that most of the Cr^{6+} was excreted in the feces (Visek et al., 1953). Thus, knowing how much Cr^{6+} escapes inhaled paint particles into the lung fluid, and how quickly it escapes, is critical for assessing lung cancer risk to spray painters from chromate-containing primer overspray.

Paint Overspray and Particle Inhalation Dynamics

The mass and distribution of particles inhaled by a painter depends on worker respiration rate, breathing zone concentration, and breathing zone particle size distribution. Respiration rate typically ranges from about 6 L/min at rest (Fox, 1999) to 30 L/min during moderate exercise (Seinfeld, 1986), and translates to the volume of air inhaled over time. Breathing zone concentration and particle size distribution are influenced by the concentration and size distribution of the overspray, the booth air velocity, and painter orientation to the airflow and paint sources. In painting operations, overspray is produced when paint particles of smaller mass, and therefore less inertia, fail to impact the target surface and become entrained in the local airflow (Carlton and Flynn, 1997a). These localized air currents are mainly created by the nozzle air velocity and booth, or ambient, airflow. Carlton and Flynn (1997b) found that the combination of spray gun nozzle pressure and painter orientation to the booth airstream had the dominant influence on breathing zone distribution. Though that study found no correlation between the spray particle size distribution and the breathing zone distribution, the structure and composition of inhaled overspray particles is influenced by paint spray characteristics.

Paint and Overspray Particle Size Distributions

Overspray particles consisting of paint solids and unevaporated solvents and originate from spray particles produced by paint atomization. The atomized spray distribution is a function of pressure at the nozzle, paint viscosity, and relative air-to-liquid mass flow rate (Bayvel and Orzechowski, 1993). In addition to these parameters, the $SrCrO_4$ granule size distribution added to the paint by the manufacturer may influence spray particle size and composition. Figure 4 shows a typical $SrCrO_4$ granule size distribution (log scale) in the Deft® primer mixtures as analyzed by the manufacturer. This distribution contains granules with d_p ranging from .1 µm to 30 µm and a geometric mean of about 4 µm. During spraying, paint from the nozzle is atomized by shearing forces when the surrounding column of discharge air disintegrates the paint liquid into droplets (Bayvel and Orzechowski, 1993). After atomization, the spray particle size distribution may reflect some combination of solvent and epoxy-coated $SrCrO_4$ granules and "smaller" paint particles that do not contain solid $SrCrO_4$ granules. Overspray originates from this distribution but is weighted toward small particles since, by definition, it consists primarily of the smaller, lower inertia, particles.

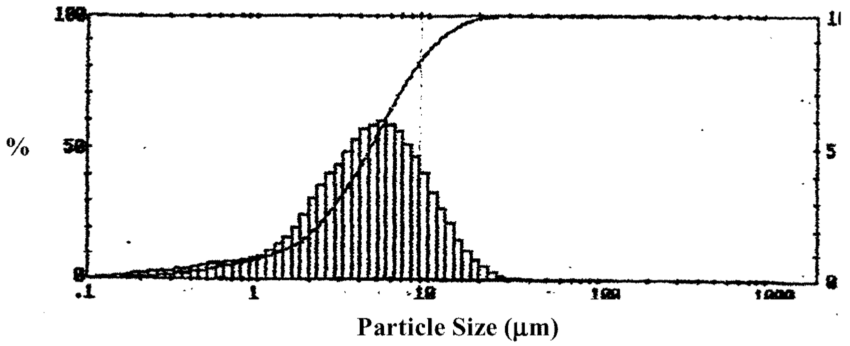


Figure 4. Deft® $SrCrO_4$ Granule Particle Size Distribution in Methanol. Measured on a Malvern Mastersizer Laser and displayed on a log scale.

Overspray Particle Composition

Post-atomization particle composition has three important implications on Cr^{6+} bioavailability. Since $SrCrO_4$ is the densest constituent in the primer, particles containing a greater volume of $SrCrO_4$ behave aerodynamically like larger particles and will tend to deposit higher in the respiratory tract. If these particles clear the lungs prior to releasing their Cr^{6+}, Cr^{6+} delivery to the target tissue may be much less than the total mass of Cr^{6+} inhaled in particles. Second, differences in composition associated with particle size may bias the Cr^{6+} deposition distribution in the lung. Previous research suggests that the larger chromate-containing primer paint particles contain significantly more chromate than smaller particles (Novy, 2001; LaPuma et al., 2001). Novy (2001) found that below 10 µm the mass of Cr^{6+} per mass of dry paint decreased linearly with particle mass median aerodynamic diameter (MMAD) [Figure 5]. Third, differences in composition related to the Cr^{6+} bias may cause some particles to release Cr^{6+} more easily than others. Novy (2001) proposed that during atomization, small particles containing mainly resins and solvents may be stripped from larger particles, increasing the relative amount of Cr^{6+} in larger "parent" particles and decreasing it in small "daughter" particles that may not contain solid chromate. If the paint matrix in larger particles holds the chromate within, then Cr^{6+} dissociation may be limited to that from chromate dissolved in unevaporated solvents on parent particle surfaces or in partly soluble daughter particles. Consequently, "smaller" particles may quickly release what little Cr^{6+} they possess while "larger" particles, containing the bulk of the Cr^{6+}, slowly release only a small portion of their Cr^{6+}.

Cr^{6+} Dissociation

In order for Cr^{6+} to enter the lung fluid it must dissociate from inhaled paint particles prior to their clearance from the lung. Two previous studies attempted to determine whether particle residence time in lung fluid was related to dissociation (Morgan, 2000; Kauth, 2001). Both studies collected MIL-P-23377G solvent-borne epoxy overspray particles in SLF using midget impingers. Though results were inconclusive, they indicated some hindrance of Cr^{6+} dissociation from the particles.

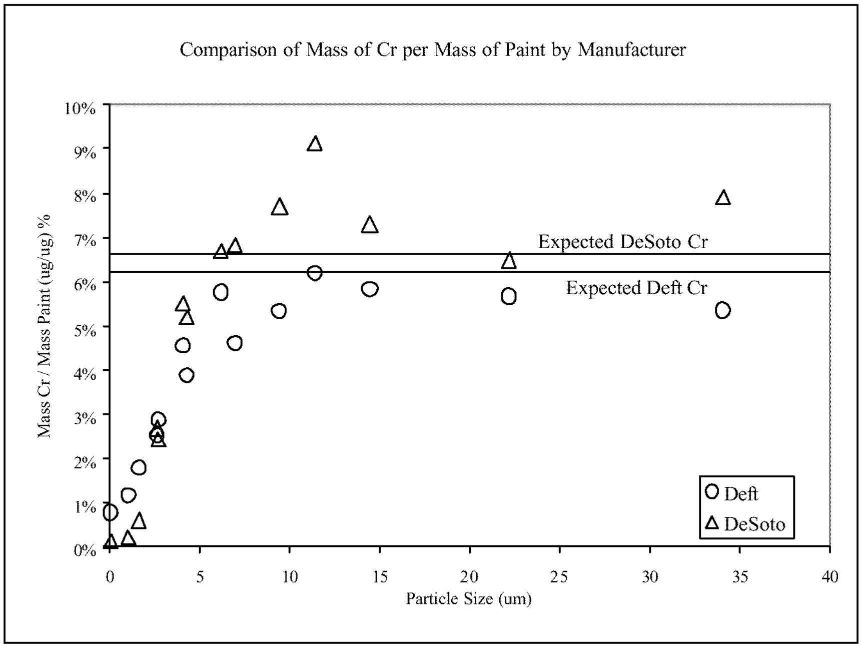


Figure 5. Comparison of Mass of Cr per Mass of Dry Paint (Novy, 2001:23)

Influencing Sample Particle Sizes

Understanding any particle size-dependent differences in Cr^{6+} dissociation behavior may lead to a more accurate evaluation of Cr^{6+} bioavailability from inhaled primer paint particles, and provide insight into the dissociation mechanisms. Previous data concerning Cr^{6+} dissociation from solvent-borne epoxy particles is limited to collections of only small particle sizes (< 5 μm). Kauth (2001) collected particles using a 1.2 L/min impinger flow rate and then characterized the collected particle size distributions using a liquid particle counter. Nearly all the particles collected were in the 1 μm to 3.5 μm bins ($d_p < 5$ μm). The author suggests that larger particles, containing significantly more $SrCrO_4$, release a much smaller proportion of their Cr^{6+}. It was noted that samples with only small particles released the same mass of Cr^{6+} as those with both large and small particles. Thus, there is indication that smaller paint particles release Cr^{6+} more easily than larger paint particles.

In order to understand the relative contributions of different particle sizes to dissociated Cr^{6+}, collections must, at a minimum, include a variety of distributions containing significant numbers of particles across the size range of interest. Since paint overspray contains a high concentration of very small particles, the challenge is to collect as many of the larger (> 5 µm) particles as feasible. Larger particle collection may be achievable by decreasing booth flow and increasing impinger flow rates. Also, varying impinger flow rates should provide some variety of particle size distributions with higher flow rates collecting more large particles.

Research Focus

This research focuses on better understanding Cr^{6+} dissociation from chromate-containing primer paint overspray particles into fluid as dependent on particle size, time, and matrix composition. First, solvent-borne epoxy overspray is collected. The amount of Cr^{6+} that dissociates from collected particles into fluid after 1 and 24 hours of residence time in the fluid is measured to assess how quickly Cr^{6+} dissociates from overspray particles and whether or not residence time is relevant. Second, the water-borne epoxy and solvent-borne polyurethane primers are analyzed similarly to compare Cr^{6+} dissociation behavior for all three paints. Primer overspray collection is designed so as to capture a broader range of particle sizes than in previous related research. This may provide added information about the relative contributions from particles of different sizes to the observed fraction of Cr^{6+} that dissolves into water from paint particles.

III. Methodology

Overview

This chapter provides a description of the methods and equipment used for sample collection, handling, and analysis. The experiment is designed to emulate respirable paint particles inhaled into serous lung fluid so that the fraction of Cr^{6+} dissolving from the particles into the fluid may be determined. This experiment makes the conservative assumption that particles are inhaled, immediately immersed in the watery serous lung fluid layer, and remain there for at least 24 hours. Deposited particles generally float atop the lung's mucous layer so that chromate must dissolve and diffuse through the mucous to the serous fluid before Cr^{6+} is available to lung epithelial cells. This experiment ignores any intervention by the mucous layer or lung clearance and Cr^{6+} reduction mechanisms, and focuses on Cr^{6+} dissociation from particles into water.

Three phases comprise the sampling and analysis plan used to obtain data in this study. First, aerosolized primer paint particles representative of those produced in field painting operations are generated using HVLP spraying equipment in a ventilated paint booth. Second, during spraying, airborne paint particles are trapped and collected in fluid for later analysis. Third, fluid collections are processed and analyzed for particle size distribution and Cr^{6+} dissociation (measured as Cr^{6+} concentration, $[Cr^{6+}]$) over time from particles into the fluid.

Painting Operation

Particle samples were generated in a climate-controlled, ventilated paint booth located at the U. S. Air Force Coatings Technology Integration Office, Wright Patterson Air Force Base, Ohio. The booth is 10' W x 14 L' x 9' H and was operated at a 100 fpm exhaust face flow rate. Booth temperature (26.0 ± 0.6°C) and humidity (6.6 ± 1.1 %) [95 % confidence] were held constant. Paint particles were generated using a DeVilbiss spray gun (product number JGHV-531), fitted with a 46MP air cap. This equipment setup is typical for aircraft painting operations. A "low" and "high" nozzle pressure setting was used for each primer (Table 4) to alter the particle size distribution generated. Prior to each collection, the paint gun nozzle pressure was calibrated using a 46MP test cap and pressure gauge. The same HVLP gun air and paint flow settings were used throughout the study to achieve the spray coarseness and uniformity desired for typical aircraft painting operations.

Table 4. Spray Gun Nozzle Pressure Settings

Primer	Low Pressure (psi)	High Pressure (psi)
Solvent-borne Epoxy	2.5	8.0
Water-borne Epoxy	7.0	10.0
Solvent-borne Polyurethane	4.0	8.0

All paints were mixed and tested for viscosity per the manufacturer's specifications. Selected information for the primers used in this experiment is summarized in Table 5. A type I primer uses standard (i.e. not low-infrared) pigments and Class C or C2 indicate that $SrCrO_4$ is added to the paint. Approximately 0.6 to 1.0 liter (L) of paint was mixed for each session using the component ratios given in Table 2. Paint collection times ranged from 8 to 30 minutes.

Spraying from the HVLP spray gun against a cardboard target generated continuous primer paint overspray. The gun was held in a fixed position 41" above the floor and its trigger was fully depressed with a cable-tie during painting. Nozzle-to-target distance was fixed at 7” (manufacturer and service technical instructions specify 6” to 8”). In order to slow airflow in the vicinity of the samplers and increase the concentration of paint particles, a cardboard baffle (27” W X 25” H X 28.5” D) was placed around the sampling equipment (Figures 6 & 7). The gun sprayed in a direction level to the floor and parallel to the box face. The target was placed at approximately a 20° angle to the center of the spray, allowing the largest particles to impact the target and smaller particles to become entrained in the local airflow as overspray.

Table 5. Paint Data Summary (Deft® Product Information Data Sheets)

	Solvent-borne Epoxy	Water-borne Epoxy	Solvent-borne Polyurethane
Specification	MIL-P-23377G	MIL-P-85582B	TT-P-2760A
Type	I	I	I
Class	C	C2	C
Deft Product Code	02-Y-40	44-GN-72	09-Y-2
Batch #’s (Base/Catalyst)	46517/46518	45699/45700	45526/45527
Viscosity spec.* (sec)	21	20	14-24
Induction Time (min)	30	None specified	None specified

*Using a #4 Ford Cup

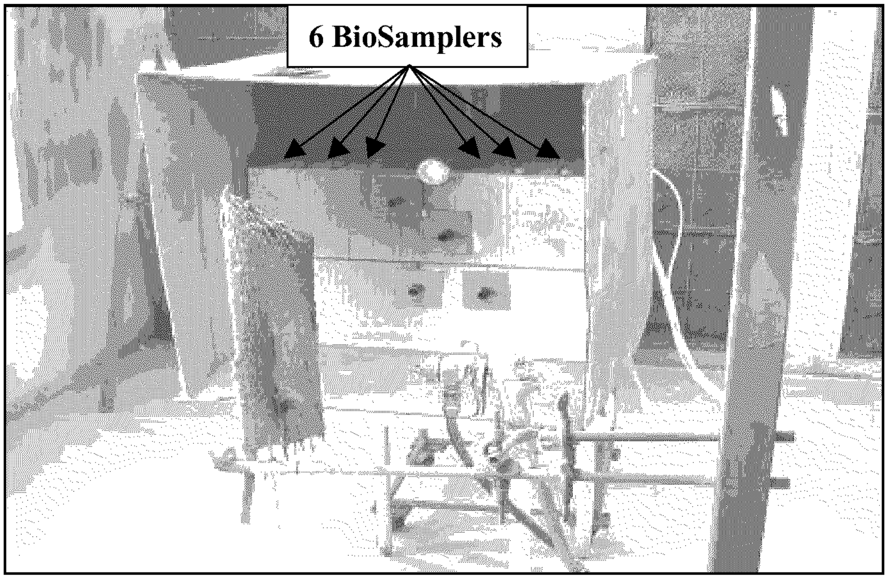


Figure 6. Paint Booth Setup and Sample Collection Apparatus

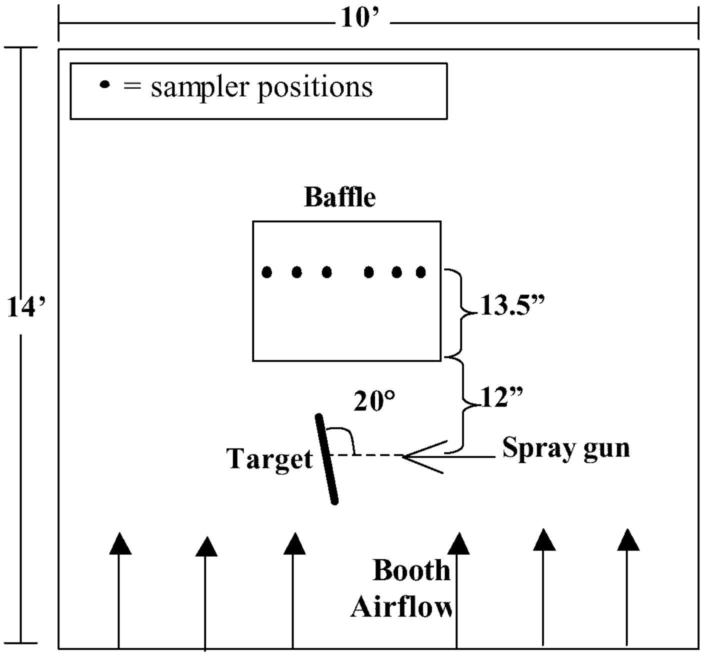


Figure 7. Paint Booth Setup Diagram (top down view)

BioSampler®

Samples were collected using six BioSampler® glass impingers manufactured by SKC Incorporated (Figure 8). Designed for collection of bio-aerosols, this device was chosen over the midget impinger due to its high collection efficiency and ability to collect particles at high flow rates. The BioSampler® uses tangential nozzles to swirl the collection fluid and continuously deposit particles to the surface of the swirling fluid. This means of capturing particles more closely resembles deposition in the lung and eliminates the bubbling of sample air through the fluid that is required by the midget impinger. In order to prevent excessive bubbling, and the resulting loss of particles, the standard midget impinger is limited to low flow rates that tend to collect very small particles (Kauth, 2001). The BioSampler® allows the use of higher flow rates while minimizing particle bounce and re-aerosolization. The ability to use higher flow rates was important in this experiment due to the desire to increase collection of larger overspray particles.

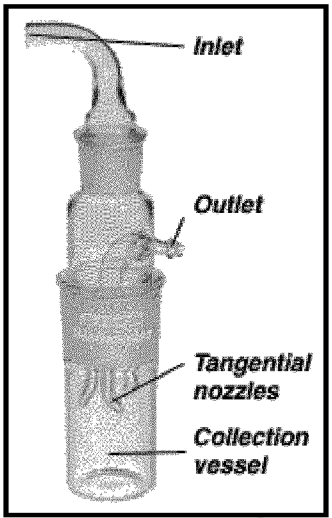


Figure 8. SKC BioSampler® (SKC, 2001)

Sampling Plan

Solvent-borne epoxy, water-borne epoxy, and polyurethane overspray samples were collected separately. A total of 117 samples were collected and Table 6 shows the sample allocation by primer type and flow rate. Six BioSamplers collected overspray samples at three different flow rates. Sampler inlet nozzle airflow rates of 2, 5, and 10 L/min enabled collection of a variety of particle size distributions. Higher flow rates increased the capture zone at the sampler inlet and enabled the collection of larger, higher inertia, particles. Samplers were arranged within the baffle as shown in Figure 9. The 1.2 L/min flow rate for positions 1 and 6 was only used to collect five samples in Teflon® midget impingers for comparison to previous studies. Gilian® GilAir 5 air pumps were connected to each 2 (or 1.2) L/min, and 5 L/min sampler, and airflow from an SKC Air Sampler sonic flow pump (Cat. No. 228-9605) was split to operate each 10 L/min sampler. All samplers were calibrated before and after each collection using a Gilibrator Airflow Calibration System #800285/286.

Table 6. Allocation of Samples by Primer Type and Flow Rate

Primer Type	Sampler Flow Rate		
	2 L/min	5 L/min	10 L/min
Solvent-borne epoxy (in DI only)	13	13	13
Water-borne epoxy	16	16	16
Solvent-borne polyurethane	10	10	10

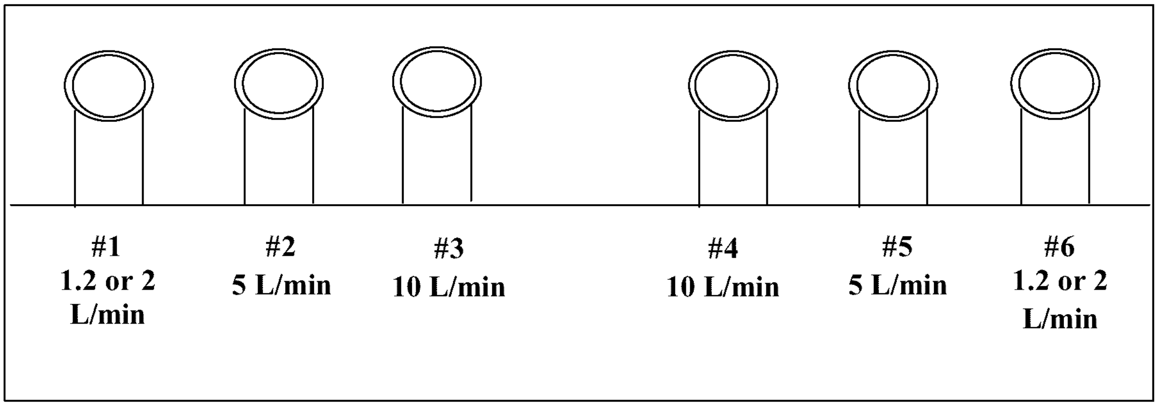


Figure 9. Sampler Layout (front view)

To better understand the relationship of particle size to Cr^{6+} bioavailability, this study attempted to collect samples with a variety of particle size distributions by varying flow rate. Ideally, the collection data set should consist of samples containing only single particle diameters covering the range of interest. Since no feasible method of isolating overspray particles of single diameters into fluid currently exists, a more realistic depiction of a desirable set of collected distributions is shown in Figure 10. Given the high concentration of very small particles in overspray, the practical limits of impinger flow rates prevent collection of the larger particle distributions in Figure 10.

Nevertheless, increasing flow rate enabled a rightward shift in collected particle size distributions as flow rate increased, providing some contrast between distributions.

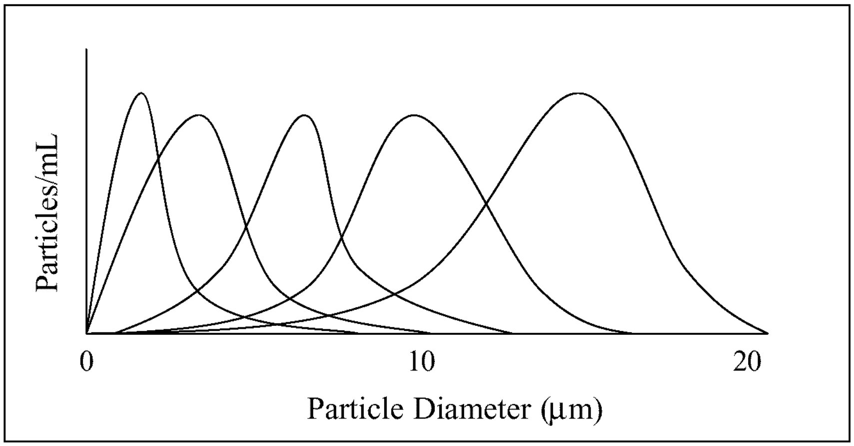


Figure 10. Desirable Set of Particle Size Distributions for Relating Cr^{6+} Dissociation to Particle Size

Background Sampling

Four booth air background collections were conducted to identify and quantify particle and Cr^{6+} background resulting from the paint booth air, collection equipment, and methodology. Background samples were collected: prior to the first paint collection, between the solvent-borne and water-borne epoxy collections, between the water-borne epoxy and polyurethane collections, and after all sampling was complete. These collections provided an estimate of the background contributed by the paint booth air, sample collection vessels, and laboratory handling and equipment. Laboratory air backgrounds were collected prior to the first and after the last booth background measurements. The lab backgrounds sampled presumably "clean" air in order to isolate equipment and process background from that due to the booth air. Procedures for background collection and analysis were identical to those for paint particle samples.

Liquid Particle Counter

The size distribution of particles collected in each de-ionized water (DI) sampler was determined using a Particle Measuring Systems, Inc. Automatic Parenteral Sampling System model 200 (APSS-200) volumetric liquid particle counter (LPC). This device is configured with a Liquilaz® S05 volumetric spectrometer. The Liquilaz® counts particles and measures their diameters by passing sample fluid through a laser beam and sensing and comparing the scattered light to diameter-dependent characteristic scattering. System software allows display of particle counts over this range in a maximum of 15 particle size bins as defined by the user. Particles counted in each bin are equal to or larger than the designated bin threshold diameter and smaller than the next larger bin threshold diameter. The result is a discrete particle size distribution over the user-defined range. The Liquilaz® S05 is capable of measuring diameters between 0.5 µm and 20 µm but counts particles with diameters up to 125 µm. All particles larger than the largest defined bin diameter (20 µm in this study) are counted as being in the largest bin.

Sample particle size analyses using the LPC were performed on 10 mL particle samples (Table 7) diluted with an additional 10 mL of pure DI. The particle counter automatically drew three 5 mL replicates from the center of each sample. Replicate particle number concentrations (counts/mL) for each bin were averaged, adjusted for dilution, and background counts/mL subtracted. Background distributions corrected for particles present due to the DI water, sample collection vessels, and paint booth air without overspray.

Residence Time Analysis

A residence time analysis was designed to determine the fraction of Cr^{6+} from each particle sample hypothetically available to human lung tissue at 1 and 24 hours. Figure 11 depicts the procedural concept used to determine the fraction of Cr^{6+} dissolved from paint particles into the collection fluid after particles are allowed to reside in the fluid for 1 or 24 hours. Samples were broken into three representative sub-samples. To determine the concentration of total Cr^{6+} collected ($[Cr]_P$), an untreated sub-sample with particles was digested and analyzed using atomic absorption spectroscopy. After 1 and 24 hours, respectively, the other sub-samples were centrifuged to separate the paint particles from the sample fluid, and the fluid analyzed to determine $[Cr^{6+}]$ resulting from Cr^{6+} dissociation from the particles ($[Cr]_{NP1}$ and $[Cr]_{NP24}$). Figure 11 shows the three sub-samples originating from the particle- and Cr^{6+}-laden sample fluid. 1- and 24-hour sub-samples are shown after centrifugal separation with paint particles deposited at the bottom of the centrifuge tube. Dashed lines highlight the supernatant portion of the sample, containing only dissolved Cr^{6+} ions, which was extracted for Cr^{6+} concentration analysis.

Quantifying Cr^{6+} Dissociation

This section explains the convention used to make quantitative comparisons between samples regarding Cr^{6+} dissociation. The size distribution and total amount of paint particles collected, and thus total $[Cr^{6+}]$, varies between samples. The $[Cr^{6+}]$ after particles were eliminated also varies depending on the total $[Cr^{6+}]$ collected and the Cr^{6+} dissociation behavior. Since comparison of dissociation behavior is central to this study,

[Cr^{6+}] after particle elimination is divided by the total [Cr^{6+}] with particles and converted to a % as shown in equation 3.

$$f_t = \frac{[Cr]_{NP}}{[Cr]_P} \times 100\% \tag{3}$$

where: f_t = the fraction (%) of Cr^{6+} dissociated at residence time t
$[Cr]_P$ = the total sample Cr^{6+} concentration including collected particles
$[Cr]_{NP}$ = sample supernatant (no-particle) Cr^{6+} concentration at residence time t (hours)

Henceforth, f_1 and f_{24} are used when referring to the 1- and 24-hour % of Cr^{6+} dissociated in a sample or set of samples, and f_t is used when referring to both f_1 and f_{24}.

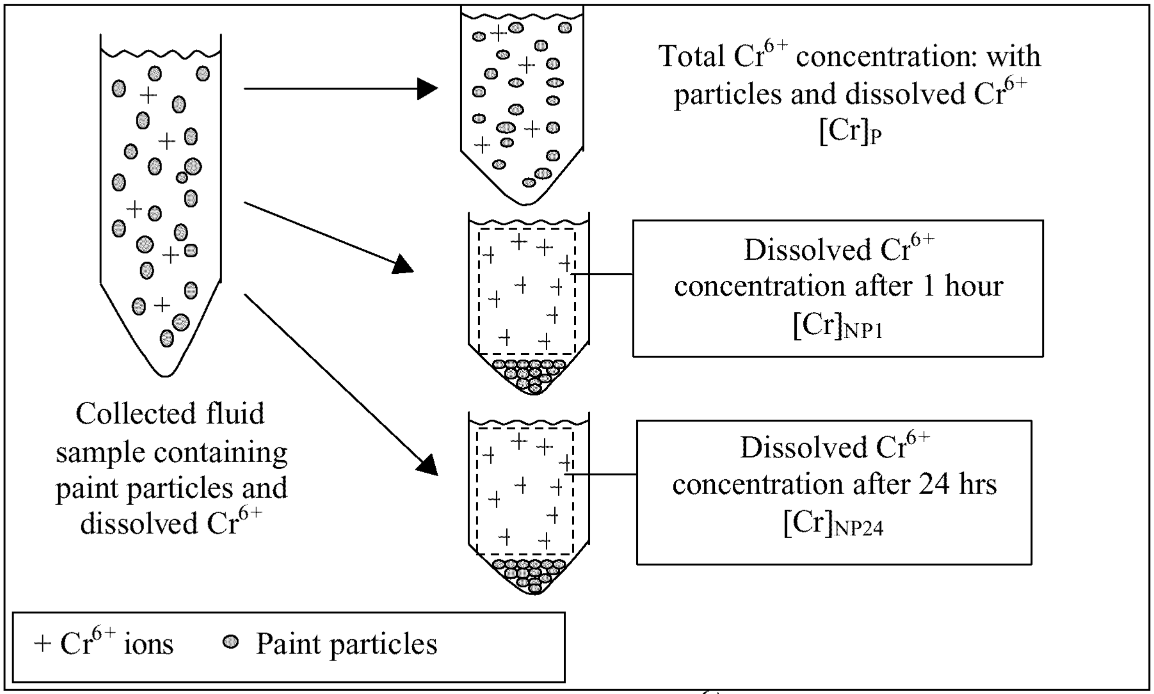


Figure 11. Procedural Concept for Determining Cr^{6+} Dissociation from Paint Particles (adapted from Kauth, 2001)

Sample Preservation and Preparation

Table 7 shows the total volume of collection fluid added to each sampler prior to sampling and the sub-sample volumes as divided in the laboratory after sampling. Total collection fluid volume varied according to sampler flow rate. These volumes were selected to enable the collection fluid to swirl while minimizing sample wall losses and fluid aspiration to the pumps.

Table 7. Sample Volume Scheduling

Sample or Sub-sample	**Sampler Flow Rate**		
	2 L/min	**5 L/min**	**10 L/min**
Total collection fluid	30 mL	25 mL	20 mL
Total Cr^{6+} sample ($[Cr]_P$)	3 mL	2 mL	2 mL
1-hr sample ($[Cr]_{NP1}$)	7 mL	4-5 mL	3 mL
24-hr sample ($[Cr]_{NP24}$)	7 mL	4-5 mL	3 mL
Particle sample	10 mL	10 mL	10 mL

After each collection, samples were transferred into wide-mouth Nalgene® polypropylene containers and capped for transport to the laboratory. At the laboratory, samples were divided for analyses. 10 mL of each sample was pipetted into a glass Pyrex® beaker for particle size distribution analysis on the LPC. In order to determine the total [Cr^{6+}] collected in each sampler, 2 to 3 mL of the remaining sample was pipetted into a Teflon®-lined microwave digestion vessel and an equal volume of 70% HNO_3 was added. Equal amounts of the remaining sample were then pipetted into two polypropylene centrifuge tubes. The paint particles in one centrifuge tube were allowed to remain in the DI water for 1 hour and in the other tube for 24 hours at 37° C. This simulated 1 and 24 hours of paint particle contact with serous lung fluid. Both samples were centrifuged after 1 or 24 hours for a minimum of 30 minutes at 4000 RPM and 37° C in order to separate the paint particles from the DI water. 2 to 3 mL of supernatant was then extracted and prepared for digestion in a similar manner to the total [Cr^{6+}] sample.

It is assumed that the supernatant [Cr^{6+}] represents only the amount of Cr^{6+} dissolved from the particles after 1 or 24 hours.

Sample Digestion

Complete decomposition of collected paint particles ensures the availability of collected Cr^{6+} for spectroscopic analysis. Microwave acid digestion was used to digest all samples. This study used an OI Analytical microwave and employed a digestion method modified from EPA (3050A) and NIOSH (7300 and 7800) methods for paint chip digestion. Each digestion vessel was sealed and placed in the OI Analytical microwave carousel. Samples were then digested using a three to five minute temperature rise to 150°C followed by 20 minutes at 150°C. Digestion pressures ranged between 20 and 50 psig. Vessels were allowed to cool to ambient conditions and each sample was poured into a 30 mL Nalgene® High Density Polyethylene (HDPE) storage bottle. A volume of DI water equal to the sample plus HNO_3 volume was added to reduce HNO_3 concentration for analysis.

Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) was used to analyze the [Cr^{6+}] in each sample's total collection (with particles) and the 1- and 24-hour residence time samples (without particles). AAS sample atomization is accomplished with either a flame or electrothermal (graphite furnace) heat source. Electrothermal AAS (EAAS) is the more sensitive, though less precise, method and requires much less sample volume. EAAS is also more effective in releasing refractory metals from their matrices and is considered appropriate for samples containing less than 1 mg/L of analyte (Willard et al., 1988). EAAS analyses were performed on a GBC Avanta Atomic Absorption Spectrometer

(AAS) configured with a PAL 3000 autosampler, graphite furnace, and deuterium background correction lamp. Selected AAS settings are summarized in Table 8. Samples with concentrations less than or equal to 4 mg/L were diluted into the EAAS calibration range and EAAS analysis performed.

EAAS calibrations were performed using a 75 µg/L Cr^{6+} in 2% HNO_3 standard from High Purity Standards. A five-point calibration (7.5, 20, 40, 60, 75 µg/L) using a concentration least-squares curve was conducted before and after every 12 samples. A minimum R^2 of .98 was required for acceptance. EAAS samples were prepared in 1 mL polyethylene cuvettes by pipetting and weighing 900 µL of DI and 100 µL of sample for a 0.1 dilution factor. This dilution lowered sample Cr^{6+} concentrations into the calibration range and reduced the HNO_3 concentration to 2-3%, making the sample matrix similar to the 75 µg/L standard. After every 6 samples, a 75 µg/L check sample and DI blank were analyzed as quality control measures.

Table 8. Summary of AAS Parameters

System Type	Furnace
Element	Cr
Matrix	2% HNO_3
Lamp Current	6.0 mA
Wavelength	357.9 nm
Slit Width	0.2 mm
Slit Height	Reduced (furnace) Normal (flame)
Instrument Mode	Absorbance Background Correction Selection
Measurement Mode	Peak Area

The AAS was programmed for a five-step EAAS graphite furnace program (Table 9). After a sample is auto-injected into the graphite furnace tube, the drying step (Step

1), heats the sample to remove all water. The drying is accomplished slowly to avoid splattering and possible loss of sample. Argon gas flows through the tube to remove evaporated vapors. Steps 2 and 3 perform sample charring and pyrolysis. These steps destroy the organic matrix components at a temperature low enough to avoid liberating the Cr. Step 4 atomizes Cr and an absorbance measurement is taken. The last step (5) cleans any residual substances from the furnace tube by raising the temperature again and forcing gas through it, preparing it for the next sample.

Re-analysis by flame AAS was conducted for all samples with Cr^{6+} concentrations greater than 4 mg/L. Flame analyses were performed on the same AAS configured with an air-acetylene burner and FS 3000 autosampler. Calibration standards were made from a 1000 mg/L Cr^{6+} standard from High Purity Standards by diluting with DI water containing 7% HNO_3. A four-point calibration curve (1, 5, 10, 15 mg/L) was used for the flame method. Calibration R^2 acceptance criteria, check sample (5 mg/L) frequency, and DI blank frequency were the same as for the graphite furnace method.

Table 9. Atomic Absorption Graphite Furnace Program

Step	Final Temp (°C)	Ramp Time (s)	Hold Time (s)	Gas	Read Signal
1: Drying	80	5.0	10.0	Argon	Off
2: Charring	130	30.0	10.0	Argon	Off
3: Pyrolysis	1400	15.0	15.0	Argon	Off
4: Atomization	2500	1.4	1.6	None	On
5: Clean	2700	0.5	1.5	Argon	Off

Comparing SLF to Pure De-ionized Water (DI)

Though DI does not imitate lung fluid as well as SLF, the ability to count particles in each sample was necessary for examining the role of particle size in Cr^{6+}

bioavailability. In earlier primer paint Cr^{6+} bioavailability research, SLF particle samples could not be reliably analyzed with a liquid particle counter. Instead, these studies assumed that a particle size distribution collected in a surrogate sample of DI represented the SLF particle size distribution (Kauth, 2001). This method introduces inaccuracies that limit the ability to relate a sample's particle size distribution to its Cr^{6+} dissociation. Therefore, the objectives of this study required collection of all samples in DI.

DI and SLF were tested side-by-side to verify that no significant difference exists between the fluids with regard to Cr^{6+} dissociation from paint particles. Solvent-borne epoxy primer particles were collected in DI and SLF and analyzed for Cr^{6+} dissociation. A modified version of Gamble's 1952 SLF formula (Table 10) reported by Fisher and Briant (1994) was mixed in a 1.0 L batch for use in SLF samplers. Paired t-tests were used to compare mean f_1 and f_{24} for each SLF sample to a mean f_1 and f_{24} for a corresponding DI sample collected simultaneously and at the same flow rate.

Table 10. Simulated Lung Fluid Ingredients

Description	Molecular Formula	Concentration (mg/L)
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	101
Sodium chloride	$NaCl$	6019
Potassium chloride	KCl	298
Sodium phosphate	$Na_2HPO_4 \cdot 7H_2O$	268
Sodium sulfate	Na_2SO_4	71
Calcium chloride	$CaCl_2 \cdot 2H_2O$	184
Sodium acetate	$NaH_3C_2O_2 \cdot 3H_2O$	952
Sodium bicarbonate	$NaHCO_3$	97
Sodium citrate	$Na_3H_5C_6O_7 \cdot 2H_2O$	97

Table 11 summarizes the test results. Samples are compared by flow rate since each flow rate may collect a characteristic particle size distribution that could influence the amount of Cr^{6+} that dissociates from the primer particles. All statistical comparisons indicate no statistically significant difference between SLF and DI values of f_1 and f_{24}. Substituting pure DI for SLF as the collection fluid does not appear to significantly alter Cr^{6+} dissociated from solvent-borne epoxy primer overspray particles.

Table 11. SLF vs. DI Paired t-test Comparison [Solvent-Borne Epoxy Tests]

Residence Time (hours)	Sampler Air Flow Rate (L/min)	n	% of Cr^{6+} Dissociated (f_t) SLF#	% of Cr^{6+} Dissociated (f_t) DI#	Mean (paired) |Difference|	t statistic	$t_{critical}$ (2-tail)*	P-value (2-tail)	Statistically Significant Difference?
1	2	3	81 ± 42%	86 ± 44%	5%	0.524	9.925	0.652	NO
	5	4	79 ± 30%	74 ± 33%	6%	0.543	5.841	0.625	NO
	10	4	59 ± 20%	69 ± 18%	10%	1.31	5.841	0.280	NO
Aggregate Mean		11	73 ± 12%	75 ± 11%	3%	0.415	3.169	0.687	NO
24	2	4	84 ± 31%	97 ± 9%	14%	1.19	5.841	0.319	NO
	5	4	88 ± 29%	71 ± 31%	16%	2.45	4.604	0.071	NO
	10	4	76 ± 27%	88 ± 24%	12%	4.00	5.841	0.028	NO
Aggregate Mean		12	83 ± 12%	84 ± 12%	2%	0.27	3.055	0.793	NO

* Significance level .01
# Shown with 95% confidence intervals (based on a t-distribution)

Limits of Detection and Quantitation

The typical method 3σ limits of detection (LOD), 10σ limits of quantitation (LOQ) [at 95% confidence], and sensitivities observed for both furnace and flame AAS sample analyses in this study are summarized in Table 12. LOD and LOQ represent the mean background concentration, as determined by sample blanks, plus 3σ and 10σ, respectively. Method sensitivity is defined for AAS as the concentration in μg/mL of analyte that produces an absorbance of 0.0043 absorbance units (1.0% absorbance) [Willard, et al., 1988]. Sensitivity is shown here in μg/L for consistency within the table.

Table 12. AAS Method Limits of Detection and Quantitation

Method	3σ LOD (μg/L)	10σ LOQ (μg/L)	Sensitivity (μg/L)
Furnace	3.7 ± 0.4	7.3 ± 0.7	0.301 ± .003
Flame	38 ± 15	74 ± 31	65 ± 6

Quality Control

BioSamplers were cleaned between paint particle collections to prevent buildup of paint deposits and minimize Cr^{6+} contamination from the glass samplers. The BioSampler® inlet nozzles and collection vessels were cleaned with solvents after each sample collection and then thoroughly rinsed with DI. Collection vessels were also rinsed daily using a 1:1 HNO_3 solution followed by a DI triple rinse. Tangential nozzle stages were soaked overnight in MEK following the initial solvent cleaning, and prior to sampling they were thoroughly rinsed with DI and dried.

Despite cleaning procedures, a Cr^{6+} background, was detected throughout this study and only isolated following the final lab background collection. The tangential nozzle stages appeared to be the source of contamination, either from sample air passing over paint residue in the nozzles or Cr^{6+} leaching from the outside of the nozzles into collection fluid. Cr^{6+} Background from this source should have been reasonably consistent between sub-samples with particles ($[Cr]_P$) and those without ($[Cr]_{NP}$) since they originate from the same sample. Subtracting background decreases both $[Cr]_P$ and $[Cr]_{NP}$ by the same amount, but the change in $\frac{[Cr]_{NP}}{[Cr]_P}$ depends on the % change of each concentration. The larger the correction relative to either concentration, the more f_t decreases. For example, if the uncorrected $[Cr]_P$ and $[Cr]_{NP1}$ are 3,000 µg/L and 2000 µg/L, respectively, then $f_t = 67\%$. If both concentrations are corrected for a 200 µg/L background, then $f_t = 64\%$, showing that the uncorrected f_t is a small overestimation. However, if the background is 1000 µg/L, then $f_t = 50\%$, a much more significant change. Background was quantified and corrected for in this study's Cr^{6+} concentration data. Correction factors specific to each sampler ranged from 200 µg/L to 700 µg/L. Still, unknown day-to-day inconsistencies in actual background concentration may not be represented by background correction factors. Therefore, over- or under-correcting for background possibly added variability to the data in the form of small under- or over-estimations of f_t.

IV. Results

Primer Particle Cr^{6+} Dissociation Results

Two general goals of this research were: to quantify the Cr^{6+} dissociation from primer particles into DI at residence times of 1 and 24 hours in order to relate dissociation to residence time and particle size, and to compare the behavior of three different types of primers. Table 13 summarizes the results for all three paints with 95% confidence intervals. The mean fraction of Cr^{6+} dissociated at the indicated residence time t, (f_t), is shown for each flow rate and paint type, followed by an aggregate f_t for each paint over all flow rates. Tabular and graphic summaries of the background corrected concentrations of Cr^{6+} collected ($[Cr]_P$), 1- and 24-hour sample concentrations, and the associated f_t for all three primers are contained in Appendices A, B, and C.

Table 13. Paint Particle Cr^{6+} Dissociation Summary

Paint Type

		Solvent-borne Epoxy (MIL-P-23377G)$^{\#}$		Water-borne Epoxy (MIL-P-85582B)		Polyurethane (TT-P-2760A)	
Residence Time (hours)	**Sampler Air Flow Rate (L/min)**	**n**	**Mean % of Cr^{6+} Dissociated* (f_t)**	**n**	**Mean % of Cr^{6+} Dissociated* (f_t)**	**n**	**Mean % of Cr^{6+} Dissociated* (f_t)**
1	1.2	5	76 ± 23%				
	2	10	79 ± 15%	16	76 ± 7%	10	95 ± 4%
	5	16	68 ± 10%	15	79 ± 8%	10	98 ± 2%
	10	16	63 ± 7%	15	66 ± 7%	10	91 ± 7%
	Aggregate	47	70 ± 5%	46	74 ± 4%	30	94 ± 3%
24	1.2	5	90 ± 10%				
	2	11	91 ± 8%	16	82 ± 7%	10	96 ± 3%
	5	16	81 ± 10%	15	90 ± 4%	10	98 ± 2%
	10	16	82 ± 7%	15	80 ± 7%	10	92 ± 4%
	Aggregate	48	85 ± 5%	46	84 ± 4%	30	95 ± 2%

* Shown with 95% confidence intervals (based on a t-distribution)

$^{\#}$ Includes both DI and SLF samples

In general, the solvent-borne epoxy exhibited substantial Cr^{6+} dissociation at both 1 and 24 hours. The aggregate mean f_1 was 70 ± 5% and f_{24} was 85 ± 5% suggesting that particles release the majority of their Cr^{6+} in the first hour and then release Cr^{6+} more slowly over the next 23 hours. On average, the water-borne epoxy dissociated only slightly more Cr^{6+} by 1 hour (f_1 = 74 ± 4%) than the solvent-borne epoxy and essentially the same amount by 24 hours (f_{24} = 84 ± 4%). On the other hand, data indicate that the polyurethane primer consistently released almost all of its Cr^{6+} by 1 hour (f_1 = 94 ± 3% and f_{24} = 95 ± 2%). This primer demonstrated strong hydrophobic characteristics, which caused a portion of the paint particles to separate from the DI water and visibly "cling" to the sides of the collection vessel producing a paint film. Collection vessel wall losses could exaggerate Cr^{6+} dissociation estimates. If primer on the vessel wall leached Cr^{6+} into the fluid but retained Cr^{6+} that was not accounted for in the total $[Cr^{6+}]$ with particles estimate, $[Cr]_P$, then f_t for the polyurethane would be an overestimation of the dissociation from particles residing in the fluid.

Primer Volatiles Testing

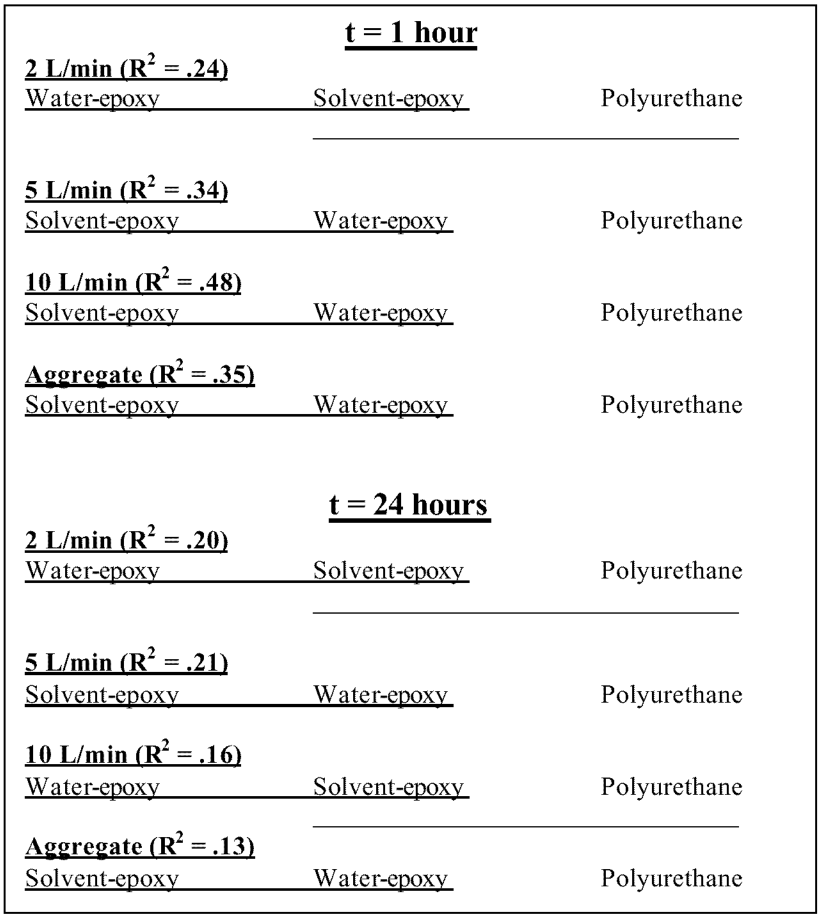
It was theorized that Cr^{6+} dissociation into fluid from primer overspray particles might be limited to that from unevaporated solvents (volatiles) containing dissolved chromate. Based on this hypothesis, a significant increase in the water-borne f_t was expected due to an increase in: the solubility of $SrCrO_4$ in the water-borne primer's volatile fraction (which includes water), the solubility of the mainly-water volatiles in lung fluid, or the fraction of volatiles in the paint mixture. As discussed earlier, solvent-borne primer volatiles consist of solvents while water-borne primer volatiles include both water and solvents. The water-borne epoxy volatiles represent 74 % of that primer by volume and water makes up 77% (by volume) of the volatiles. By contrast, both solvent-borne primers contain only 41% volatiles by volume.

Quantitative tests were conducted to assess the [Cr^{6+}] in each primer's volatile fraction after paint mixing and equilibration. Three 10 mL samples of each paint were centrifuged for 20 minutes at 4000 RPM in order to separate the less dense volatiles in each paint. A sample of the solvent- or solvent-and-water-comprised supernatant was then extracted, microwave-digested using HNO_3, and analyzed using furnace and flame AAS. The solvent-borne epoxy volatiles had a mean [Cr^{6+}] of 586 ± 181 μg/L (n = 3) and the water-borne epoxy volatiles a mean of 374,000 ± 90,000 μg/L (n = 3) [95% confidence], a more than 600 fold increase in dissolved Cr^{6+}. Based on the $SrCrO_4$ solubilities given in Chapter 2 (45,000 μg/L in MEK and 1,200,000 μg/L in water) neither primer volatile sample was near $SrCrO_4$ saturation. Further calculations show that the observed [Cr^{6+}] in the solvent- and water-borne volatiles represents only .0009% and 1.3% of the total mass of Cr^{6+} per volume of paint, respectively. This means that most of the $SrCrO_4$ in the mixed paint is in solid particle form and a very small fraction is dissolved in the volatiles when the primer is sprayed.

The polyurethane volatile fraction mean [Cr^{6+}] was 492,000 ± 139,000 μg/L (n = 3). This far exceeds the expected $SrCrO_4$ saturation limit but is still only 1.4% of the total Cr^{6+} mass per volume of paint. Unfortunately, the validity of this primer's samples is questionable due to difficulty separating and sampling a "pure" solvent supernatant. As a result, polyurethane volatile samples may have contained non-volatile paint constituents including un-dissolved $SrCrO_4$ pigment.

Primer Type Comparison

Quantitative comparison of mean f_t by paint type, residence time, and sampler flow rate indicates some minor differences in dissociation behavior. Using JMP 4.0, an analysis of variance (ANOVA) and a Tukey-Kramer all pairs analysis were performed. The Tukey-Kramer analysis is a simultaneous multiple comparison of the means and was performed at an overall significance level of $\alpha = .05$. Figure 12 shows the results of each comparison with underlines connecting data sets that indicate no statistically significant difference in f_t. In no case do the solvent- and water-borne epoxies show a significant difference in their mean f_t.



t = 1 hour

2 L/min (R^2 = .24)
Water-epoxy Solvent-epoxy Polyurethane

5 L/min (R^2 = .34)
Solvent-epoxy Water-epoxy Polyurethane

10 L/min (R^2 = .48)
Solvent-epoxy Water-epoxy Polyurethane

Aggregate (R^2 = .35)
Solvent-epoxy Water-epoxy Polyurethane

t = 24 hours

2 L/min (R^2 = .20)
Water-epoxy Solvent-epoxy Polyurethane

5 L/min (R^2 = .21)
Solvent-epoxy Water-epoxy Polyurethane

10 L/min (R^2 = .16)
Water-epoxy Solvent-epoxy Polyurethane

Aggregate (R^2 = .13)
Solvent-epoxy Water-epoxy Polyurethane

Figure 12. Tukey-Kramer All Pairs Analysis by Flow Rate and Residence Time

Though ANOVA and the Tukey-Kramer comparison do indicate a difference in the polyurethane f_t, high variability in the solvent- and water-borne data limits the amount of overall variance that can be attributed to the difference in primers (note the small values of R^2). Figure 13 compares the data using a box and whiskers plot of each primer's aggregate f_1 and f_{24} data. The "whiskers" at the top and bottom of each plot denote the highest and lowest values. Long horizontal lines represent the mean f_t, short lines within each box are at the median, and the lower and upper end of each box depict the 25th and 75th percentiles, respectively. Data points outside the "whiskers" represent outliers, defined as values > 1.5 times the fourth spread (i.e. 75th percentile – 25th percentile) from closest end of the box (Devore, 2000). Ultimately, the data suggest no evidence for a difference in Cr^{6+} dissociation from the solvent- and water-borne primers, but do point toward a different behavior for the polyurethane.

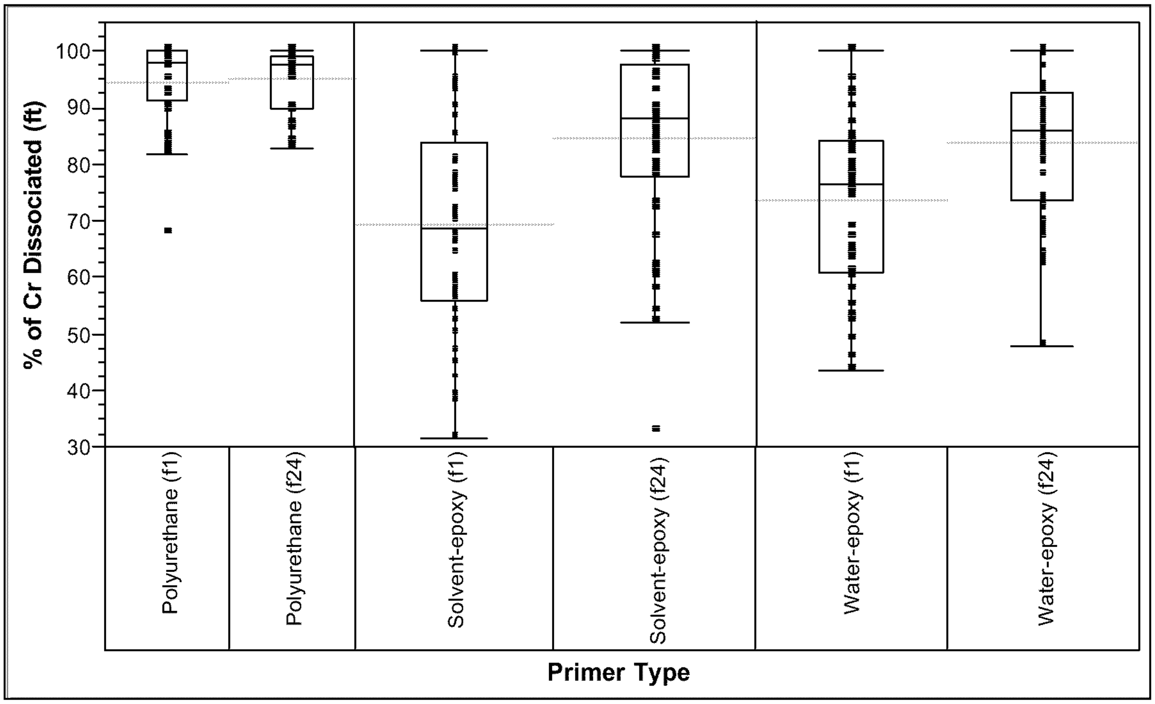


Figure 13. Box and Whiskers Comparison (f_1 & f_{24} by primer type)

Residence Time Comparison

The results indicate that the majority of Cr^{6+} dissociation takes place in the first hour after which there is generally some further dissociation through at least 24 hours. An indication of this behavior is the relatively small mean differences ($f_{24} - f_1$) for paired samples, and the associated mean percent increase in f_t (Table 14). The mean percent increase is defined here as the amount of change relative to f_1, or $[(f_{24} - f_1)/f_1] \times 100\%$. Table 14 also shows paired t-test results comparing mean f_1 and f_{24} for each paint and flow-rate combination. Despite the appearance of little change, the t-tests indicate that a statistically significant increase in the fraction of Cr^{6+} dissociated from the solvent- and water-borne epoxy primer particles does occur. The polyurethane primer's lack of significant additional dissociation after 1 hour is, at least partly, due to its near complete dissociation at 1 hour.

Table 14. Residence Time Comparison (Paired t-tests)

Primer	Sampler Air Flow Rate (L/min)	n	1-hr Mean % of Cr^{6+} Dissociated[1] (f_1)	24-hr Mean % of Cr^{6+} Dissociated[1] (f_{24})	Mean (paired) Diff. (f_{24} - f_1)	Mean % Increase	t statistic	$t_{critical}$ (right-tail)[2]	P-value (1-tail)	Statistically Significant Increase?[2]
Solvent Epoxy[3] (MIL-P-23377G)	1.2	5	76%	90%	14%	18%	2.48	2.132	0.034	YES
	2	10	79%	91%	12%	15%	2.03	1.833	0.037	YES
	5	16	68%	81%	12%	18%	3.95	1.753	0.001	YES
	10	16	63%	82%	19%	29%	5.45	1.753	< .0001	YES
	Aggregate	47	70%	84%	15%	21%	7.01	1.68	< .0001	YES
Water Epoxy (MIL-P-85582B)	2	16	76%	82%	7%	9%	3.17	1.753	0.003	YES
	5	15	79%	90%	11%	14%	3.48	1.761	0.002	YES
	10	15	66%	80%	13%	20%	7.14	1.761	< .0001	YES
	Aggregate	46	74%	84%	10%	14%	7.14	1.681	< .0001	YES
Polyurethane (TT-P-2760)	2	10	95%	96%	1%	1%	0.657	1.833	0.264	NO
	5	10	98%	98%	0%	0%	<<.0001	1.833	0.500	NO
	10	10	91%	92%	1%	2%	0.756	1.833	0.234	NO
	Aggregate	30	94%	95%	1%	1%	0.897	1.699	0.377	NO

[1] Means for *paired* samples only

[2] Significance level .05

[3] Includes both DI and SLF samples

Primer Particle Distributions

Figures 14, 15, and 16 display the background corrected particle size distributions, averaged by sampler flow rate, collected in this study. Generally, increasing sampler air flow rates produced the desired increase in the number of larger particles, as seen by the rightward shift with flow rate. All collected distributions are shown graphically in Appendices A, B, and C by paint and flow rate. The LPC counts particles per bin per mL of sample. Though these counts are in discrete bins, they are depicted as continuous distributions for ease of comparison. The midpoint d_p of each bin is used to represent the particle sizes collected. Since the LPC counts particles ≥ 20 and < 125 μm in the 20 μm bin, particles in the 20 μm bin were extrapolated out to smooth the distributions for display and later calculations. Extrapolation methods are described in Appendix D.

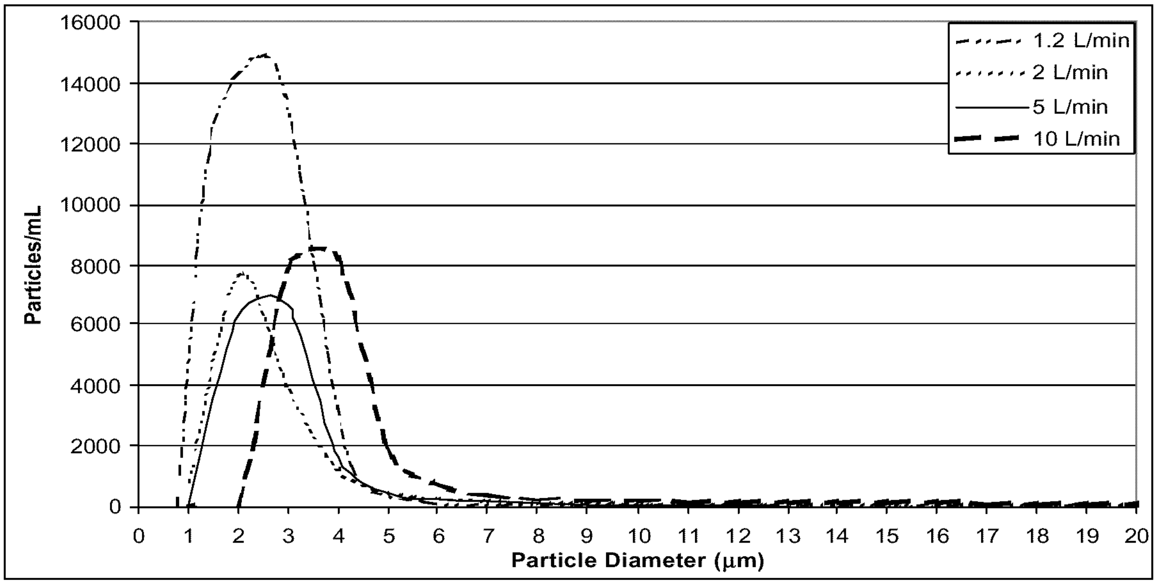


Figure 14. Solvent-borne Epoxy Average Particle Size Distributions by Flow Rate

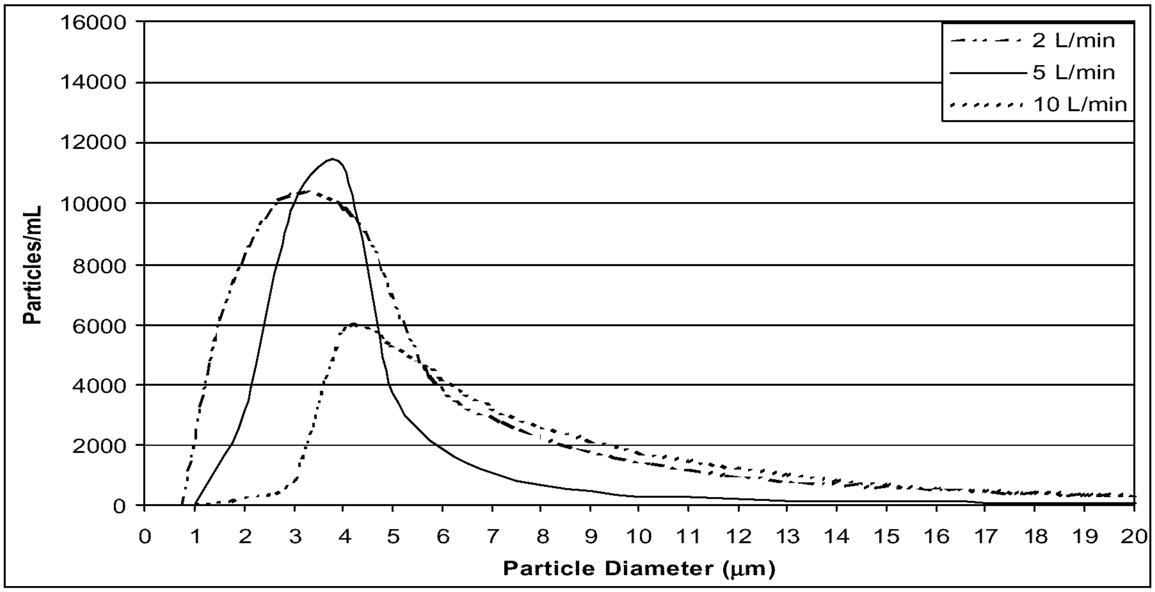


Figure 15. Water-borne Epoxy Average Particle Size Distributions by Flow Rate

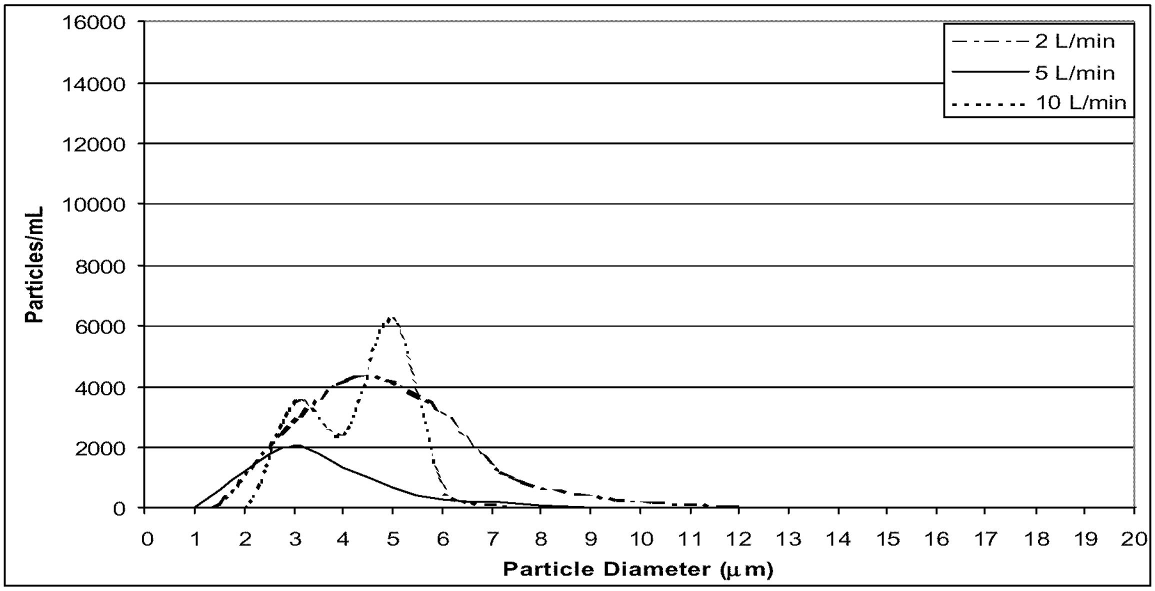


Figure 16. Polyurethane Average Particle Size Distributions by Flow Rate

In general, the 1.2 and 2 L/min samplers collected small particles very efficiently but very few particles larger than 5 µm. On the other hand, the typical 10 L/min distribution had very few particles < 2 µm and contained particles in all bins, including ≥ 20 µm. Six of the 10 L/min water-borne epoxy samples showed a notably different distribution, containing only particles larger than 3.5 μm (Appendix B-2) and significant numbers of particles in all bins up through 20 μm. These six distributions all occurred in high flow rate samples collected in the same three sampling sessions, and had similar numbers of total particles and $[Cr]_P$ to other samples, but cannot be explained. Finally, note that the polyurethane samples show a substantial decrease in the quantity of particles collected, and a distinctly different set of average distributions. The tendency of polyurethane particles to "cling" to collection vessel walls may explain why fewer particles were collected during spray times comparable in duration to those of the other paints.

Calculating Aerodynamic Diameters and the Cr^{6+} Distribution

Two conversions were necessary to interpret the collected particle distributions in terms pertinent to lung physiology and Cr^{6+} bioavailability. First, since inhaled particles distribute in the lung based on aerodynamic diameter (d_{ae}), each particle size bin (midpoint) d_p was converted to an equivalent d_{ae}. Particle density directly influences d_{ae}, such that the more particle density exceeds 1 g/cm^3 the more its d_{ae} exceeds its d_p (see Ch. 2). Due to the high density of Cr relative to the other paint constituents, Cr^{6+} (as $SrCrO_4$) is largely responsible for the difference between d_p and d_{ae} for chromate-containing primer particles. The increase in % mass of Cr^{6+} with particle size causes paint particle density (ρ_p) to increase as d_p increases (see Figure 5) [LaPuma et al., 2001; Novy, 2001; Rhodes, 2002]. Therefore, conversions of d_p to d_{ae} are unique to each d_p, and also to each paint since the Cr^{6+} bias differs between paints. The second conversion involved determining the volume of Cr^{6+} collected at each particle size by incorporating the Cr^{6+} bias into collected particle volume distributions. Conversion of each bin d_p to d_{ae}

and calculation of the % volume of Cr^{6+} in particles of each bin d_p was needed to determine the Cr^{6+} volume distribution as a function of d_{ae}.

A summary of data obtained from MSDSs and Deft® Product Information Data Sheets is given in Table 15. The calculated % mass of Cr^{6+} in the "wet" paint mixture for each primer is included with this data. Paint mixture composition data from Table 3 was used to determine the density of the non-$SrCrO_4$ fraction of each primer and the % volume of $SrCrO_4$ in the paint mixture. Table 16 shows the Cr^{6+} bias data from the Novy (2001) and Rhodes (2002) studies as a mass % (mass of Cr^{6+} to mass of dry paint) for each bin, defined by a lower-limiting effective cutoff diameter (ECD).

Table 15. Calculation Data (MSDS and Deft® Product Information Data Sheets)

Primer Type	Mixed paint density (ρ_{wet}) [g/L]	% Volume of solids (v_{solids})	Solids density (ρ_{dry}) [g/L]	Paint mixture % mass Cr^{6+}
Solvent-epoxy	1240.2	58.55%	1539.8	5.19%
Water-epoxy	1102.3	26.39%	1447.5	2.58%
Polyurethane	1173.1	59.63%	1393.6	3.03%

Note: Data represents the paint mixture as sprayed and units have been converted from English to SI

Table 16. Cr^{6+} Content Bias Data (Novy[1], 2001; Rhodes[2], 2002)

Particle Size (ECD) [μm]	Mean % Cr^{6+} (mass Cr^{6+}/mass dry paint)		
	Solvent-epoxy[1] (Deft® 02-Y-40)	Water-Epoxy[2] (Deft® 44-GN-72)	Polyurethane[2] (Deft® 09-Y-2)
0.7	0.8 %	0.67%	0.36%
1.0	1.2 %	0.72%	0.51%
1.6	1.8 %	1.15%	0.90%
2.6	2.5 %	2.89%	1.65%
2.7	2.9 %	1.89%	1.70%
4.1	4.5 %	4.95%	2.51%
4.3	3.9 %	4.97%	2.79%
6.2	5.8 %	6.50%	3.77%
7.0	4.6 %	6.56%	3.72%
9.5	5.3 %	6.67%	3.86%
11.4	6.2 %	N/A	N/A
14.5	5.8 %	6.27%	3.76%
22.2	5.7 %	5.57%	3.60%
34.1	5.3 %	6.03%	4.34%

Appendix E describes in detail the calculations necessary to determine ρ_p, d_{ae}, and the Cr^{6+} volume fraction for each d_p collected. The calculations make several key assumptions:

1) Collected paint particles are spherical
2) Cr^{6+} in the paint droplets is in the form of $SrCrO_4$
3) Collected paint particles comprise a mixture that is homogeneous with respect to all constituents except $SrCrO_4$, and is otherwise representative of the batch paint mixture
4) Dry paint contains only paint solids such that the solids density may be used to approximate the dry paint density
5) Linear interpolation of dry paint particle Cr^{6+} content data may be used to approximate the % mass of Cr^{6+} in each particle size

Figure 17 depicts the conceptual model for calculating the density ($\boldsymbol{\rho}_\mathbf{p}$) and Cr^{6+} volume fraction (v_{Cr}) of a particular size particle. Though ECD is a function of particle aerodynamic diameter, it is assumed to be a valid first approximation of d_p. Based on this assumption, each computation started by interpolating the mass fraction (%) of Cr^{6+} in a *dry* paint particle of each bin midpoint d_p (hereafter denoted as the bold $\mathbf{d_p}$) from Table 16 (Step 1). The *dry* Cr^{6+} mass fraction was then converted to the mass fraction (%) of $SrCrO_4$ in a *wet* particle of size $\mathbf{d_p}$ (Step 2) by first "returning" the volatiles to the particle and adjusting the Cr^{6+} mass fraction for the accompanying increase in particle volume. In step 3, the $SrCrO_4$ mass fraction is converted to the volume fraction (%) of $SrCrO_4$ in a *wet* particle of size $\mathbf{d_p}$. Using the volume fraction of $SrCrO_4$ and that of the other paint constituents the density specific to each $\mathbf{d_p}$, denoted as the bold $\boldsymbol{\rho}_\mathbf{p}$, was computed using the known densities of $SrCrO_4$ and non-$SrCrO_4$ constituents. Each $\boldsymbol{\rho}_\mathbf{p}$ was then used to determine a d_{ae} and Cr^{6+} volume fraction (v_{Cr}) for each $\mathbf{d_p}$. The v_{Cr} values were applied as a correction factor to the total particle volume per mL of sample collected in each bin to account for the difference in Cr^{6+} content with particle size. The result is a Cr^{6+}

volume distribution (µm^3 Cr^{6+}/mL sample) for each sample (Figures 18, 19, and 20). Computed v_{Cr} values for each bin are shown in the data summary tables of Appendices A, B, and C.

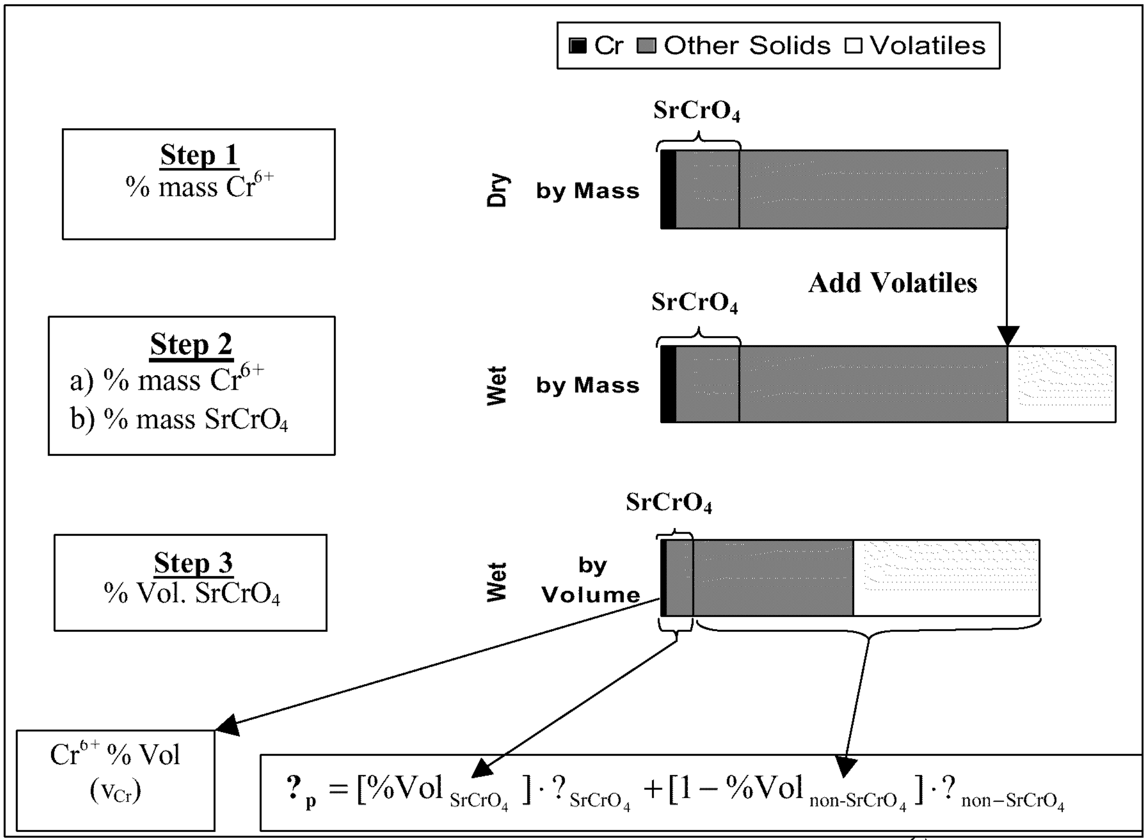


Figure 17. Determining Size-Specific Particle Density and Cr^{6+} % Volume

Cr^{6+} volume distributions demonstrate that a majority of the Cr^{6+} volume resides in particles with aerodynamic diameter larger than those that deposit in the pulmonary or tracheobronchial regions (reference Figure 3), despite collecting many more smaller particles than larger ones. More importantly, for this study, the Cr^{6+} distributions have been corrected for the bias in Cr^{6+}, which adjusts for the fact that different particle sizes contain unequal fractions of Cr^{6+}.

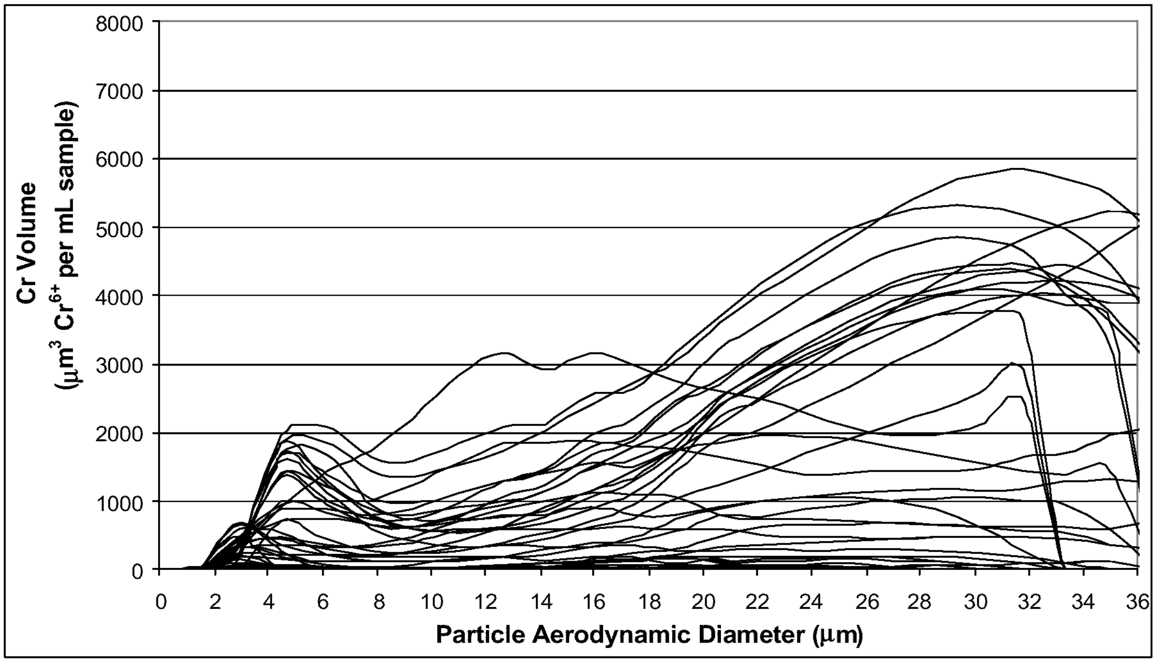


Figure 18. Solvent-borne Epoxy Cr^{6+} Volume Distributions Collected

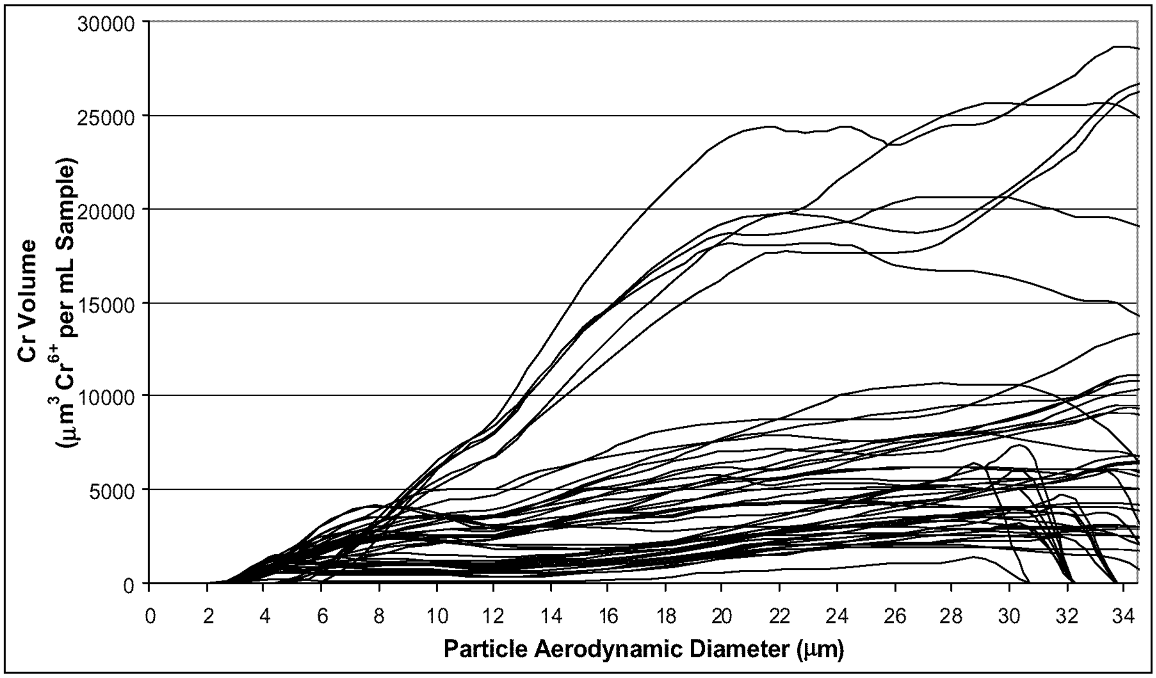


Figure 19. Water-borne Epoxy Cr^{6+} Volume Distributions Collected

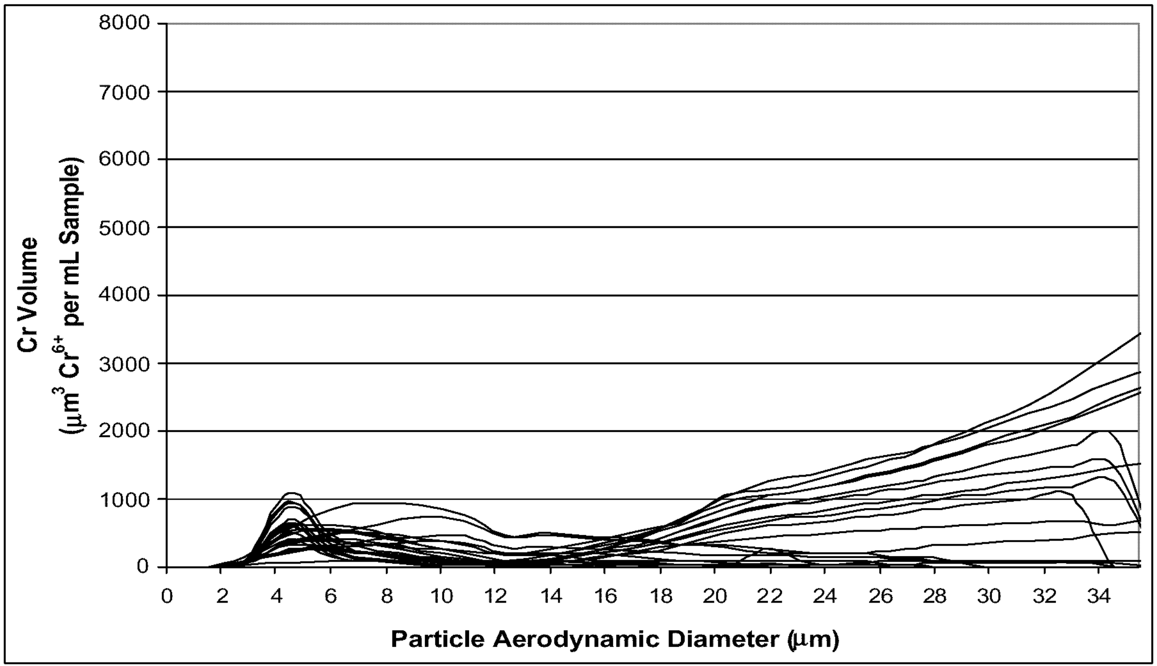


Figure 20. Polyurethane Cr^{6+} Volume Distributions Collected

Relating Particle Size to Cr^{6+} Dissociation Behavior

An important objective in this study was to assess the relative contributions of various particle sizes to Cr^{6+} dissociation from primer particles. One hypothesis was that smaller overspray particles release Cr^{6+} more readily than larger particles. If this is true there should be a positive correlation between the samples with many small particles and the fraction of Cr^{6+} that dissociates from the particles (f_t). It follows that samples with a greater proportion of large particles would have a relatively smaller f_t. Correlations comparing the volume of Cr^{6+} collected in each particle size bin to sample f_t were used to see if data indicate the existence of particle size-dependent Cr^{6+} dissociation.

Prior to statistical analyses, data conversion was necessary to obtain accurate and unbiased parameters for comparison. First, particle number concentrations (N_i) in particles/mL for each bin (i) of each sample were converted to a volume of Cr^{6+} per mL of sample for each bin (V_{Cr_i}) using equation 4, such that:

$$\frac{\text{Cr Volume/mL}}{\text{Bin}} = \frac{\text{\# of particles/ mL}}{\text{Bin}} \times \frac{\text{Particle Volume}}{\text{particle}} \times \frac{\text{Cr Volume}}{\text{Particle Volume}} .$$

$$V_{Cr_i} = N_i \cdot \left(p \cdot \frac{d_i^3}{6} \right) \cdot v_{Cr_i} \tag{4}$$

where: V_{Cr_i} = volume of Cr^{6+} per mL sample in bin i
N_i = particle number concentration in bin i (particles/mL)
$p \cdot \frac{d_i^3}{6}$ = the volume of a spherical particle with bin i mean diameter, d_i
v_{Cr_i} = (Vol. of Cr)/(Vol. of wet paint) in a particle mean bin diameter d_i, [corrects for Cr^{6+} bias]
i = the bin number ranging from i = 1 for the 0.5 μm bin to i = 15 for the ≥ 20 μm bin

Next, the volume of Cr^{6+} per mL in each bin was divided by the total volume of Cr^{6+} per mL collected in the same sample ($V_{Cr_{total}}$) as in equation 5. The result is an estimate of the fraction of collected Cr^{6+} residing in each particle size bin (i) for each sample, denoted as F_{Cr_i}. By normalizing the Cr^{6+} volume in each bin to the total Cr^{6+} volume, F_{Cr_i} is adjusted for both the bias in Cr^{6+} content (using v_{Cr}) and in particle volume ($V = \frac{p \cdot d_i^3}{6}$). This adjustment corrects for the fact that different particle sizes have inherently different volumes and % Cr^{6+} and, therefore, unequal supplies of Cr^{6+} to contribute to the collection fluid through dissociation. As a result of these corrections F_{Cr_i} is an unbiased parameter, and is appropriate for correlations to f_t.

$$F_{Cr_i} = \frac{\text{(Cr Volume/mL) /Bin}}{\text{Total Cr Volume/mL}} = \frac{V_{Cr_i}}{V_{Cr_{total}}} = \frac{\left[N_i \cdot \left(p \cdot \frac{d_i^3}{6} \right) \cdot v_{Cr_i} \right]}{\sum_{i=1}^{15} \left[N_i \cdot \left(p \cdot \frac{d_i^3}{6} \right) \cdot v_{Cr_i} \right]} \tag{5}$$

To gain information about the relationship between the amount of Cr^{6+} collected in particular particle sizes or size ranges and Cr^{6+} dissociation, each F_{Cr_i} was statistically correlated with its accompanying sample f_1, f_{24}, and the change ($\Delta f_t = f_{24} - f_1$). The underlying relationship between the fraction of the total Cr^{6+} that dissociates from collected particles (f_t) and the distribution of that Cr^{6+} with particle size (F_{Cr_1}, F_{Cr_2},... $F_{Cr_{23}}$) is depicted by equation 6.

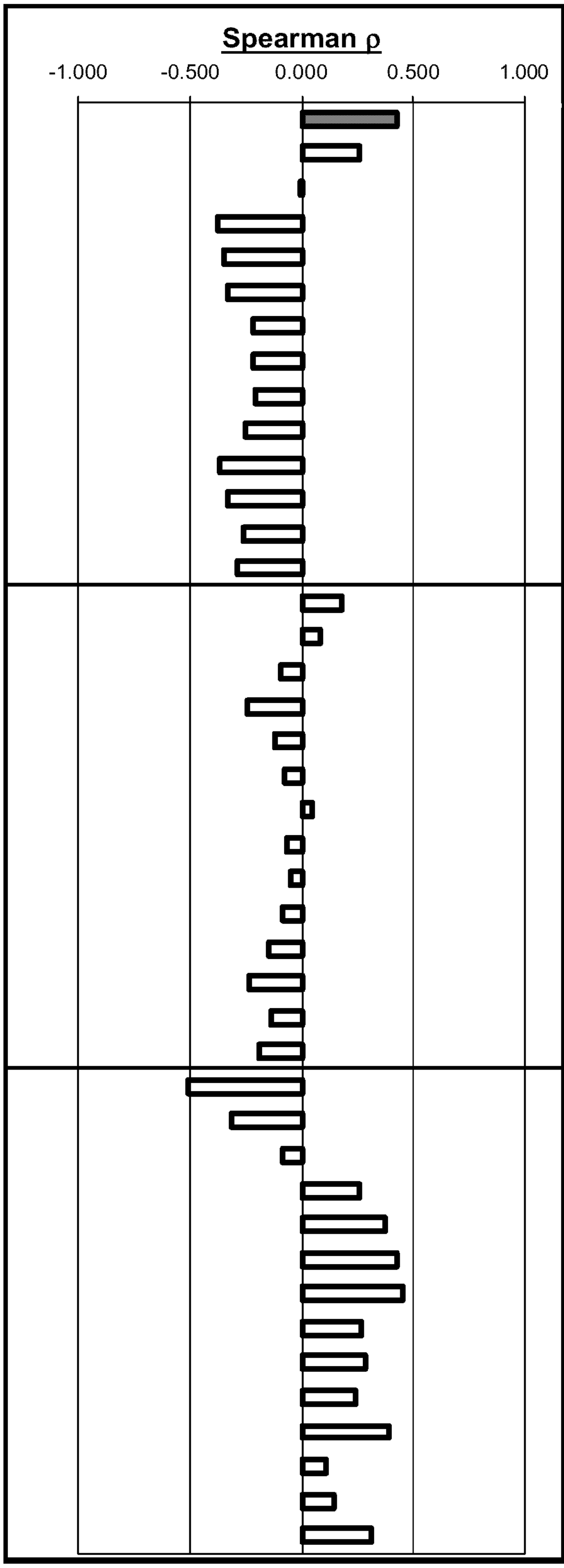
$$f_t = \sum_{i=1}^{15} F_{Cr_i} \cdot F_{t,i} \qquad (6)$$

where: $F_{t,i}$ = the probability that, or frequency with which, the fraction of Cr^{6+} resident in bin i (F_{Cr_i}) dissociates by time t

In other words, within each sample, particles of every size release some portion ($F_{t,i}$) of their Cr^{6+} to the DI (0 to 100%), and in so doing contribute to the fraction of total Cr^{6+} dissociation, f_t. Hence, equation 6 may be thought of as defining a theoretical expected value (mean) for the fraction of Cr^{6+} that dissociates from a given particle sample (f_t). In this analogy the fraction of Cr^{6+} resident in each bin (F_{Cr_i}) is a discrete random variable and $F_{t,i}$ is a hypothetical probability mass function.

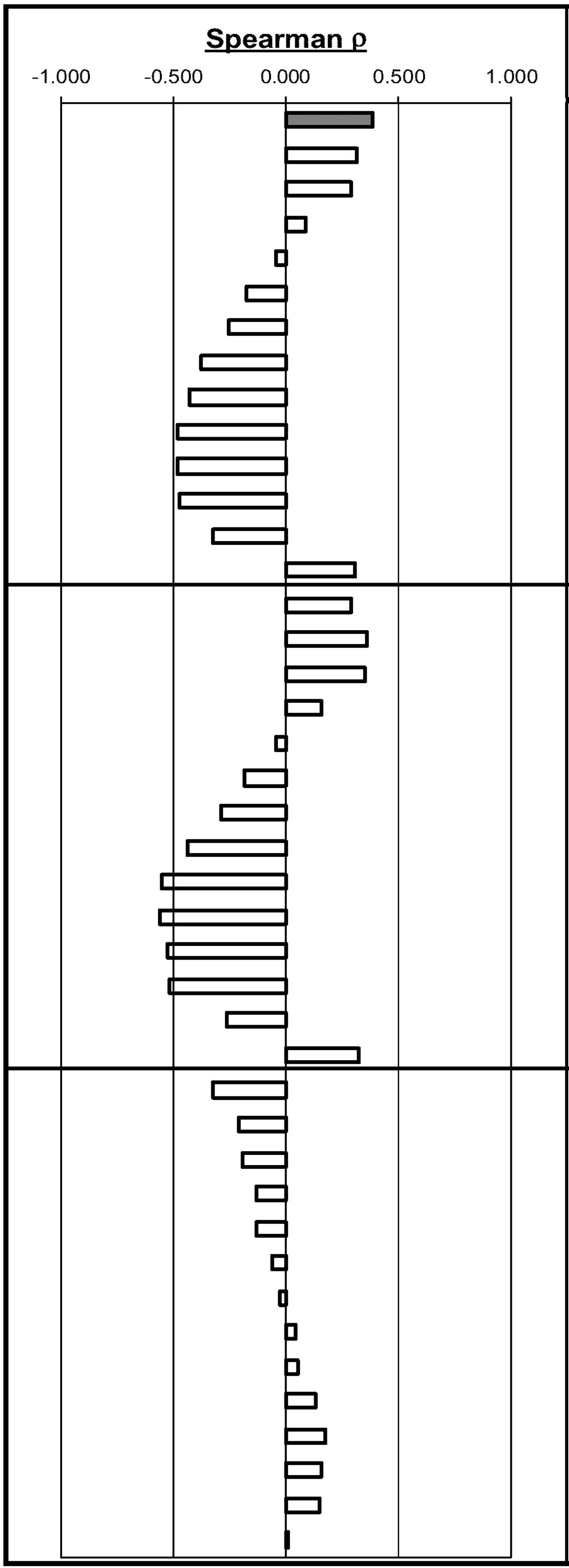
Spearman Correlations

Figures 21, 22, and 23 depict the results of a correlation analysis for the three primers. The 0.5 μm bin (bin 1) correlations are not shown for the solvent- and water-borne epoxies as particle counts in these bins were below background in all but two (solvent epoxy) samples. This bin is subject to substantial interference from non-paint particles. The distribution of F_{Cr_i} for a single particle size bin over all samples was not normally distributed for bin sizes less than 14 μm and greater than 20 μm, therefore the non-parametric Spearman Correlation Coefficient (ρ) was used as the test statistic. This coefficient is a distribution-free estimate of the degree of linearity between two variables and has a range of +1 (positive relationship) to –1 (inverse relationship). Spearman ρ coefficients are depicted in graphic and tabular form for pairs of correlated variables, and P values are shown as an indication of the statistical significance of those coefficients. $\mathbf{d_p}$ for each bin (i) is also included as a reference.



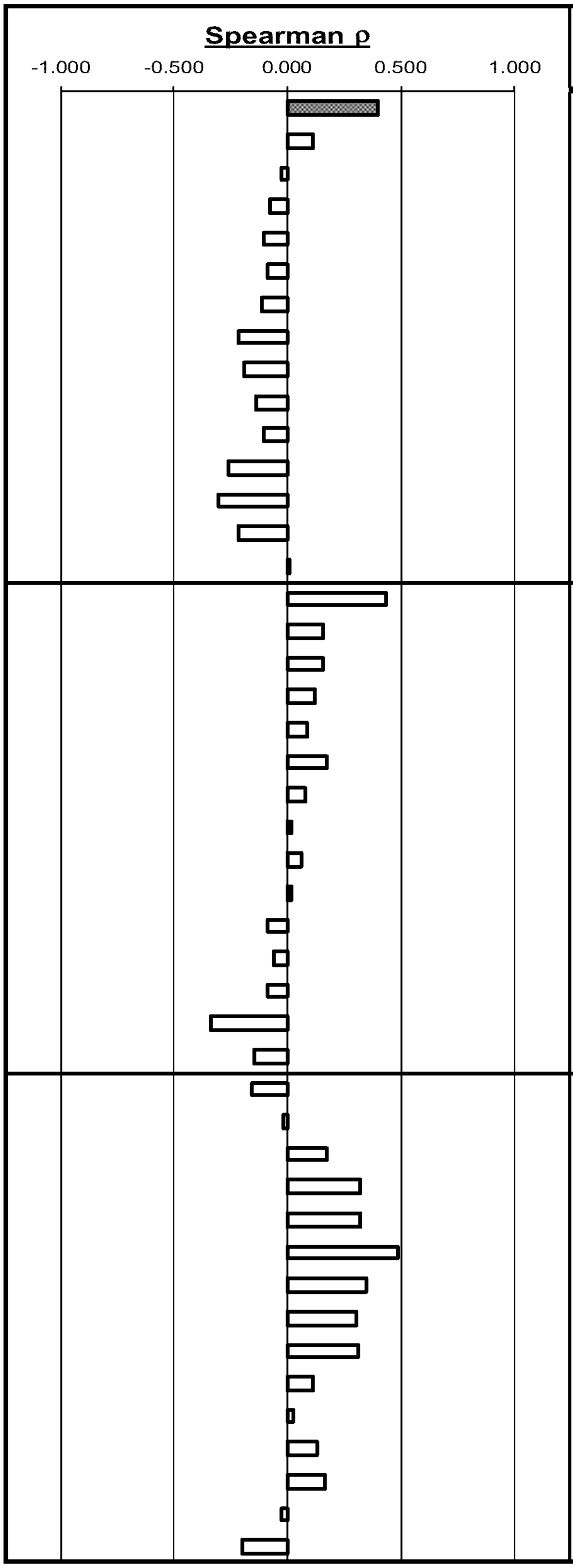
Correlated Variables (f_t by F_{Cri})	d_p (μm)	Spearman ρ	P-value
f_1 by F_{Cr2}	1.5	0.429	0.010
f_1 by F_{Cr3}	2.8	0.264	0.126
f_1 by F_{Cr4}	4.3	-0.001	0.997
f_1 by F_{Cr5}	5.8	-0.378	0.025
f_1 by F_{Cr6}	7.3	-0.345	0.043
f_1 by F_{Cr7}	8.8	-0.334	0.050
f_1 by F_{Cr8}	10.3	-0.219	0.205
f_1 by F_{Cr9}	11.8	-0.219	0.207
f_1 by F_{Cr10}	13.3	-0.205	0.236
f_1 by F_{Cr11}	14.8	-0.252	0.144
f_1 by F_{Cr12}	16.3	-0.363	0.032
f_1 by F_{Cr13}	17.8	-0.329	0.053
f_1 by F_{Cr14}	19.3	-0.263	0.127
f_1 by F_{Cr15}	≥ 20	-0.282	0.101
f_{24} by F_{Cr2}	1.5	0.182	0.297
f_{24} by F_{Cr3}	2.8	0.085	0.629
f_{24} by F_{Cr4}	4.3	-0.095	0.586
f_{24} by F_{Cr5}	5.8	-0.243	0.160
f_{24} by F_{Cr6}	7.3	-0.122	0.485
f_{24} by F_{Cr7}	8.8	-0.074	0.673
f_{24} by F_{Cr8}	10.3	0.044	0.801
f_{24} by F_{Cr9}	11.8	-0.063	0.720
f_{24} by F_{Cr10}	13.3	-0.049	0.779
f_{24} by F_{Cr11}	14.8	-0.087	0.618
f_{24} by F_{Cr12}	16.3	-0.150	0.391
f_{24} by F_{Cr13}	17.8	-0.234	0.175
f_{24} by F_{Cr14}	19.3	-0.132	0.449
f_{24} by F_{Cr15}	≥ 20	-0.194	0.265
Δf_t by F_{Cr2}	1.5	-0.509	0.002
Δf_t by F_{Cr3}	2.8	-0.314	0.066
Δf_t by F_{Cr4}	4.3	-0.083	0.635
Δf_t by F_{Cr5}	5.8	0.256	0.138
Δf_t by F_{Cr6}	7.3	0.376	0.026
Δf_t by F_{Cr7}	8.8	0.426	0.011
Δf_t by F_{Cr8}	10.3	0.455	0.006
Δf_t by F_{Cr9}	11.8	0.267	0.121
Δf_t by F_{Cr10}	13.3	0.283	0.099
Δf_t by F_{Cr11}	14.8	0.238	0.169
Δf_t by F_{Cr12}	16.3	0.395	0.019
Δf_t by F_{Cr13}	17.8	0.110	0.531
Δf_t by F_{Cr14}	19.3	0.148	0.397
Δf_t by F_{Cr15}	≥ 20	0.316	0.064

Figure 21. Solvent-borne Epoxy Spearman Correlations
Shaded bars indicate correlations with P-values < .100.



Correlated Variables (f_t by F_{Cri})	d_p (μm)	Spearman ρ	P-value
f_1 by F_{Cr2}	1.5	0.382	0.009
f_1 by F_{Cr3}	2.8	0.320	0.030
f_1 by F_{Cr4}	4.3	0.289	0.052
f_1 by F_{Cr5}	5.8	0.086	0.571
f_1 by F_{Cr6}	7.3	-0.047	0.758
f_1 by F_{Cr7}	8.8	-0.175	0.246
f_1 by F_{Cr8}	10.3	-0.254	0.088
f_1 by F_{Cr9}	11.8	-0.374	0.011
f_1 by F_{Cr10}	13.3	-0.431	0.003
f_1 by F_{Cr11}	14.8	-0.483	0.001
f_1 by F_{Cr12}	16.3	-0.483	0.001
f_1 by F_{Cr13}	17.8	-0.469	0.001
f_1 by F_{Cr14}	19.3	-0.326	0.027
f_1 by F_{Cr15}	≥20	0.302	0.041
f_{24} by F_{Cr2}	1.5	0.286	0.054
f_{24} by F_{Cr3}	2.8	0.362	0.013
f_{24} by F_{Cr4}	4.3	0.349	0.017
f_{24} by F_{Cr5}	5.8	0.157	0.299
f_{24} by F_{Cr6}	7.3	-0.048	0.751
f_{24} by F_{Cr7}	8.8	-0.180	0.233
f_{24} by F_{Cr8}	10.3	-0.291	0.050
f_{24} by F_{Cr9}	11.8	-0.436	0.003
f_{24} by F_{Cr10}	13.3	-0.550	<.0001
f_{24} by F_{Cr11}	14.8	-0.556	<.0001
f_{24} by F_{Cr12}	16.3	-0.521	0.0002
f_{24} by F_{Cr13}	17.8	-0.515	0.0002
f_{24} by F_{Cr14}	19.3	-0.265	0.075
f_{24} by F_{Cr15}	≥20	0.325	0.028
Δf_t by F_{Cr2}	1.5	-0.326	0.027
Δf_t by F_{Cr3}	2.8	-0.212	0.158
Δf_t by F_{Cr4}	4.3	-0.194	0.197
Δf_t by F_{Cr5}	5.8	-0.131	0.387
Δf_t by F_{Cr6}	7.3	-0.134	0.375
Δf_t by F_{Cr7}	8.8	-0.061	0.688
Δf_t by F_{Cr8}	10.3	-0.024	0.874
Δf_t by F_{Cr9}	11.8	0.046	0.761
Δf_t by F_{Cr10}	13.3	0.052	0.734
Δf_t by F_{Cr11}	14.8	0.136	0.369
Δf_t by F_{Cr12}	16.3	0.175	0.246
Δf_t by F_{Cr13}	17.8	0.156	0.302
Δf_t by F_{Cr14}	19.3	0.147	0.330
Δf_t by F_{Cr15}	≥20	0.010	0.949

Figure 22. Water-borne Epoxy Spearman Correlations
Shaded bars indicate correlations with P-values < .100.



Correlated Variables (f_t by F_{Cri})	d_p (μm)	Spearman ρ	P-value
f_1 by F_{Cr1}	0.75	0.402	0.028
f_1 by F_{Cr2}	1.5	0.117	0.539
f_1 by F_{Cr3}	2.8	-0.023	0.906
f_1 by F_{Cr4}	4.3	-0.076	0.689
f_1 by F_{Cr5}	5.8	-0.108	0.572
f_1 by F_{Cr6}	7.3	-0.089	0.641
f_1 by F_{Cr7}	8.8	-0.113	0.551
f_1 by F_{Cr8}	10.3	-0.220	0.243
f_1 by F_{Cr9}	11.8	-0.194	0.304
f_1 by F_{Cr10}	13.3	-0.138	0.469
f_1 by F_{Cr11}	14.8	-0.100	0.600
f_1 by F_{Cr12}	16.3	-0.265	0.158
f_1 by F_{Cr13}	17.8	-0.300	0.107
f_1 by F_{Cr14}	19.3	-0.221	0.241
f_1 by F_{Cr15}	≥ 20	0.011	0.953
f_{24} by F_{Cr1}	0.75	0.433	0.017
f_{24} by F_{Cr2}	1.5	0.155	0.413
f_{24} by F_{Cr3}	2.8	0.157	0.406
f_{24} by F_{Cr4}	4.3	0.121	0.525
f_{24} by F_{Cr5}	5.8	0.088	0.642
f_{24} by F_{Cr6}	7.3	0.174	0.358
f_{24} by F_{Cr7}	8.8	0.080	0.674
f_{24} by F_{Cr8}	10.3	0.014	0.941
f_{24} by F_{Cr9}	11.8	0.058	0.762
f_{24} by F_{Cr10}	13.3	0.019	0.919
f_{24} by F_{Cr11}	14.8	-0.087	0.649
f_{24} by F_{Cr12}	16.3	-0.061	0.749
f_{24} by F_{Cr13}	17.8	-0.085	0.657
f_{24} by F_{Cr14}	19.3	-0.342	0.064
f_{24} by F_{Cr15}	≥ 20	-0.145	0.445
Δf_t by F_{Cr1}	0.75	-0.153	0.420
Δf_t by F_{Cr2}	1.5	-0.014	0.941
Δf_t by F_{Cr3}	2.8	0.169	0.371
Δf_t by F_{Cr4}	4.3	0.319	0.086
Δf_t by F_{Cr5}	5.8	0.326	0.079
Δf_t by F_{Cr6}	7.3	0.486	0.007
Δf_t by F_{Cr7}	8.8	0.349	0.058
Δf_t by F_{Cr8}	10.3	0.308	0.098
Δf_t by F_{Cr9}	11.8	0.312	0.094
Δf_t by F_{Cr10}	13.3	0.112	0.556
Δf_t by F_{Cr11}	14.8	0.030	0.877
Δf_t by F_{Cr12}	16.3	0.134	0.480
Δf_t by F_{Cr13}	17.8	0.168	0.376
Δf_t by F_{Cr14}	19.3	-0.024	0.899
Δf_t by F_{Cr15}	≥ 20	-0.204	0.281

Figure 23. Polyurethane Spearman Correlations
Shaded bars indicate correlations with P-values < .100.

All three primers show some significant correlations. The solvent- and water-borne epoxy primer data demonstrate generally higher significance than the polyurethane, as indicated by the P-values. Shaded bars in Figures 21, 22, and 23 highlight correlations with P-values < 0.1. Correlation coefficients for both epoxy primers show a positive correlation for the smallest particle sizes and a negative correlation for larger particles. Though this pattern is significant for the solvent epoxy f_1 correlations, the f_{24} correlations are much weaker and none show statistical significance. To the contrary, the water epoxy results show a similar pattern at both 1 *and* 24 hours with even stronger correlation and high statistical significance. The water epoxy also shows a feature that cannot be explained. The largest particles ($\mathbf{d_p} \geq 20\ \mu m$) demonstrate a positive correlation with f_t that is similar in magnitude and significance to the smallest particles ($1.5\ \mu m \leq \mathbf{d_p} \leq 4.3\ \mu m$). Finally, the polyurethane data only show a significant correlation (positive) at 1 and 24 hours for the smallest particle bin ($\mathbf{d_p} = 0.75\ \mu m$), though its overall trend is similar to the epoxy primers. Given that the polyurethane showed very little variability in f_t, the lack of significant correlation between f_t and F_{Cr_i} for that primer is understandable. The observed patterns indicate that the amount of Cr^{6+} contained in smaller primer particles has a stronger influence on how much Cr^{6+} is released to the collection fluid during the first 24 hours than does Cr^{6+} residing in larger particles.

Correlations of F_{Cr_i} with Δf_t, particularly for the solvent epoxy, add further insight into the data. The solvent epoxy shows a significant negative relationship ($\rho = -0.51$ to -0.31) between F_{Cr_i} and Δf_t for particles $\leq 2.8\ \mu m$ and a positive relationship ($\rho = +0.46$ to $+0.11$) for all particles larger than $4.3\ \mu m$. A similar pattern was observed in the water epoxy primer, but correlations are weaker and less significant. The polyurethane data show a positive correlation between F_{Cr_i} and Δf_t over the range 4.3 μm to 11.8 μm, though statistical significance is somewhat limited. The pattern seen in the Δf_t correlations, when combined with those for f_1 and f_{24}, supports the theory that very small particles release their Cr^{6+} rapidly (the observed positive correlation to f_t), but contribute little to the dissociation between 1 and 24 hours (the observed negative correlation with Δf_t). Furthermore, the indication is that large particles are slower to release their Cr^{6+} (the observed negative correlation to f_t) but do provide a residual source of dissolvable Cr^{6+} over the first 24 hours in DI (the observed positive correlation with Δf_t). This implies that distributions with greater numbers of small particles release a larger proportion of Cr^{6+} and do so quickly.

V. Discussion

Summary and Conclusions

The objectives of this study were to examine three aspects of Cr^{6+} dissociation from chromate-containing primer particles into a fluid:

1) The influence of particle residence time in pure DI (water) on the quantity of Cr^{6+} dissociated
2) Differences in Cr^{6+} dissociation between three different primer compositions (solvent-borne epoxy, water-borne epoxy, and solvent-borne polyurethane)
3) The relationship between particle size and Cr^{6+} dissociation

These objectives have direct implications for bioavailability, and ultimately the toxicological impact, of Cr^{6+} inhaled in this form. Time-dependent dissociation (objective 1) is important due to the body's ability to escalate and remove Cr^{6+}-containing particles from the lung. It follows that understanding any size-dependent dissociation (objective 3) is important because the location of particle deposition in the lung, and thus the time required to escalate and clear those particles, depends on particle (aerodynamic) diameter. Finally, it was proposed that encapsulation of Cr^{6+} in a paint matrix may render it less available in lung fluid after some initial release of Cr^{6+}, and that this effect may vary depending on paint composition (objective 2).

The data suggest that, for the three aircraft primers tested, a substantial release of Cr^{6+} into DI from overspray particles does occur during the first hour of contact with the DI. The solvent-borne epoxy primer did not show the apparent Cr^{6+}-binding observed in earlier research and, was not significantly different from the water-borne epoxy. Between 1 and 24 hours of particle residence time, the solvent- *and* water-borne primers show a statistically significant increase in the fraction of Cr^{6+} dissociated, though the additional fraction dissociated is relatively small. During the first hour in DI, solvent epoxy particles dissociate Cr^{6+} at a rate of 70 ± 5% and the water epoxy 74 ± 4%, but only dissociate an additional 15% and 10%, respectively, by 24 hours. Testing of the $[Cr^{6+}]$ in each primer's mixed volatile fraction confirmed that almost 100% of the $SrCrO_4$ in these primers remains in solid, undissolved, form in these primers. Therefore, the f_t data indicate that paint constituents other than the volatiles, including solid $SrCrO_4$, must be sources of Cr^{6+} to the DI. Consequently, the hypothesis that the water-borne epoxy releases significantly more Cr^{6+} into a watery fluid than the solvent-borne epoxy is not supported.

The polyurethane primer demonstrated a distinctly different pattern, releasing essentially all of its Cr^{6+} within the first hour (94 ± 2%). However, some doubt is cast on this paint type based on the observation that it tended to "cling" to collection vessel walls. This observation inspired a separate qualitative test. Small volumes (< 10 mL) of mixed polyurethane primer were poured directly into a 1.0 L beaker of DI and swirled. The paint appeared to immediately separate some of its components, possibly the solvents separating from the pigment and resin solids. Swirling moved the majority of the solids to the walls of the vessel where they formed a hydrophobic film. These observations coincide with the clear appearance of the polyurethane samples and the film observed on collection vessel walls. It may be that polyurethane particles released some amount of Cr^{6+} dissolved in the more water-soluble constituents upon contact with the DI, but separated the bulk of the $SrCrO_4$ (the source) from the fluid to the vessel walls. Loss of Cr^{6+}-containing paint constituents to collection vessel walls would result in systematic overestimation of f_t due to underestimating the total amount of Cr^{6+} ($[Cr]_P$) that had the opportunity to release Cr^{6+}.

Although study data indicate a large fraction of Cr^{6+} dissociates from chromate-containing primer particles, calculations show that most of the Cr^{6+} mass collected was in the larger overspray particles. This implies that despite the large number of small particles ($d_p < 5$ µm or $d_{ae} < \approx 6$ µm) in primer overspray, most of the Cr^{6+} volume exists in larger particles that are less likely to be inhaled or are quickly cleared from the upper respiratory system upon deposition. Correlations indicate that Cr^{6+} contained in smaller overspray particles dissociates more quickly and more completely than the Cr^{6+} in larger particles. Observed sample f_I and f_{24} ranged from complete (100%) dissociation to as low as $f_I = 32\%$ and $f_{24} = 33\%$ for the solvent epoxy, and $f_I = 44\%$ and $f_{24} = 48\%$ for the water epoxy. This range of f_t appears to result from a dependency on sample particle size distribution. The significance of such a dependency is that Cr^{6+} may be released more slowly from larger particles that deposit higher in the respiratory system.

Several factors, when considered together, point toward a difference in the character of Cr^{6+} exposure from chromate-containing primer overspray as compared to other industrial exposures to chromate-containing particles. These are: the tendency of Cr^{6+} to remain predominantly in an undissolved (solid $SrCrO_4$) form in primer paint, the small Cr^{6+} mass in respirable overspray particles, and the degree of Cr^{6+} dissociation from deposited paint particles. Limited Cr^{6+} dissociation from larger particles, containing the preponderance of Cr^{6+}, may be the reason for the lack of significant lung cancer incidence among painters relative to other chromate-exposed workers. If painters inhale only a small amount of overspray that contains only the smallest, $d_{ae} < 6$ µm, particles possessing very little Cr^{6+} then exposure may be limited, even if ventilation and respirator protection fail or are improperly used.

Study Limitations

Limitations exist in this study. As mentioned, daily variations in $[Cr^{6+}]$ background could not be quantified and may have introduced bias even after a mean correction was applied. Second, values of f_t may be exaggerated if a portion of collected primer particles were in contact with the fluid long enough to leach Cr^{6+} into the DI, but were lost prior to $[Cr]_P$ analysis. As mentioned earlier, this may have occurred as a result of particle adhesion to collection vessel walls, which was especially noticeable for the polyurethane primer.

Recommendations

This study points to several possible ways to improve future research regarding Cr^{6+} bioavailability from primer paints, and generates new questions for further study. Future studies using BioSamplers to collect primer paint particles must control contamination. In addition to rinsing the collection vessels with 1:1 HNO_3, the tangential nozzle stages should be soaked in 1:1 HNO_3 followed by ultrasonic cleaning to remove paint residue. A second 1:1 HNO_3 rinse should then be performed to eliminate adsorbed Cr from the glass nozzle stages prior to DI rinse. Second, any future study concerning the bioavailability of Cr^{6+} from primer paint particles or other similar chemical matrices should include a chemical analysis of the matrix. Better understanding about Cr^{6+} solubility in the various paint constituents, the solvent polarities, and mechanisms for Cr^{6+} transfer would provide useful insight into the questions posed in this study. For example, a surface mass transfer model with some matrix limiting may explain the dissociation behavior seen in this study. Microscopic analyses may add further understanding as to overspray particle behavior in fluid, to include particle shape, composition, whether or not particle agglomeration occurs, etc. Finally, using a lung mucous layer surrogate as the particle collection medium would more closely represent particle deposition and subsequent Cr^{6+} dissociation in the mucous layer. Although particle size analysis may be more difficult for collections in mucous, primer particle or chromate solubility in the mucous may differ from that in water or SLF.

Modifications to methodology are necessary to develop a firmer quantitative estimate of the apparently size-dependent Cr^{6+} dissociation behavior observed in this study. Determining the Cr^{6+} dissociation (0 to 100%) from different size particles is possible by solving equation 7 for $F_{t,i}$. An accurate solution requires samples that contain single particle diameters (or as close to this as possible), so as to reduce or eliminate multiple dependencies within samples. The particle size distributions collected in this study, though somewhat variable, were not distinct enough to allow consistently meaningful solutions even when particle sizes were grouped to reduce the number of variables. The inherently high concentration of small particles in overspray makes the technique of varying sampler flow rate within feasible limits inadequate for collecting distinctly different distributions. Though ultrasonic nebulizer technology may enable mono-disperse overspray particle size distributions to be generated and collected, it may not be representative of spray gun atomization. Instead, it may be desirable to focus on changing collection methodology.

Combining a particle separation technology, such as cascade impaction or electrostatic precipitation, with impinger-type collection may allow different particle sizes to be selectively collected into fluid by using the separation apparatus as a band-pass filter. Then, applying the concepts developed in this study, direct quantitative determination and, therefore, prediction of the mass of Cr^{6+} released as a function of particle size becomes possible. This capability may have tremendous value to bioavailability studies concerning inhalation of particles containing toxic compounds in a complex matrix.

Glossary

The following list defines terms and symbols used in the text and Appendices:

Term or Symbol	**Meaning**
Particle Number Concentrations	Background corrected particles/mL
Particle Size Bins	Bin minimum, or lower threshold, particle diameter
$\mathbf{d_p}$	The midpoint of particle diameters (µm) in the given bin
$\mathbf{d_{ae}}$	The midpoint of aerodynamic particle diameters (µm) in the given bin
v_{Cr}	Volume fraction of Cr^{6+} (as % vol.) in a wet particle of size $\mathbf{d_p}$
ΣN_i	Total particles/mL collected in all bins (i) for the given sample
$[Cr]_P$	Initial sample (Total Collection) Cr^{6+} concentration (µg/L) including collected particles
$[Cr]_{NP1}$	Sample supernatant (no-particle) Cr^{6+} concentration (µg/L) at particle residence time t = 1 hour
$[Cr]_{NP24}$	Sample supernatant (no-particle) Cr^{6+} concentration (µg/L) at particle residence time t = 24 hours
f_1	Fraction (as %) of Cr^{6+} dissociated at particle residence time t = 1 hour such that $f_1 = \frac{[Cr]_{NP1}}{[Cr]_P}$
f_{24}	Fraction (as %) of Cr^{6+} dissociated at particle residence time t = 24 hours such that $f_{24} = \frac{[Cr]_{NP24}}{[Cr]_P}$
Δf_t	Change in the fraction (as %) of Cr^{6+} dissociated between particle residence times of 1 and 24 hours ($f_{24} - f_1$)
MSDS	Material Safety Data Sheet

Appendix A:

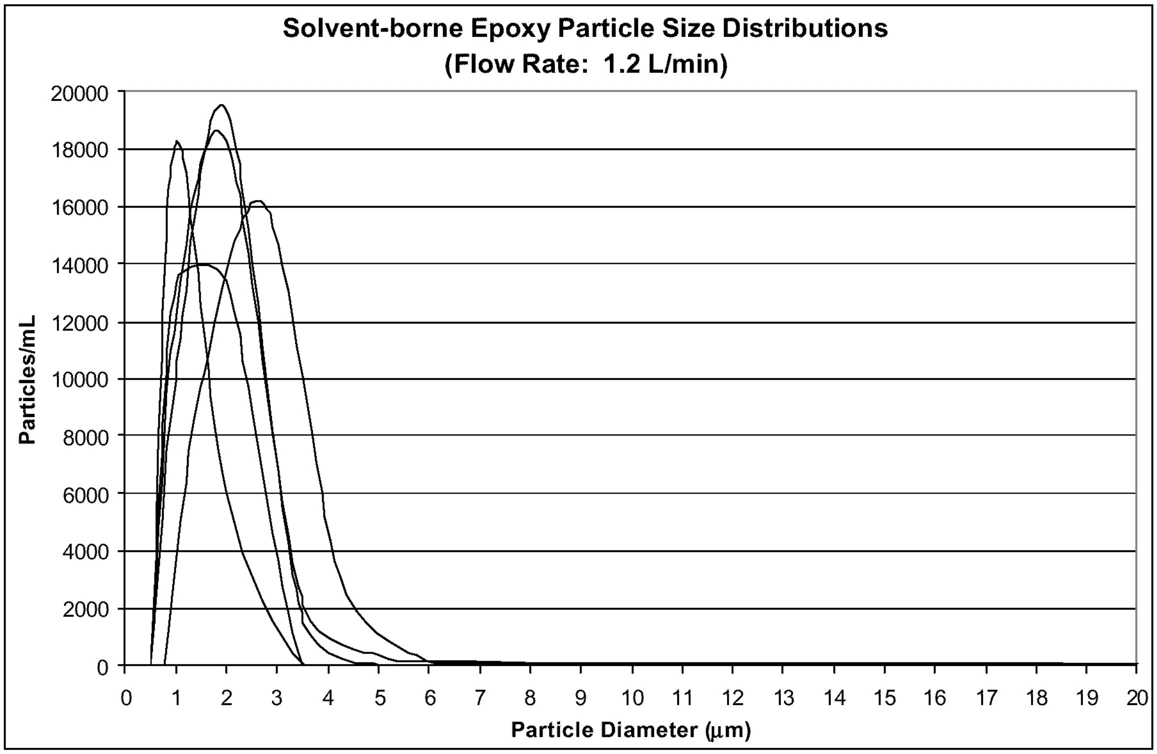
Deft® 02-Y-40 Solvent-borne Epoxy Polyamide Primer (MIL-P-23377G)

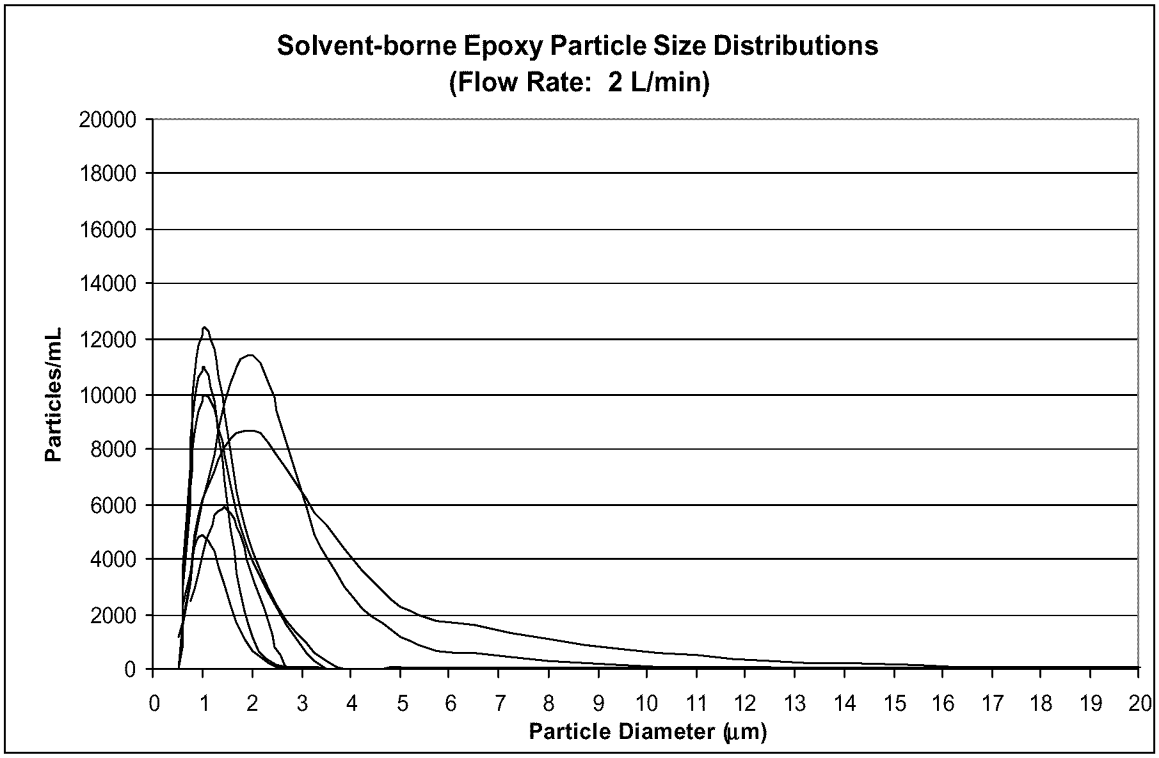
Appendix A-1: Solvent-borne Epoxy Data Summary

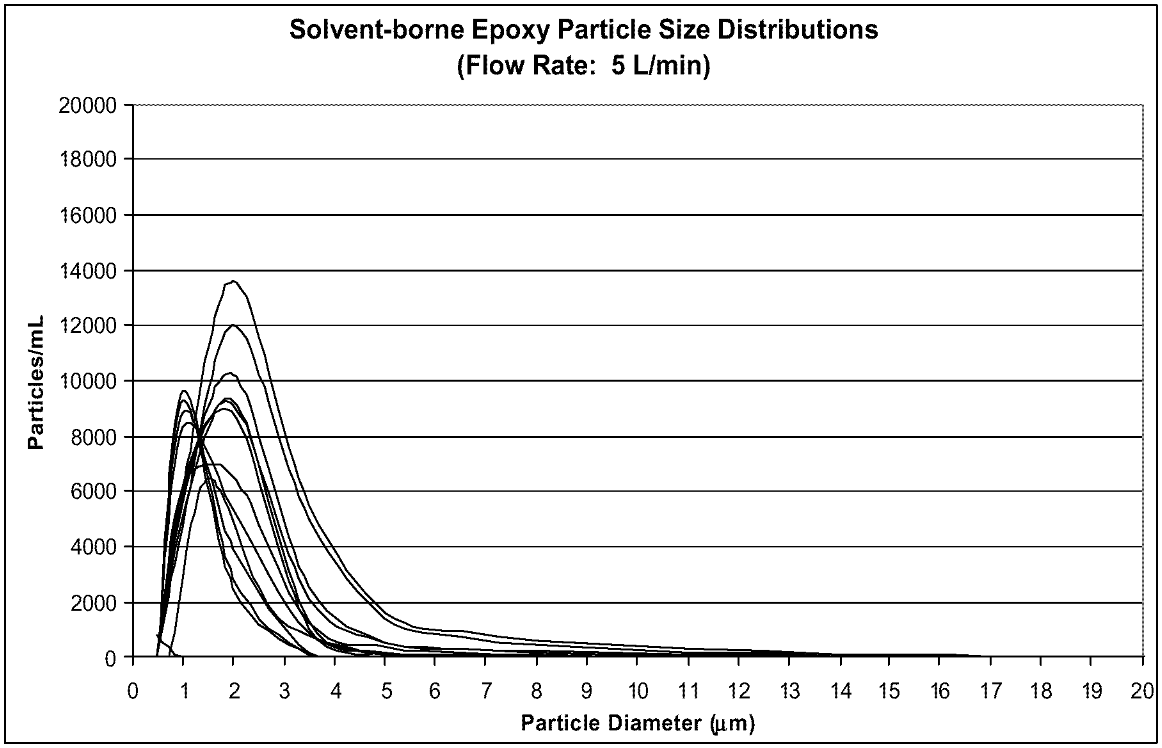
Fluid	Flow Rate (L/min)	Particle Number Concentrations																				
		Particle Size Bins (µm)															ΣN_i	$[Cr]_P$ (µg/L)	$[Cr]_{NP1}$ (µg/L)	f_1	$[Cr]_{NP24}$ (µg/L)	f_{24}	Δf_t
		0.5	1.0	2.0	3.5	5.0	6.5	8.0	9.5	11.0	12.5	14.0	15.5	17.0	18.5	≥20							
SLF	2	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	638	935	147%	749	118%	-29%
SLF	2	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	851	328	39%	612	72%	33%
SLF	2	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	2,347	1,584	68%	1,459	62%	-5%
SLF	2	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	1,479	1,112	75%	1,597	108%	33%
SLF	5	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	3,857	2,694	70%	4,320	112%	42%
SLF	5	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	1,617	942	58%	1,770	109%	51%
SLF	5	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	2,046	2,059	101%	1,951	95%	-5%
SLF	5	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	2,022	1,776	88%	1,944	96%	8%
SLF	10	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	20,150	8,513	42%	10,958	54%	12%
SLF	10	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	4,961	2,884	58%	4,216	85%	27%
SLF	10	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	9,822	6,853	70%	7,209	73%	4%
SLF	10	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	6,434	4,267	66%	5,961	93%	26%
DI	1.2	0	9,687	16,070	3,100	352	117	54	32	29	27	28	31	38	36	183	29,784	6,210	3,470	56%	4,823	78%	22%
DI	1.2	0	9,998	19,363	1,520	0	0	0	0	0	0	12	16	15	20	97	31,039	5,903	3,369	57%	5,084	86%	29%
DI	1.2	0	12,203	18,235	2,083	342	179	126	113	104	109	95	97	90	86	603	34,463	4,952	4,217	85%	4,923	99%	14%
DI	1.2	0	13,339	13,348	0	0	0	0	0	0	0	11	8	11	13	66	26,796	3,635	3,190	88%	3,279	90%	2%
DI	1.2	0	18,213	6,047	78	0	0	0	0	0	0	0	0	0	1	0	24,338	1,790	1,703	95%	1,712	96%	0%
DI	2	2,478	5,806	0	0	0	0	0	0	0	0	0	0	0	0	0	8,285	478	475	99%	469	98%	-1%
DI	2	0	10,983	1,180	0	0	0	0	0	0	0	0	0	0	0	0	12,163	649	691	106%	578	89%	-17%
DI	2	1,200	4,883	734	0	0	0	0	0	0	0	0	0	1	1	1	6,820	539	lost	lost	558	104%	-----
DI	2	0	9,874	3,969	0	0	0	0	0	0	0	0	0	0	0	2	13,845	1,063	991	93%	1,065	100%	7%
DI	2	0	6,138	11,412	4,100	1,215	578	305	190	132	96	76	54	41	37	126	24,499	1,089	719	66%	1,084	100%	34%
DI	2	0	6,216	8,714	5,244	2,309	1,574	1,079	769	524	346	261	200	142	105	304	27,788	767	345	45%	648	84%	39%
DI	2	0	12,363	4,266	336	54	42	35	41	29	15	13	12	5	6	0	17,217	743	757	102%	956	129%	27%
DI	5	0	6,439	1,766	383	73	23	8	0	1	0	1	1	2	2	1	8,700	2,791	897	32%	922	33%	1%
DI	5	0	9,303	2,531	188	10	1	0	0	2	3	2	0	2	2	4	12,047	1,833	1,717	94%	1,620	88%	-5%
DI	5	0	8,862	3,917	201	3	4	3	6	12	12	11	10	9	7	24	13,080	1,572	700	45%	913	58%	14%
DI	5	0	6,158	6,542	1,263	356	196	122	83	59	39	28	24	14	11	38	14,933	5,204	4,046	78%	4,558	88%	10%
DI	5	0	9,637	2,879	146	0	4	3	5	11	6	6	4	4	2	5	12,712	1,419	1,087	77%	1,279	90%	14%
DI	5	0	4,768	11,992	5,009	1,423	721	437	297	213	165	129	100	89	75	273	25,690	2,898	1,748	60%	2,272	80%	20%
DI	5	0	5,542	10,274	2,581	584	333	235	187	144	120	91	72	54	32	111	20,360	1,850	1,239	67%	1,461	79%	12%
DI	5	0	5,924	13,618	5,496	1,610	918	604	423	302	222	155	120	91	67	247	29,796	3,033	1,430	47%	1,573	52%	5%
DI	5	0	5,054	9,333	1,336	123	17	6	8	8	11	8	8	7	5	22	15,946	2,249	1,174	52%	1,380	61%	9%
DI	5	0	6,216	8,783	1,064	105	20	6	4	6	4	5	5	3	2	9	16,234	1,693	1,186	70%	1,387	82%	12%
DI	5	0	5,848	9,118	2,140	566	303	196	148	95	72	50	42	30	24	73	18,703	2,094	1,482	71%	1,994	95%	24%
DI	5	0	8,320	5,406	871	204	103	59	35	26	15	14	8	8	4	17	15,091	961	865	90%	924	96%	6%
DI	10	0	0	280	4,075	693	249	117	73	59	53	52	51	53	50	270	6,074	3,912	2,799	72%	2,628	67%	-4%
DI	10	0	0	6,685	8,065	1,632	664	357	259	211	175	162	146	134	130	650	19,270	4,192	2,258	54%	4,238	101%	47%
DI	10	0	0	9,866	7,971	1,947	792	389	246	164	136	124	119	105	102	546	22,508	4,148	3,353	81%	3,667	88%	8%
DI	10	0	0	6,820	5,741	1,334	579	312	213	155	135	122	108	97	96	450	16,163	4,487	3,043	68%	4,309	96%	28%
DI	10	0	0	8,865	7,856	1,548	590	308	211	177	147	138	125	124	110	619	20,818	3,572	2,108	59%	3,922	78%	19%
DI	10	0	0	10,626	9,801	2,250	940	476	303	212	169	149	128	126	112	613	25,903	3,572	2,108	59%	3,922	110%	51%
DI	10	0	0	9,536	10,553	2,973	1,293	664	411	286	241	199	182	156	146	800	27,441	▨ 2,996	▨ 1,494	▨ 50%	▨ 2,169	▨ 72%	▨ 23%
DI	10	0	0	9,363	11,294	3,365	1,476	781	492	344	252	211	175	163	149	771	28,835	4,908	1,882	38%	2,947	60%	22%
DI	10	0	0	5,965	9,204	1,802	549	204	89	63	64	58	63	74	77	498	18,710	4,567	2,913	64%	3,880	85%	21%
DI	10	0	0	4,343	9,556	2,011	720	291	146	94	81	73	74	81	89	532	18,092	3,640	2,916	80%	3,158	87%	7%
DI	10	0	0	8,820	10,794	2,078	687	286	154	105	92	88	85	88	96	574	23,947	3,065	2,325	76%	2,553	83%	7%
DI	10	0	0	10,679	9,709	2,701	852	360	197	129	99	95	88	91	100	599	25,701	3,254	2,464	76%	2,941	90%	15%
	d_p	0.750	1.50	2.75	4.25	5.75	7.25	8.75	10.3	11.8	13.3	14.8	16.3	17.8	19.3	≥20.8							
	d_{ae}	0.754	1.53	2.89	4.49	6.17	7.76	9.33	11.0	12.6	14.2	15.9	17.4	19.0	20.6	≥22.2							
	v_{Cr}	0.09%	0.18%	0.33%	0.43%	0.62%	0.55%	0.58%	0.66%	0.71%	0.69%	0.72%	0.67%	0.66%	0.66%	0.66%							

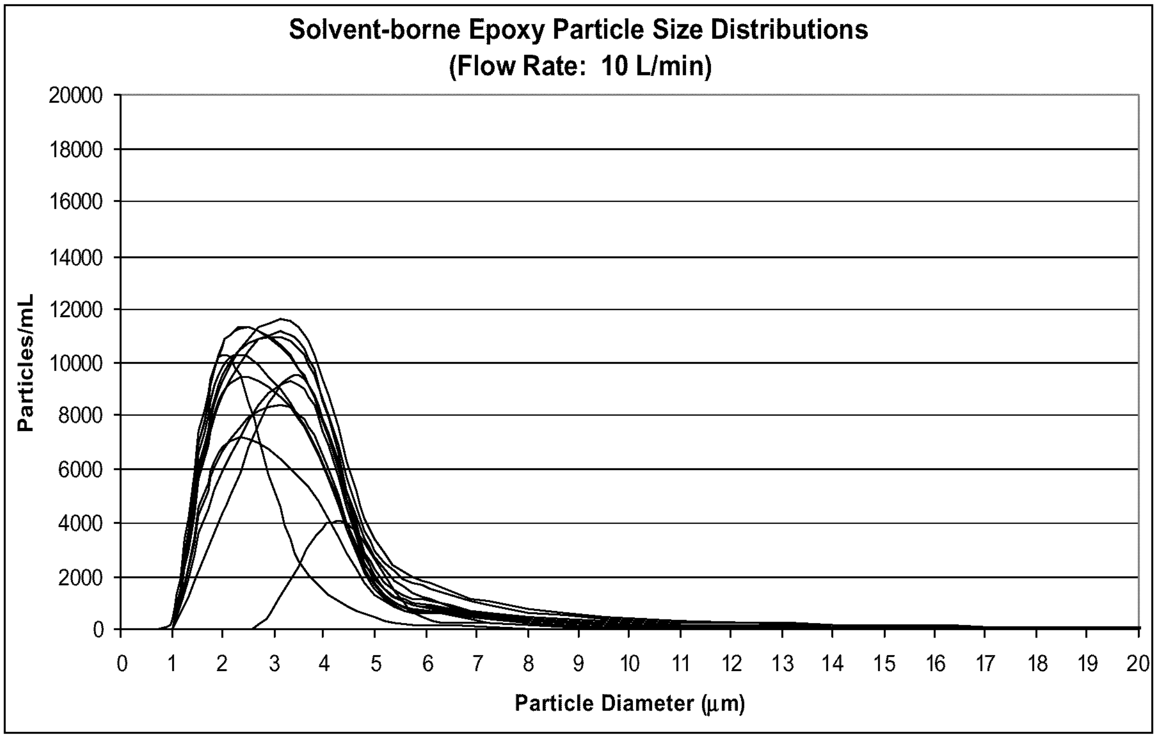
▨ = Flame AAS results

Appendix A-2: Solvent-borne Epoxy Particle Size Distributions by Flow Rate

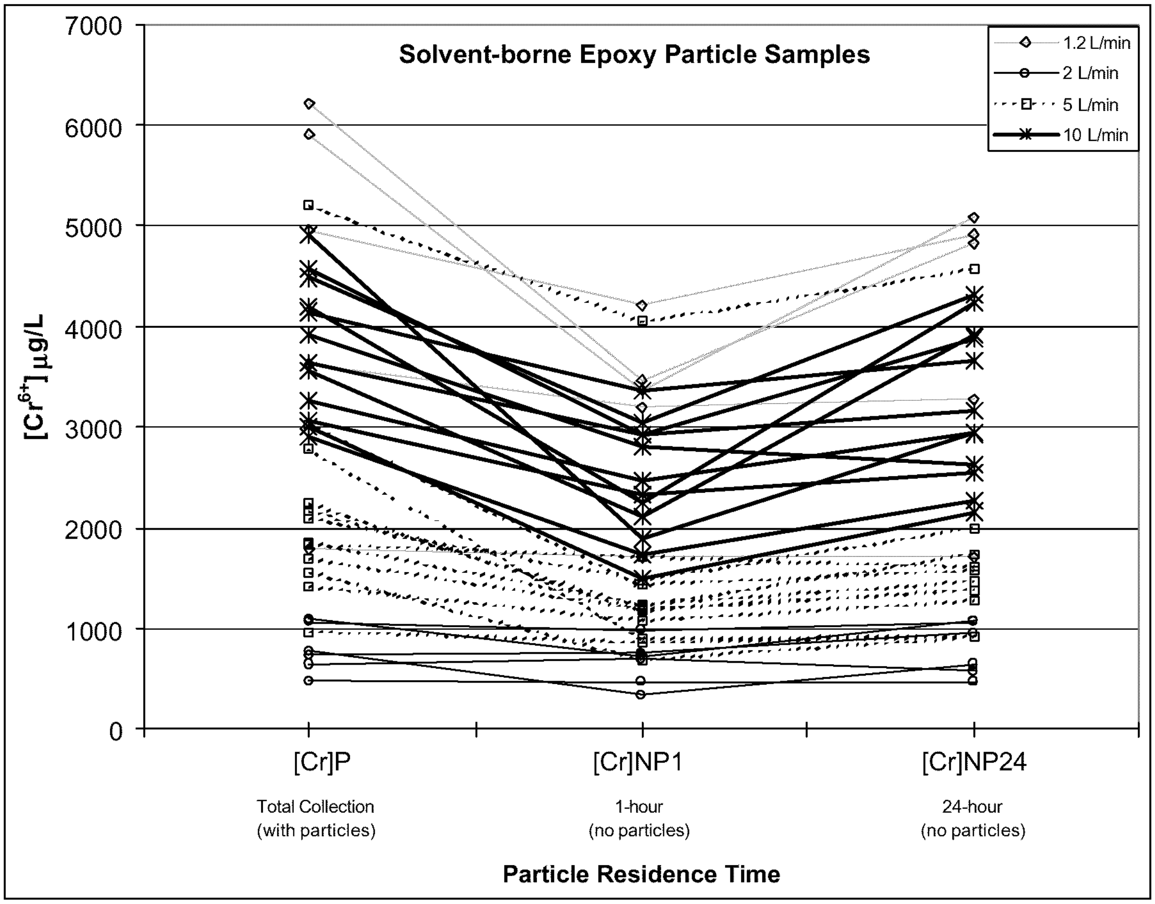





Solvent-borne Epoxy Particle Size Distributions
(Flow Rate: 5 L/min)
Particles/mL
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Particle Diameter (µm)

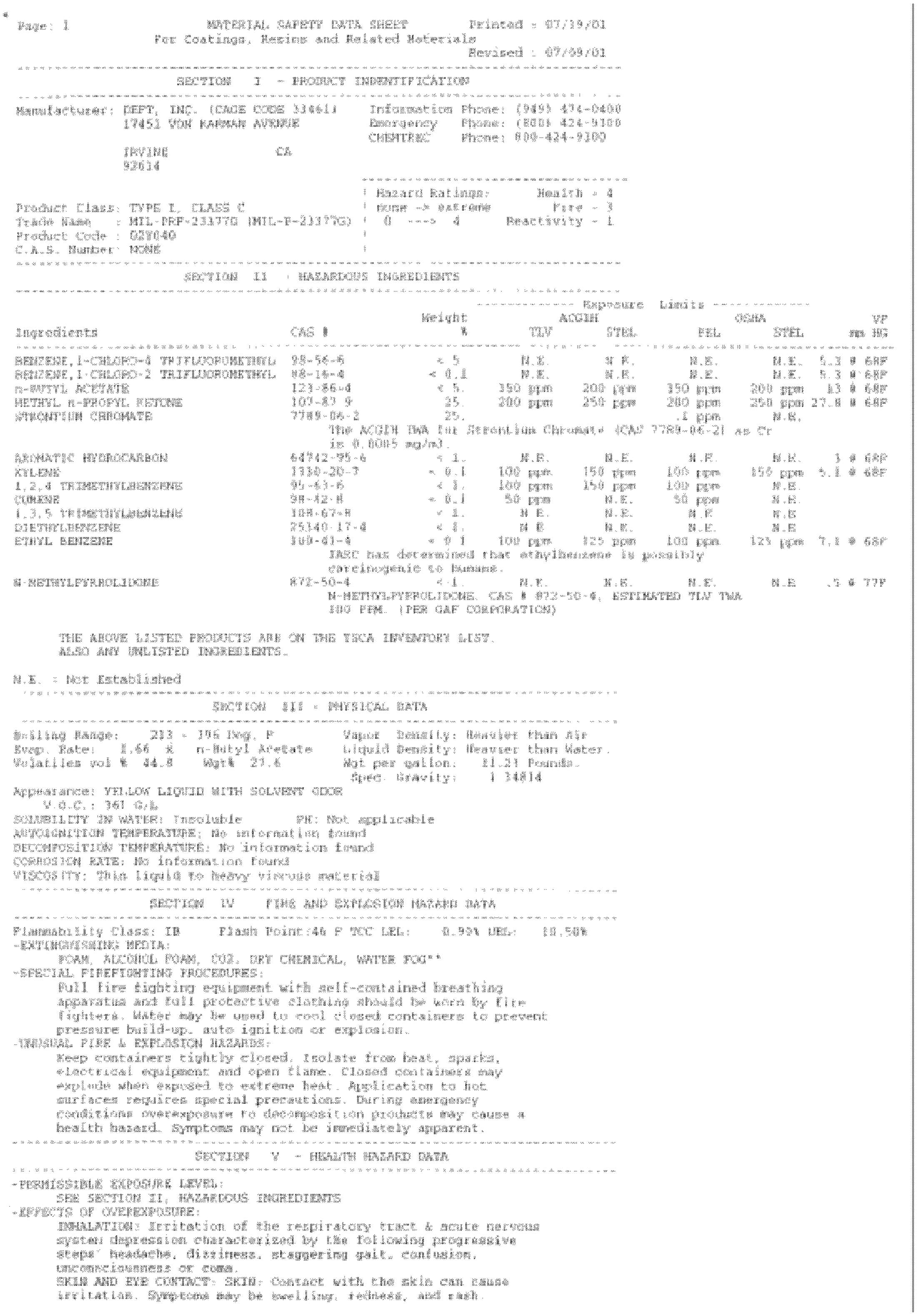

Solvent-borne Epoxy Particle Size Distributions
(Flow Rate: 10 L/min)
Particles/mL
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Particle Diameter (µm)

Appendix A-3: Solvent-borne Epoxy Particle Sample DI [Cr^{6+}] vs. Time



The chart above depicts the Cr^{6+} concentration data from the data summary table (Appendix A-1). Lines connect [Cr]P, the concentration of total Cr^{6+} collected (including that in particles) in each sample, to that sample's 1-hour ([Cr]NP1) and 24-hour ([Cr]NP24) concentration from dissociated Cr^{6+} (i.e. with particles removed).

Appendix A-4a: Deft® Solvent-borne Epoxy Primer (Base) MSDS Excerpt



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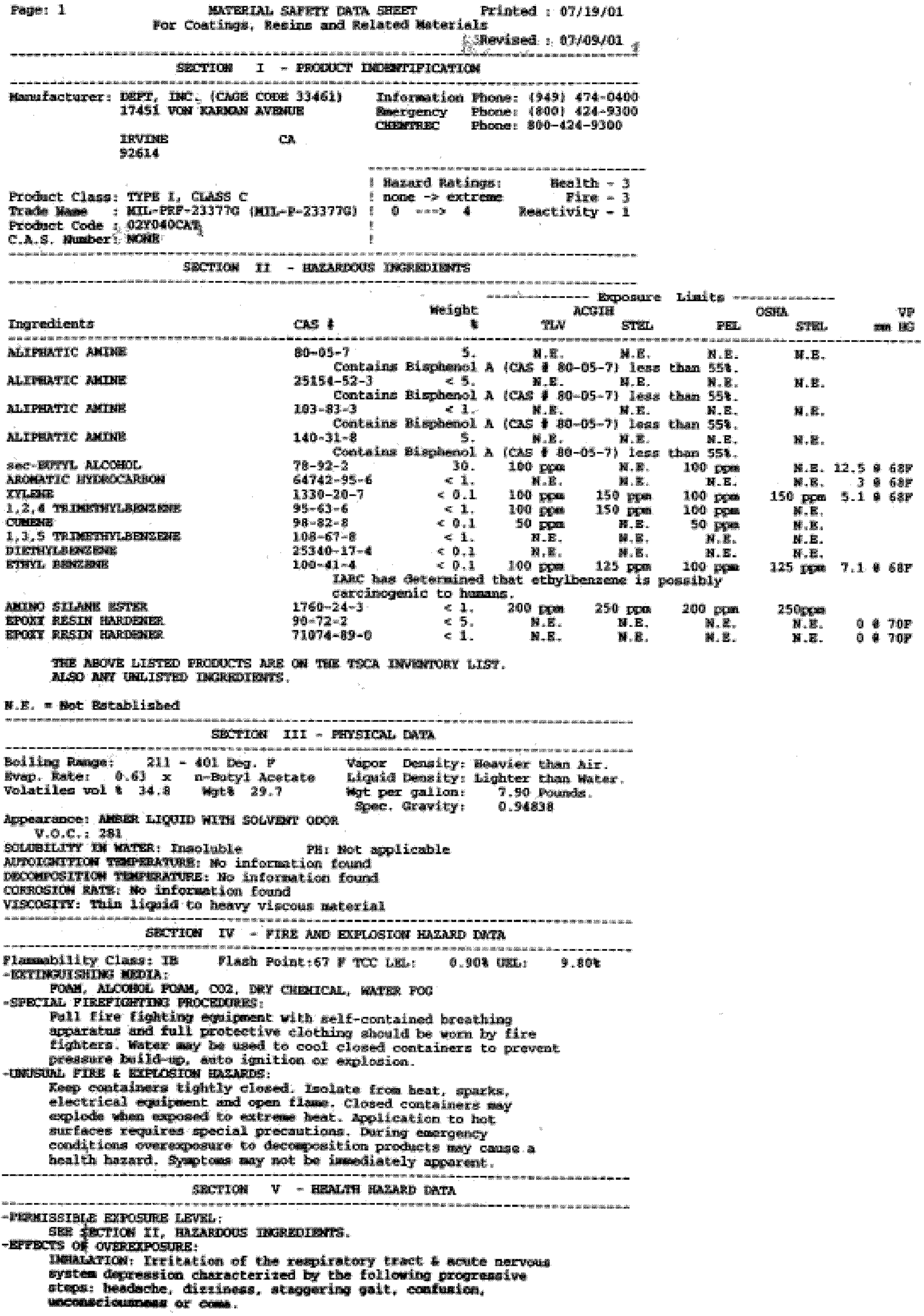
Page: 1                  MATERIAL SAFETY DATA SHEET        Printed : 07/19/01
                For Coatings, Resins and Related Materials
                                                          Revised : 07/09/01
------------------------------------------------------------------------------
                     SECTION   I  - PRODUCT INDENTIFICATION
------------------------------------------------------------------------------
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
                                               ------------------------------------
                                               | Hazard Ratings:       Health - 4
Product Class: TYPE I, CLASS C                 | none -> extreme        Fire - 3
Trade Name    : MIL-PRF-23377G (MIL-P-23377G)  |  0 ---> 4        Reactivity - 1
Product Code : 02Y040                          |
C.A.S. Number: NONE                            |
------------------------------------------------------------------------------
                      SECTION  II  - HAZARDOUS INGREDIENTS
------------------------------------------------------------------------------
                                                      ------------- Exposure  Limits -------------
                                            Weight          ACGIH                    OSHA              VP
Ingredients                      CAS #         %         TLV        STEL         PEL        STEL      mm HG
----------------------------------------------------------------------------------------------------------
BENZENE,1-CHLORO-4 TRIFLUOROMETHYL  98-56-6      < 5        N.E.        N.E.        N.E.        N.E.   5.3 @ 68F
BENZENE,1-CHLORO-2 TRIFLUOROMETHYL  88-16-4      < 0.1      N.E.        N.E.        N.E.        N.E.   5.3 @ 68F
n-BUTYL ACETATE                     123-86-4     < 5.     150 ppm     200 ppm     150 ppm     200 ppm   13 @ 68F
METHYL n-PROPYL KETONE              107-87-9       25.    200 ppm     250 ppm     200 ppm     250 ppm 27.8 @ 68F
STRONTIUM CHROMATE                  7789-06-2      25.                             .1 ppm       N.E.
                                        The ACGIH TWA for Strontium Chromate (CAS 7789-06-2) as Cr
                                        is 0.0005 mg/m3.
AROMATIC HYDROCARBON                64742-95-6   < 1.       N.E.        N.E.        N.E.        N.E.     3 @ 68F
XYLENE                              1330-20-7    < 0.1    100 ppm     150 ppm     100 ppm     150 ppm  5.1 @ 68F
1,2,4 TRIMETHYLBENZENE              95-63-6      < 1.     100 ppm     150 ppm     100 ppm       N.E.
CUMENE                              98-82-8      < 0.1     50 ppm       N.E.       50 ppm       N.E.
1,3,5 TRIMETHYLBENZENE              108-67-8     < 1.       N.E.        N.E.        N.E.        N.E.
DIETHYLBENZENE                      25340-17-4   < 1.       N.E.        N.E.        N.E.        N.E.
ETHYL BENZENE                       100-41-4     < 0.1    100 ppm     125 ppm     100 ppm     125 ppm  7.1 @ 68F
                                        IARC has determined that ethylbenzene is possibly
                                        carcinogenic to humans.
N-METHYLPYRROLIDONE                 872-50-4     < 1.       N.E.        N.E.        N.E.        N.E.    .5 @ 77F
                                        N-METHYLPYRROLIDONE, CAS # 872-50-4, ESTIMATED TLV TWA
                                        100 PPM. (PER GAF CORPORATION)

       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 - 396 Deg. F          Vapor  Density: Heavier than Air
Evap. Rate:    1.66  X   n-Butyl Acetate     Liquid Density: Heavier than Water.
Volatiles vol %  44.8    Wgt%  27.6          Wgt per gallon:   11.21 Pounds.
                                              Spec. Gravity:     1.34814
Appearance: YELLOW LIQUID WITH SOLVENT ODOR
    V.O.C.: 361 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  IV    FIRE AND EXPLOSION HAZARD DATA
------------------------------------------------------------------------------
Flammability Class: IB      Flash Point:46 F TCC LEL:     0.99% UEL:   10.50%
-EXTINGUISHING MEDIA:
      FOAM, ALCOHOL FOAM, CO2, DRY CHEMICAL, WATER FOG**
-SPECIAL FIREFIGHTING PROCEDURES:
      Full fire fighting equipment with self-contained breathing
      apparatus and full protective clothing should be worn by fire
      fighters. Water may be used to cool closed containers to prevent
      pressure build-up. auto ignition or explosion.
-UNUSUAL FIRE & EXPLOSION HAZARDS:
      Keep containers tightly closed. Isolate from heat, sparks,
      electrical equipment and open flame. Closed containers may
      explode when exposed to extreme heat. Application to hot
      surfaces requires special precautions. During emergency
      conditions overexposure to decomposition products may cause a
      health hazard. Symptoms may not be immediately apparent.
------------------------------------------------------------------------------
                       SECTION   V  - HEALTH HAZARD DATA
------------------------------------------------------------------------------
-PERMISSIBLE EXPOSURE LEVEL:
      SEE SECTION II, HAZARDOUS INGREDIENTS
-EFFECTS OF OVEREXPOSURE:
      INHALATION: Irritation of the respiratory tract & acute nervous
      system depression characterized by the following progressive
      steps: headache, dizziness, staggering gait, confusion,
      unconsciousness or coma.
      SKIN AND EYE CONTACT: SKIN: Contact with the skin can cause
      irritation. Symptoms may be swelling, redness, and rash.
```

Appendix A-4b: Deft® Solvent-borne Epoxy Primer (Catalyst) MSDS Excerpt



Page: 1 MATERIAL SAFETY DATA SHEET Printed : 07/19/01
For Coatings, Resins and Related Materials
Revised : 07/09/01

SECTION I - PRODUCT INDENTIFICATION

Manufacturer: DEFT, INC. (CAGE CODE 33461)
17451 VON KARMAN AVENUE

IRVINE CA
92614

Information Phone: (949) 474-0400
Emergency Phone: (800) 424-9300
CHEMTREC Phone: 800-424-9300

Product Class: TYPE I, CLASS C
Trade Name : MIL-PRF-23377G (MIL-P-23377G)
Product Code : 02Y040CAT
C.A.S. Number: NONE

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

SECTION II - HAZARDOUS INGREDIENTS

			Exposure Limits				
		Weight	ACGIH			OSHA	VP
Ingredients	CAS #	%	TLV	STEL	PEL	STEL	mm HG
ALIPHATIC AMINE	80-05-7	5.	N.E.	N.E.	N.E.	N.E.	
	Contains Bisphenol A (CAS # 80-05-7) less than 55%.						
ALIPHATIC AMINE	25154-52-3	< 5.	N.E.	N.E.	N.E.	N.E.	
	Contains Bisphenol A (CAS # 80-05-7) less than 55%.						
ALIPHATIC AMINE	103-83-3	< 1.	N.E.	N.E.	N.E.	N.E.	
	Contains Bisphenol A (CAS # 80-05-7) less than 55%.						
ALIPHATIC AMINE	140-31-8	5.	N.E.	N.E.	N.E.	N.E.	
	Contains Bisphenol A (CAS # 80-05-7) less than 55%.						
sec-BUTYL ALCOHOL	78-92-2	30.	100 ppm	N.E.	100 ppm	N.E.	12.5 @ 68F
AROMATIC HYDROCARBON	64742-95-6	< 1.	N.E.	N.E.	N.E.	N.E.	3 @ 68F
XYLENE	1330-20-7	< 0.1	100 ppm	150 ppm	100 ppm	150 ppm	5.1 @ 68F
1,2,4 TRIMETHYLBENZENE	95-63-6	< 1.	100 ppm	150 ppm	100 ppm	N.E.	
CUMENE	98-82-8	< 0.1	50 ppm	N.E.	50 ppm	N.E.	
1,3,5 TRIMETHYLBENZENE	108-67-8	< 1.	N.E.	N.E.	N.E.	N.E.	
DIETHYLBENZENE	25340-17-4	< 0.1	N.E.	N.E.	N.E.	N.E.	
ETHYL BENZENE	100-41-4	< 0.1	100 ppm	125 ppm	100 ppm	125 ppm	7.1 @ 68F
	IARC has determined that ethylbenzene is possibly carcinogenic to humans.						
AMINO SILANE ESTER	1760-24-3	< 1.	200 ppm	250 ppm	200 ppm	250ppm	
EPOXY RESIN HARDENER	90-72-2	< 5.	N.E.	N.E.	N.E.	N.E.	0 @ 70F
EPOXY RESIN HARDENER	71074-89-0	< 1.	N.E.	N.E.	N.E.	N.E.	0 @ 70F

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 - 401 Deg. F
Evap. Rate: 0.63 x n-Butyl Acetate
Volatiles vol % 34.8 Wgt% 29.7

Vapor Density: Heavier than Air.
Liquid Density: Lighter than Water.
Wgt per gallon: 7.90 Pounds.
Spec. Gravity: 0.94838

Appearance: AMBER LIQUID WITH SOLVENT ODOR
V.O.C.: 281
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 IV - FIRE AND EXPLOSION HAZARD DATA

Flammability Class: IB Flash Point:67 F TCC LEL: 0.90% UEL: 9.80%

-EXTINGUISHING MEDIA:
FOAM, ALCOHOL FOAM, CO2, DRY CHEMICAL, WATER FOG

-SPECIAL FIREFIGHTING PROCEDURES:
Full fire fighting equipment with self-contained breathing apparatus and full protective clothing should be worn by fire fighters. Water may be used to cool closed containers to prevent pressure build-up, auto ignition or explosion.

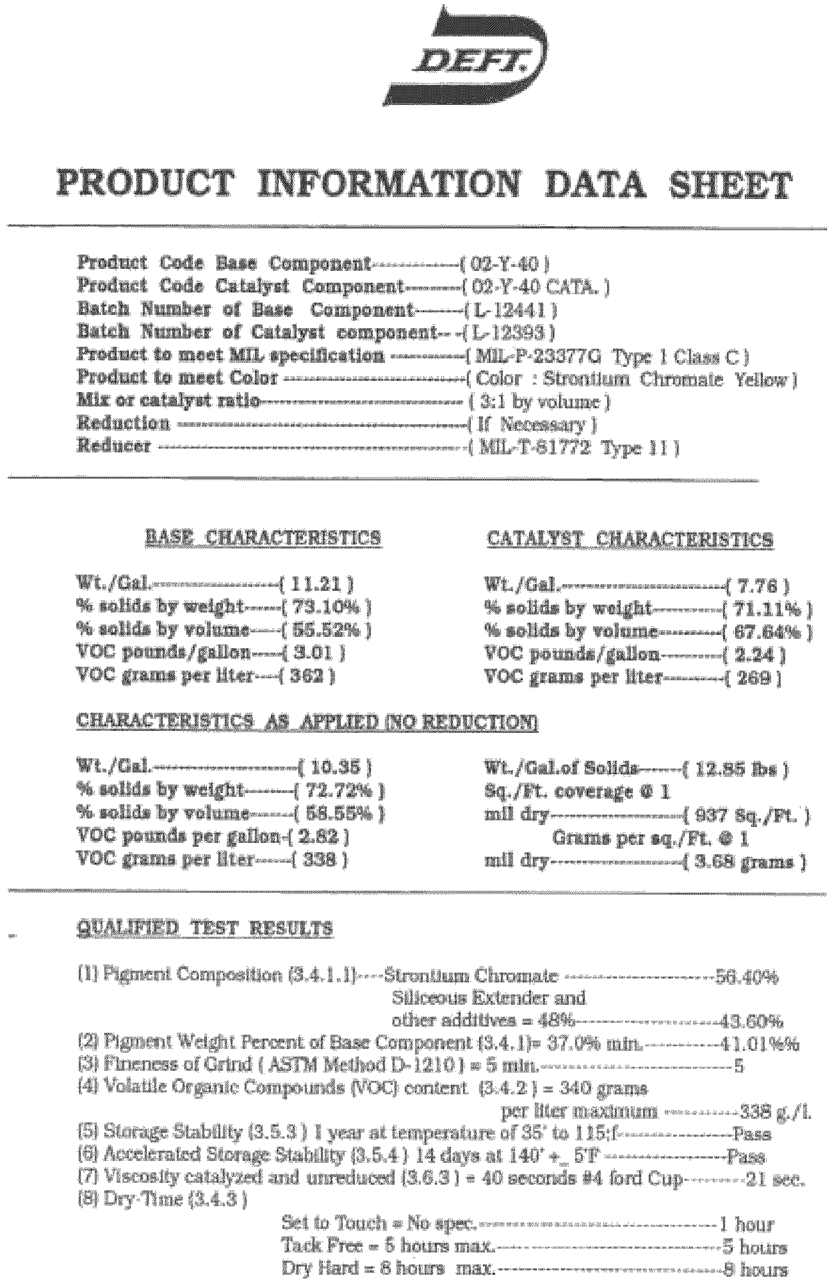
-UNUSUAL FIRE & EXPLOSION HAZARDS:
Keep containers tightly closed. Isolate from heat, sparks, electrical equipment and open flame. Closed containers may explode when exposed to extreme heat. Application to hot surfaces requires special precautions. During emergency conditions overexposure to decomposition products may cause a health hazard. Symptoms may not be immediately apparent.

SECTION V - HEALTH HAZARD DATA

-PERMISSIBLE EXPOSURE LEVEL:
SEE SECTION II, HAZARDOUS INGREDIENTS.

-EFFECTS OF OVEREXPOSURE:
INHALATION: Irritation of the respiratory tract & acute nervous system depression characterized by the following progressive steps: headache, dizziness, staggering gait, confusion, unconsciousness or coma.

Appendix A-5: Deft® Solvent Epoxy Primer Product Information Data Sheet



DEFT.

PRODUCT INFORMATION DATA SHEET

Product Code Base Component-----------(02-Y-40)
Product Code Catalyst Component--------(02-Y-40 CATA.)
Batch Number of Base Component--------(L-12441)
Batch Number of Catalyst component--(L-12393)
Product to meet MIL specification -----------(MIL-P-23377G Type I Class C)
Product to meet Color ---------------------------(Color : Strontium Chromate Yellow)
Mix or catalyst ratio------------------------------ (3:1 by volume)
Reduction ---(If Necessary)
Reducer ---(MIL-T-81772 Type II)

BASE CHARACTERISTICS

Wt./Gal.-----------------(11.21)
% solids by weight-----(73.10%)
% solids by volume----(55.52%)
VOC pounds/gallon----(3.01)
VOC grams per liter---(362)

CATALYST CHARACTERISTICS

Wt./Gal.-----------------------(7.76)
% solids by weight----------(71.11%)
% solids by volume---------(67.64%)
VOC pounds/gallon---------(2.24)
VOC grams per liter--------(269)

CHARACTERISTICS AS APPLIED (NO REDUCTION)

Wt./Gal.--------------------(10.35)
% solids by weight--------(72.72%)
% solids by volume-------(58.55%)
VOC pounds per gallon-(2.82)
VOC grams per liter-----(338)

Wt./Gal.of Solids------(12.85 lbs)
Sq./Ft. coverage @ 1 mil dry-----------------(937 Sq./Ft.)
Grams per sq./Ft. @ 1 mil dry-----------------(3.68 grams)

QUALIFIED TEST RESULTS

(1) Pigment Composition (3.4.1.1)---Strontium Chromate ----------------------56.40%
Siliceous Extender and
other additives = 48%--------------------------43.60%
(2) Pigment Weight Percent of Base Component (3.4.1)= 37.0% min.-----------41.01%%
(3) Fineness of Grind (ASTM Method D-1210) = 5 min.----------------------------5
(4) Volatile Organic Compounds (VOC) content (3.4.2) = 340 grams
per liter maximum ----------338 g./l.
(5) Storage Stability (3.5.3) 1 year at temperature of 35° to 115;f------------------Pass
(6) Accelerated Storage Stability (3.5.4) 14 days at 140° +_ 5°F -----------------Pass
(7) Viscosity catalyzed and unreduced (3.6.3) = 40 seconds #4 ford Cup--------21 sec.
(8) Dry-Time (3.4.3)
Set to Touch = No spec.------------------------------------1 hour
Tack Free = 5 hours max.----------------------------------5 hours
Dry Hard = 8 hours max.-----------------------------------8 hours

(9) Condition in Container (3.5.1) ---(**Base Component**) Will stir into a smooth,
homogeneous condition.
(**Catalyst Component**) Will be clear & clean.
(10) Adhesion (3.7.4) No loss of adhesion after 24 hours of water immersion
at temperature of 65° to 85°F -------------------No Adhesion Loss
(11) Induction Time (4.5.1) 30 minutes maximum-----------------------------------30 min.
(12) Application of primer coating (4.5.1) Apply film at 0.6 to 0.9 mils----------0.9 mils
(13) Water Resistance (3.6.1) Topcoated primer immersed for 4 days
at 120°F +_5°F = No Defects-----------------No defects
(sl. lose of color)
(14) Flexibility (3.7.5) Impact elongation = 10%-------------------------------------

(15) Lifting 3.7.3) No lifting of MIL-C-85285B Polyurethane
Topcoat after:
Topcoat @ 2 hours (no spec.)-----------------No Lifting
Topcoat @ 3 hours (no spec.)-----------------No Lifting
Topcoat @ 5 hours-----------------------------No Lifting
(16) Strippability 3.7.6) Within 60 minutes with a stripper conforming
to MIL-R-81294, Type 1 = 90% minimum---------------99%
(17) Salt Spray Resistance (3.8.2.1.1) 2000 hours with a 5% solution
No blistering, lifting or corrosion---------No Defect
(18) Topcoating (3.5.11) To be topcoated with a polyurethane conforming
to MIL-C-85285B. Color # 17925-------------------No lifting
(19) Filiform (3.8.2.2) After 1000 hours at 104°F and a relative
humidity of 80 +_5% = No Defects--------------------- -No Defects
(20) Pot-Life (3.6.4) After 4 hours at room temperature 65° to 85°F
catalyzed and unreduced =70 seconds maximum-----------30 sec.
(21) Fluid Resistance (3.8.4) No softening, blistering, loss of adhesion
or film defects after 24 hours at 250°F
MIL-L-23699-----------------------------------No Defects
MIL-H-83282-----------------------------------No Defects

EPOXY POLYAMIDE PRIMER DESCRIPTION AND APPLICATION INFORMATION

DESCRIPTION :

Chemically cured two component epoxy-polyamide primer suitable for application on aircraft and aerospace equipment. Component 1 contains the pigment and epoxy resin. Component 11 is the clear non-pigmented aliphatic polyamine-epoxy portion which acts as the hardener or curing agent for Component 1.

AIR POLLUTION REGULATIONS :

This product is formulated for use where the air pollution regulations call out for a maximum VOC of 340 grams per liter.

SPECIAL FEATURES :

This epoxy-polyamide primer is a solvent borne, corrosion inhibiting and chemical and solvent resistant primer

APPLICATION :

This primer will spray satisfactorily in all respects and shall show no running, sagging or streaking. The dry film shall show no dusting, mottling or color separation and shall present a smooth finish free from seeds. The standard film thickness shall be 0.6 to 0.9 mils dry.

Appendix B:

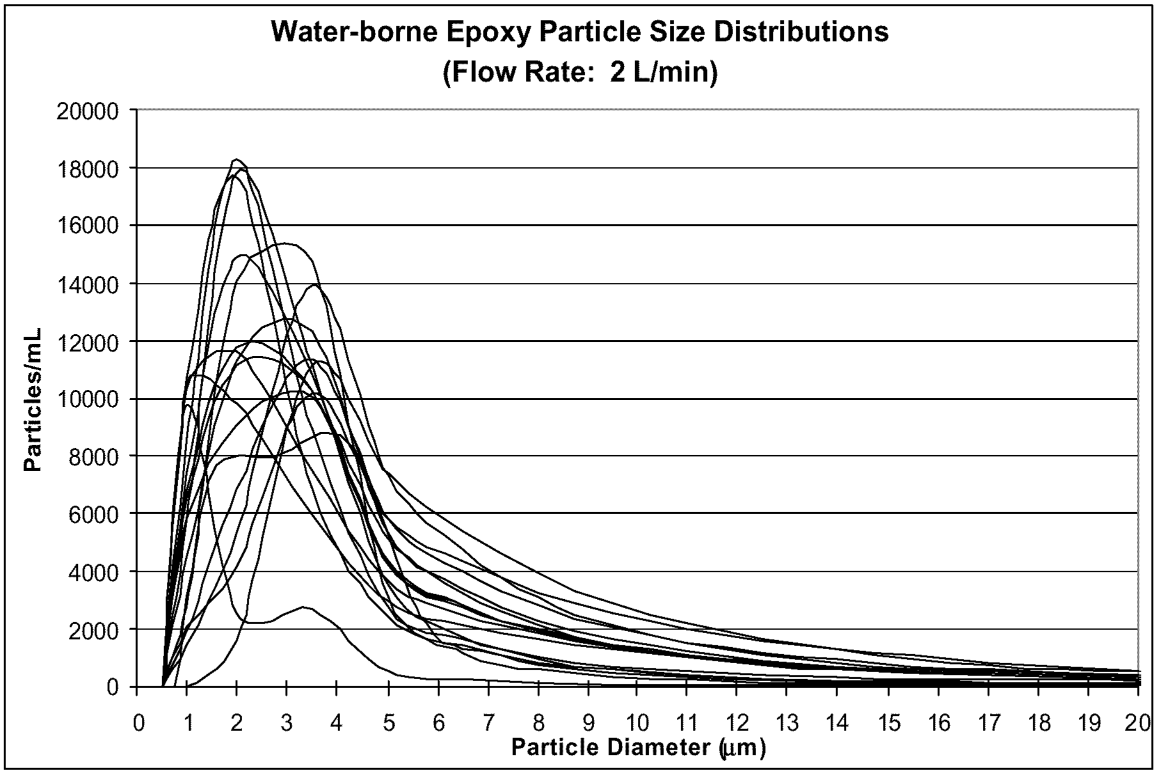
Deft® 44-GN-72 Water-borne Epoxy Polyamide Primer (MIL-P-85582B)

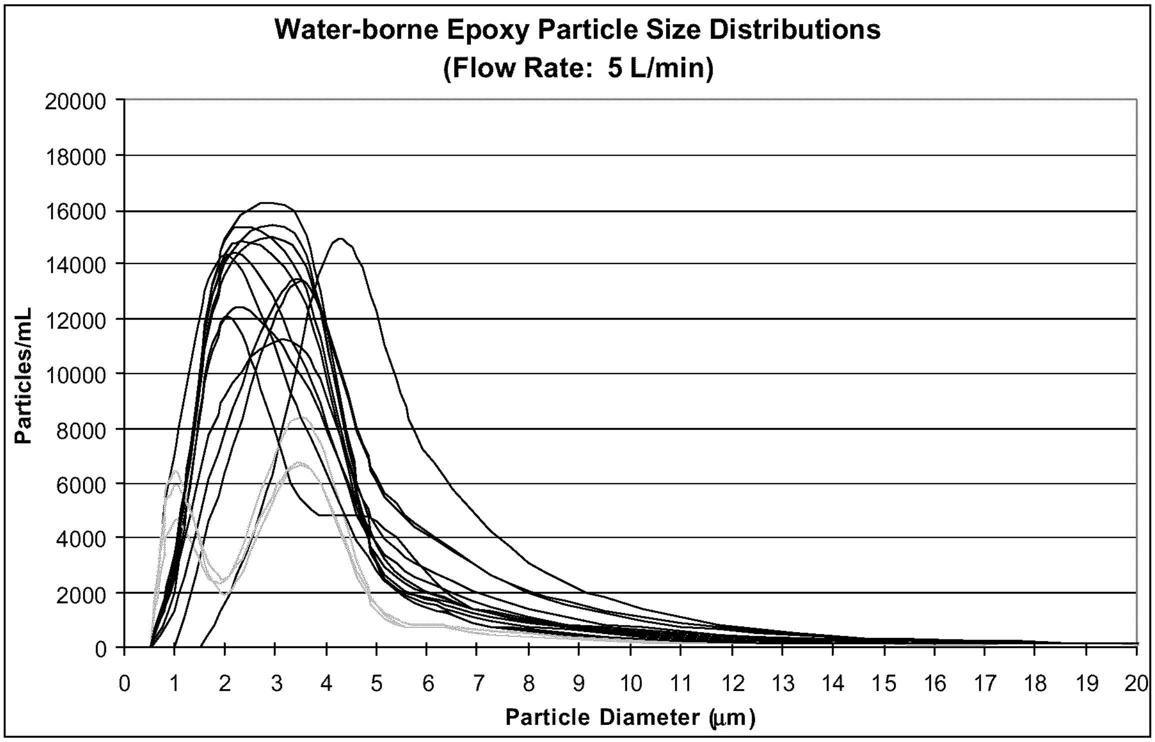
Appendix B-1: Water-borne Epoxy Data Summary

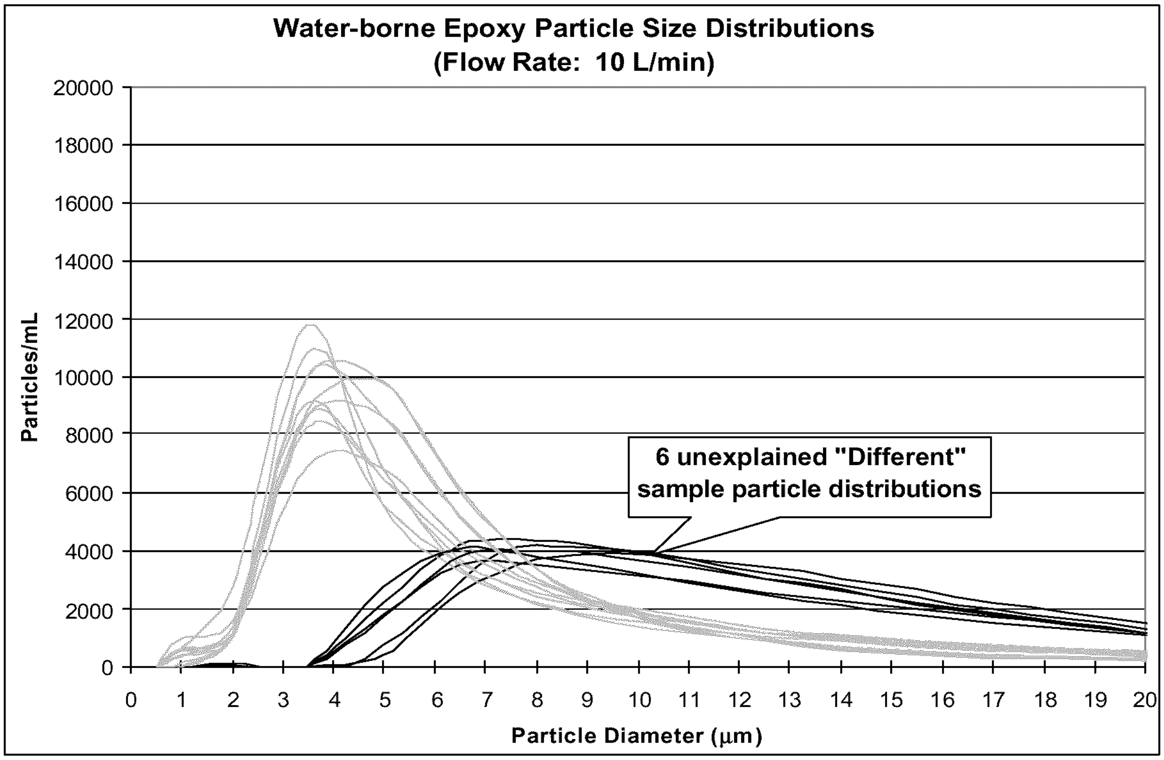
Flow Rate (L/min)	Particle Number Concentrations: Particle Size Bins (µm)																					
	0.5	1.0	2.0	3.5	5.0	6.5	8.0	9.5	11.0	12.5	14.0	15.5	17.0	18.5	≥20	ΣN_i	$[Cr]_P$ (µg/L)	$[Cr]_{NP1}$ (µg/L)	f_1	$[Cr]_{NP24}$ (µg/L)	f_{24}	Δf_t
2	0	7,386	7,929	8,443	2,164	1,060	605	388	249	174	136	121	118	119	597	29,489	6,833	3,349	49%	3,269	48%	-1%
2	0	1,899	6,852	11,352	5,832	4,004	2,798	2,042	1,560	1,162	950	722	575	462	1,705	41,916	5,600	4,137	74%	4,508	81%	7%
2	0	6,449	11,130	10,244	4,351	2,826	1,909	1,446	1,100	846	719	595	517	452	2,428	45,012	4,227	3,698	87%	3,738	88%	1%
2	0	4,515	11,300	12,333	5,301	3,297	2,127	1,496	1,078	830	637	497	411	338	1,436	45,596	4,522	3,848	85%	3,740	83%	-2%
2	0	5,764	17,791	11,160	3,504	1,741	968	594	355	255	205	166	143	139	661	43,445	4,009	2,971	74%	4,085	102%	28%
2	0	0	1,615	11,145	7,360	5,416	3,930	2,898	2,151	1,658	1,257	962	761	600	2,379	42,133	8,416	4,668	55%	5,246	62%	7%
2	0	10,299	11,623	7,476	3,660	2,520	1,829	1,332	999	772	601	480	379	331	1,283	43,582	3,881	2,857	74%	3,426	88%	15%
2	0	5,861	9,067	10,064	5,121	3,415	2,320	1,661	1,213	893	696	543	444	375	1,650	43,323	3,643	3,108	85%	2,916	80%	-5%
2	0	6,782	11,769	10,255	4,251	2,772	1,967	1,465	1,117	875	716	579	513	430	2,331	45,822	4,291	4,003	93%	3,878	90%	-3%
2	0	10,531	9,826	5,956	2,928	2,144	1,644	1,289	1,014	836	677	557	458	385	1,737	39,981	3,086	1,978	64%	2,479	80%	16%
2	0	2,022	4,162	10,211	5,852	4,347	3,276	2,574	2,014	1,587	1,274	1,060	859	681	2,992	42,909	4,151	2,288	55%	2,651	64%	9%
2	0	1,388	5,293	13,941	7,323	4,747	3,089	2,131	1,516	1,068	826	633	511	425	2,154	45,046	5,950	5,012	84%	5,744	97%	12%
2	0	7,458	14,843	10,824	4,272	2,789	1,912	1,423	1,035	773	603	483	384	335	1,240	48,374	4,084	3,219	79%	3,455	85%	6%
2	0	8,497	18,292	8,915	2,772	1,639	1,047	724	525	400	318	268	242	228	1,074	44,942	4,917	4,059	83%	4,404	90%	7%
2	0	9,741	2,532	2,697	484	231	158	89	62	38	33	35	40	46	220	16,408	1,359	1,146	84%	1,270	93%	9%
2	0	10,666	17,706	6,839	2,428	1,386	838	559	381	279	208	176	141	132	577	42,316	2,512	2,114	84%	2,104	84%	0%
5	0	0	5,172	14,914	7,893	4,273	2,326	1,400	854	542	348	247	195	170	807	39,141	8,007	6,205	77%	6,874	86%	8%
5	0	2,919	14,378	12,945	3,040	1,380	800	523	347	267	219	183	176	168	894	38,240	4,706	3,685	78%	4,189	89%	11%
5	0	2,708	14,899	13,539	3,157	1,499	904	640	436	341	260	226	189	180	922	39,900	5,245	4,189	80%	5,227	100%	20%
5	0	0	6,379	13,404	6,253	3,563	2,005	1,240	768	514	357	270	231	190	1,026	36,200	7,352	4,011	55%	5,701	78%	23%
5	0	2,571	12,030	9,916	3,822	2,005	1,128	656	414	273	202	157	132	125	562	33,993	4,789	2,123	44%	4,188	87%	43%
5	0	4,586	2,391	8,436	1,533	675	367	233	152	112	101	100	104	108	658	19,555	4,005	3,601	90%	3,579	89%	-1%
5	0	7,017	14,375	8,419	2,764	1,620	1,031	701	500	367	262	234	197	181	918	38,585	5,094	4,277	84%	4,566	90%	6%
5	0	2,751	14,037	14,764	3,075	1,139	555	333	230	160	142	130	129	137	833	38,415	4,567	3,535	77%	4,281	94%	16%
5	0	6,459	1,961	6,708	1,579	811	504	346	238	181	137	126	121	114	638	19,922	3,815	3,241	85%	3,221	84%	-1%
5	0	1,300	7,876	13,457	6,081	3,526	2,107	1,333	877	583	413	298	238	198	859	39,144	5,212	3,616	69%	3,836	74%	4%
5	0	2,499	9,133	10,950	4,407	2,432	1,399	875	585	405	302	257	224	193	1,293	34,953	6,444	4,880	76%	6,571	102%	26%
5	0	1,992	12,073	5,367	4,612	1,844	946	609	412	288	233	195	183	174	981	29,909	6,238	5,898	95%	5,784	93%	-2%
5	0	5,934	2,547	6,774	1,377	647	369	236	163	109	103	93	95	101	546	19,096	4,883	4,487	92%	4,846	99%	7%
5	0	2,888	14,967	15,541	3,063	1,186	661	411	284	208	166	150	144	140	799	40,606	3,889	3,871	100%	3,840	99%	-1%
5	0	3,382	13,659	14,269	3,741	1,697	978	646	477	365	298	259	231	215	1,187	41,405	4,815	3,925	82%	4,274	89%	7%
10	0	0	0	0	1,688	3,876	4,142	3,892	3,473	2,988	2,592	2,164	1,806	1,475	6,025	34,120	14,974	8,714	58%	10,722	72%	13%
10	0	538	1,377	10,834	6,832	3,469	2,212	1,636	1,276	1,036	852	721	602	492	2,291	34,168	7,517	6,386	85%	6,493	86%	1%
10	0	0	1,112	8,246	6,413	3,671	2,448	1,892	1,495	1,203	1,012	853	700	614	2,917	32,576	11,576	8,691	75%	11,676	101%	26%
10	0	0	0	0	1,784	3,511	3,497	3,228	2,917	2,550	2,252	1,958	1,685	1,445	7,003	31,829	10,204	5,418	53%	7,409	73%	20%
10	0	0	0	0	399	2,551	3,665	3,914	3,731	3,419	3,063	2,634	2,228	1,864	7,691	35,159	12,749	5,902	46%	8,665	68%	22%
10	0	940	1,588	9,071	5,559	3,563	2,540	1,992	1,544	1,203	997	810	682	554	2,325	33,369	8,763	5,835	67%	7,228	82%	16%
10	0	646	2,761	11,792	5,558	3,302	2,135	1,523	1,120	821	636	488	405	327	1,536	33,050	9,404	5,749	61%	6,486	69%	8%
10	0	603	1,137	6,891	6,817	4,314	2,905	2,167	1,680	1,310	1,088	877	738	606	2,817	33,949	7,483	6,270	84%	7,495	100%	16%
10	0	317	1,380	8,682	6,485	4,090	2,730	2,022	1,556	1,190	957	749	621	512	2,444	33,736	7,018	4,274	61%	4,937	70%	9%
10	0	0	137	0	2,783	4,081	3,802	3,355	2,898	2,480	2,084	1,784	1,525	1,283	5,960	32,172	9,942	7,566	76%	9,619	97%	21%
10	0	0	54	0	1,672	3,772	4,005	3,809	3,419	2,993	2,604	2,188	1,842	1,513	6,361	34,233	10,228	5,286	52%	6,492	63%	12%
10	0	583	1,135	8,568	8,615	5,207	3,059	2,091	1,498	1,116	854	690	541	441	1,830	36,227	13,336	8,058	60%	9,157	69%	8%
10	0	106	1,176	9,980	8,580	5,121	3,021	1,947	1,339	952	705	525	403	327	1,294	35,475	12,702	8,267	65%	10,960	86%	21%
10	0	404	991	8,803	9,756	6,135	3,337	1,979	1,248	855	612	458	346	287	1,389	36,600	9,171	7,815	85%	8,344	91%	6%
10	0	0	1,015	9,991	9,828	6,056	3,404	2,070	1,309	838	574	408	292	241	902	36,927	13,113	8,293	63%	8,811	67%	4%
d_p	0.750	1.50	2.75	4.25	5.75	7.25	8.75	10.3	11.8	13.3	14.8	16.3	17.8	19.3	≥20.8							
d_{ae}	0.750	1.50	2.77	4.35	5.92	7.48	9.03	10.6	12.1	13.6	15.2	16.7	18.3	19.9	≥21.5							
v_{Cr}	0.036%	0.051%	0.095%	0.24%	0.31%	0.34%	0.34%	0.31%	0.28%	0.30%	0.31%	0.32%	0.33%	0.34%	0.35%							

▨ = Flame AAS results

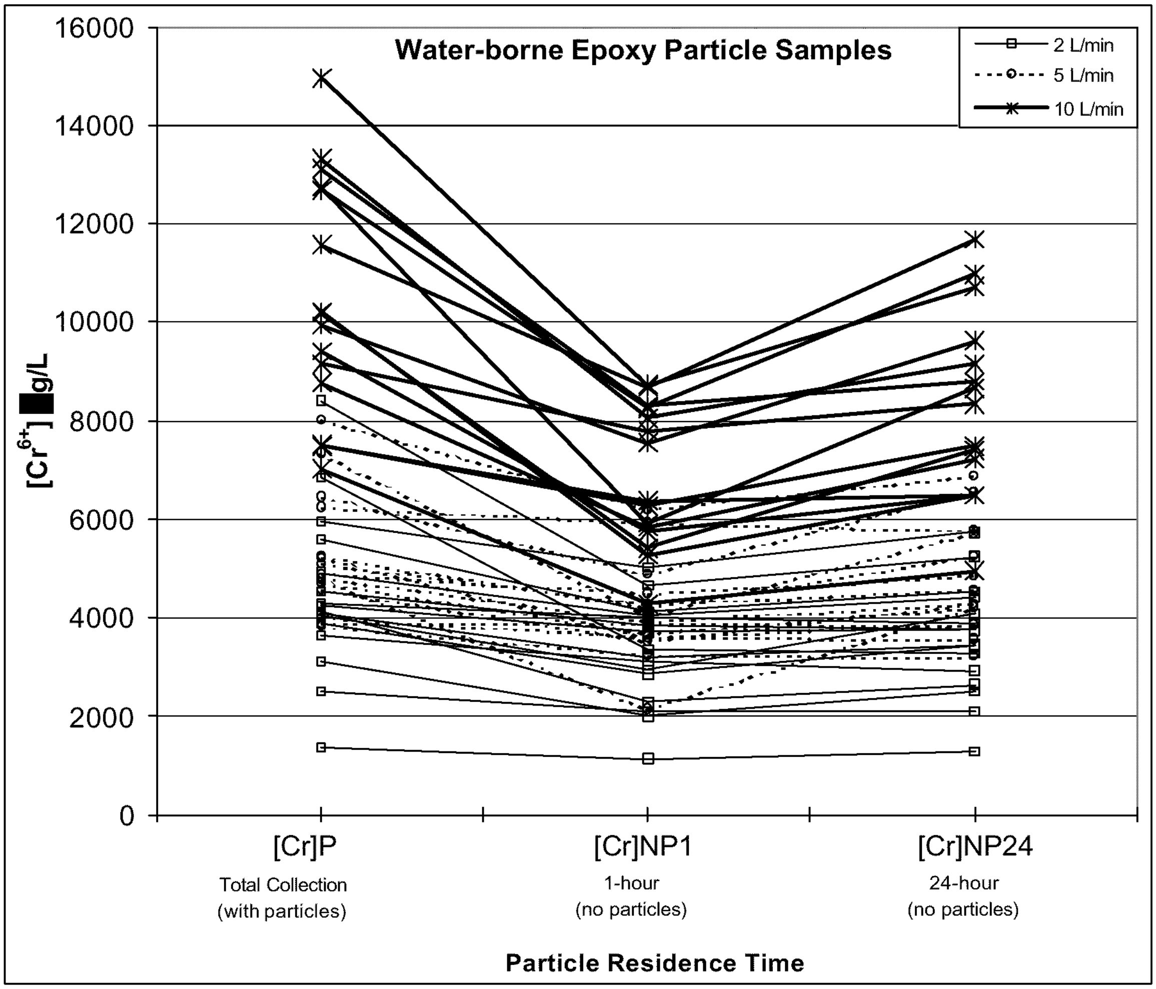
Appendix B-2: Water-borne Epoxy Particle Size Distributions by Flow Rate





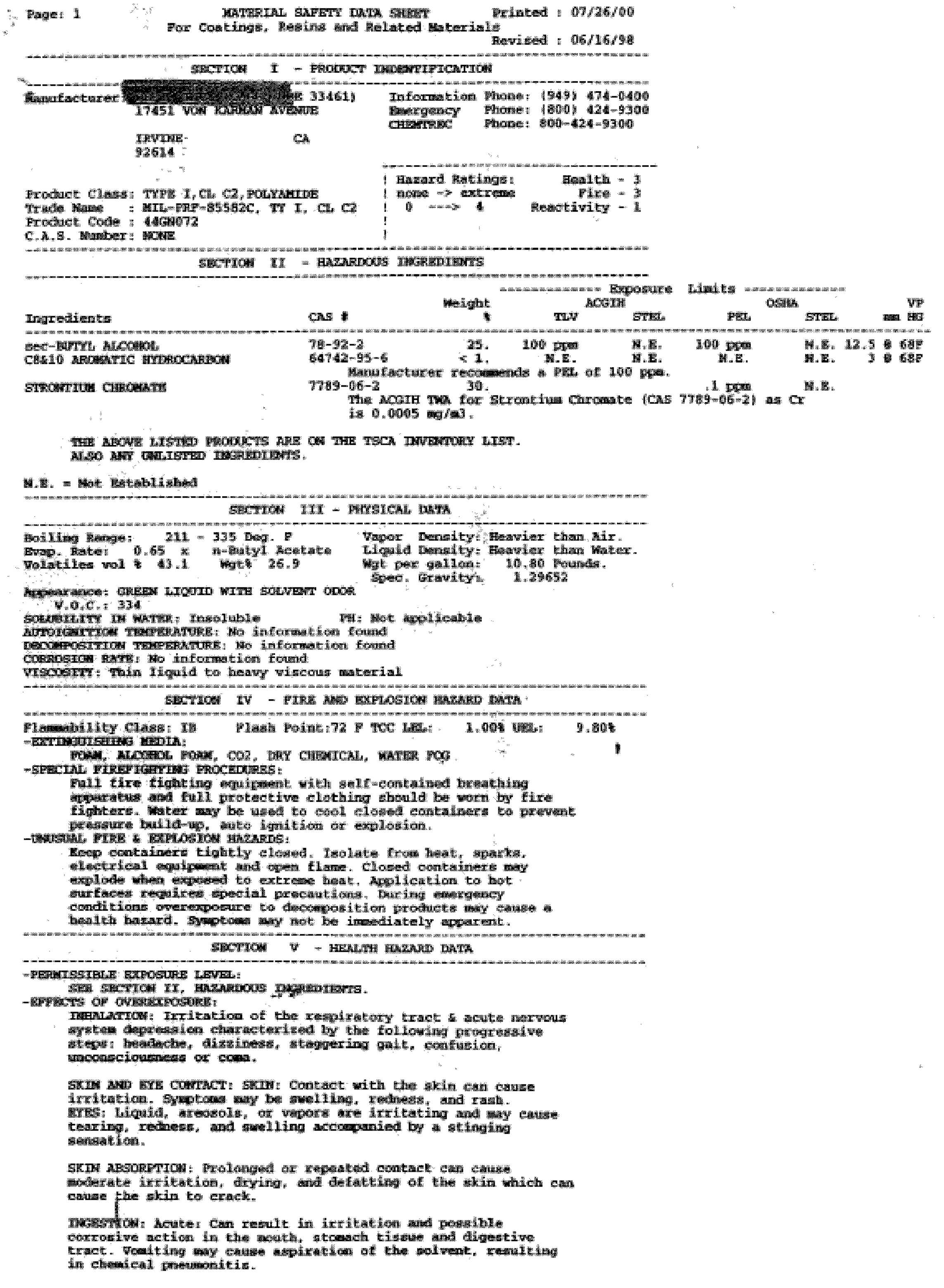

Water-borne Epoxy Particle Size Distributions
(Flow Rate: 10 L/min)
Particles/mL
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Particle Diameter (μm)
6 unexplained "Different" sample particle distributions

Appendix B-3: Water-borne Epoxy Particle Sample DI [Cr^{6+}] vs. Time



The chart above depicts the Cr^{6+} concentration data from the data summary table (Appendix B-1). Lines connect [Cr]P, the concentration of total Cr^{6+} collected (including that in particles) in each sample, to that sample's 1-hour ([Cr]NP1) and 24-hour ([Cr]NP24) concentration from dissociated Cr^{6+} (i.e. with particles removed).

Appendix B-4a: Deft® Water-borne Epoxy Primer (Base) MSDS Excerpt



Page: 1 MATERIAL SAFETY DATA SHEET Printed : 07/26/00
For Coatings, Resins and Related Materials
Revised : 06/16/98

SECTION I - PRODUCT INDENTIFICATION

Manufacturer: [redacted] 33461)
17451 VON KARMAN AVENUE

IRVINE CA
92614

Information Phone: (949) 474-0400
Emergency Phone: (800) 424-9300
CHEMTREC Phone: 800-424-9300

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

Product Class: TYPE I, CL C2, POLYAMIDE
Trade Name : MIL-PRF-85582C, TY I, CL C2
Product Code : 44GN072
C.A.S. Number: NONE

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	ACGIH TLV	ACGIH STEL	OSHA PEL	OSHA STEL	VP mm HG
sec-BUTYL ALCOHOL	78-92-2	25.	100 ppm	N.E.	100 ppm	N.E.	12.5 @ 68F
C8&10 AROMATIC HYDROCARBON	64742-95-6	< 1.	N.E.	N.E.	N.E.	N.E.	3 @ 68F
	Manufacturer recommends a PEL of 100 ppm.						
STRONTIUM CHROMATE	7789-06-2	30.			.1 ppm	N.E.	
	The ACGIH TWA for Strontium Chromate (CAS 7789-06-2) as Cr is 0.0005 mg/m3.						

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 - 335 Deg. F
Evap. Rate: 0.65 x n-Butyl Acetate
Volatiles vol % 43.1 Wgt% 26.9
Vapor Density: Heavier than Air.
Liquid Density: Heavier than Water.
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

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

Flammability Class: IB Flash Point:72 F TCC LEL: 1.00% UEL: 9.80%

-EXTINGUISHING MEDIA:
FOAM, ALCOHOL FOAM, CO2, DRY CHEMICAL, WATER FOG

-SPECIAL FIREFIGHTING PROCEDURES:
Full fire fighting equipment with self-contained breathing apparatus and full protective clothing should be worn by fire fighters. Water may be used to cool closed containers to prevent pressure build-up, auto ignition or explosion.

-UNUSUAL FIRE & EXPLOSION HAZARDS:
Keep containers tightly closed. Isolate from heat, sparks, electrical equipment and open flame. Closed containers may explode when exposed to extreme heat. Application to hot surfaces requires special precautions. During emergency conditions overexposure to decomposition products may cause a health hazard. Symptoms may not be immediately apparent.

SECTION V - HEALTH HAZARD DATA

-PERMISSIBLE EXPOSURE LEVEL:
SEE SECTION II, HAZARDOUS INGREDIENTS.

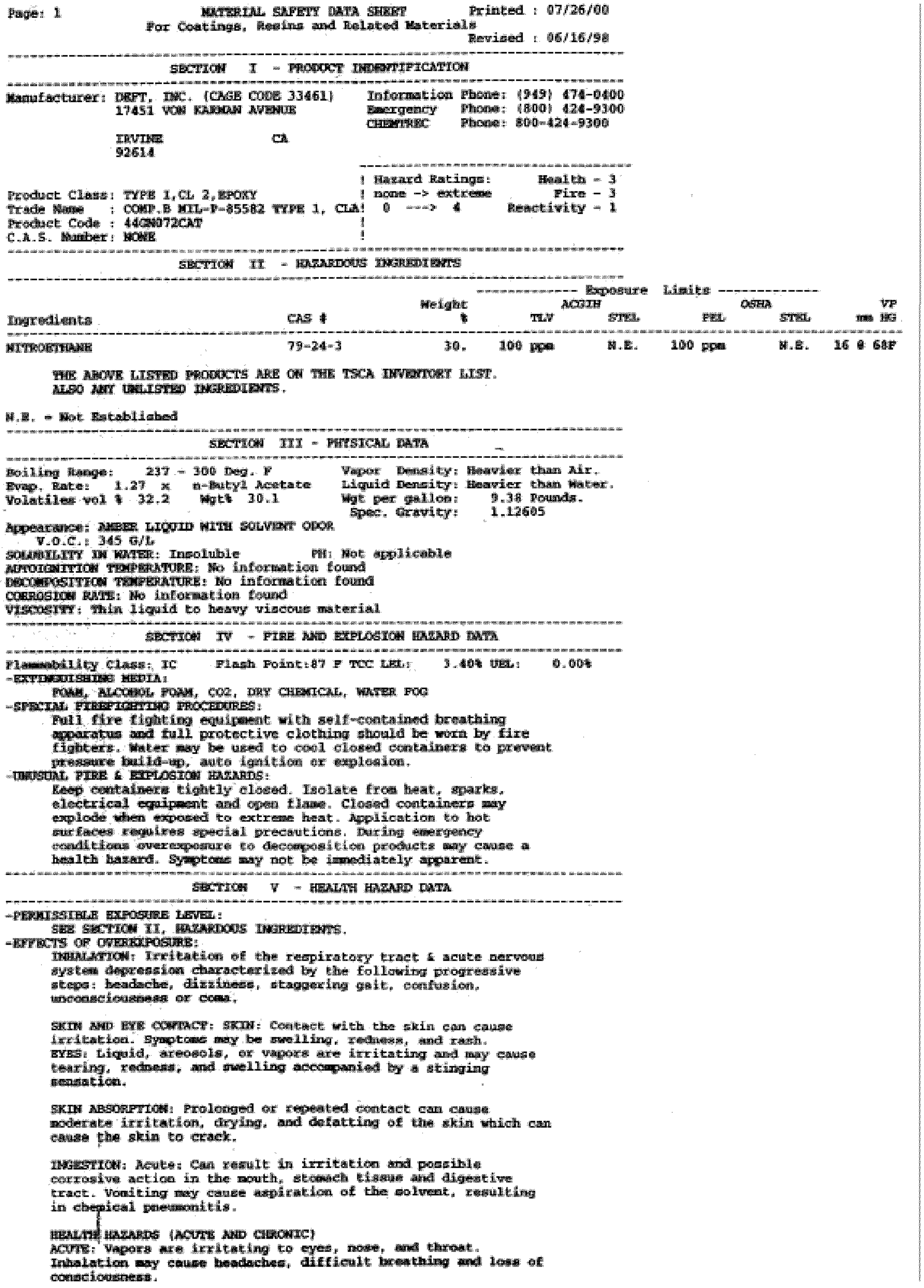
-EFFECTS OF OVEREXPOSURE:
INHALATION: Irritation of the respiratory tract & acute nervous system depression characterized by the following progressive steps: headache, dizziness, staggering gait, confusion, unconsciousness or coma.

SKIN AND EYE CONTACT: SKIN: Contact with the skin can cause irritation. Symptoms may be swelling, redness, and rash. EYES: Liquid, areosols, or vapors are irritating and may cause tearing, redness, and swelling accompanied by a stinging sensation.

SKIN ABSORPTION: Prolonged or repeated contact can cause moderate irritation, drying, and defatting of the skin which can cause the skin to crack.

INGESTION: Acute: Can result in irritation and possible corrosive action in the mouth, stomach tissue and digestive tract. Vomiting may cause aspiration of the solvent, resulting in chemical pneumonitis.

Appendix B-4b: Deft® Water-borne Epoxy Primer (Catalyst) MSDS Excerpt



Page: 1 MATERIAL SAFETY DATA SHEET Printed : 07/26/00
For Coatings, Resins and Related Materials
Revised : 06/16/98

SECTION I - PRODUCT INDENTIFICATION

Manufacturer: DEFT, INC. (CAGE CODE 33461)
17451 VON KARMAN AVENUE

IRVINE CA
92614

Information Phone: (949) 474-0400
Emergency Phone: (800) 424-9300
CHEMTREC Phone: 800-424-9300

Product Class: TYPE 1,CL 2,EPOXY
Trade Name : COMP.B MIL-P-85582 TYPE 1, CLA
Product Code : 44GN072CAT
C.A.S. Number: NONE

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

SECTION II - HAZARDOUS INGREDIENTS

			Exposure Limits				
			ACGIH		OSHA		
Ingredients	CAS #	Weight %	TLV	STEL	PEL	STEL	VP mm HG
NITROETHANE	79-24-3	30.	100 ppm	N.E.	100 ppm	N.E.	16 @ 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: 237 - 300 Deg. F
Evap. Rate: 1.27 x n-Butyl Acetate
Volatiles vol % 32.2 Wgt% 30.1
Vapor Density: Heavier than Air.
Liquid Density: Heavier than Water.
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: Insolubile 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 IV - FIRE AND EXPLOSION HAZARD DATA

Flammability Class: IC Flash Point:87 F TCC LEL: 3.40% UEL: 0.00%

-EXTINGUISHING MEDIA:
FOAM, ALCOHOL FOAM, CO2, DRY CHEMICAL, WATER FOG

-SPECIAL FIREFIGHTING PROCEDURES:
Full fire fighting equipment with self-contained breathing apparatus and full protective clothing should be worn by fire fighters. Water may be used to cool closed containers to prevent pressure build-up, auto ignition or explosion.

-UNUSUAL FIRE & EXPLOSION HAZARDS:
Keep containers tightly closed. Isolate from heat, sparks, electrical equipment and open flame. Closed containers may explode when exposed to extreme heat. Application to hot surfaces requires special precautions. During emergency conditions overexposure to decomposition products may cause a health hazard. Symptoms may not be immediately apparent.

SECTION V - HEALTH HAZARD DATA

-PERMISSIBLE EXPOSURE LEVEL:
SEE SECTION II, HAZARDOUS INGREDIENTS.

-EFFECTS OF OVEREXPOSURE:
INHALATION: Irritation of the respiratory tract & acute nervous system depression characterized by the following progressive steps: headache, dizziness, staggering gait, confusion, unconsciousness or coma.

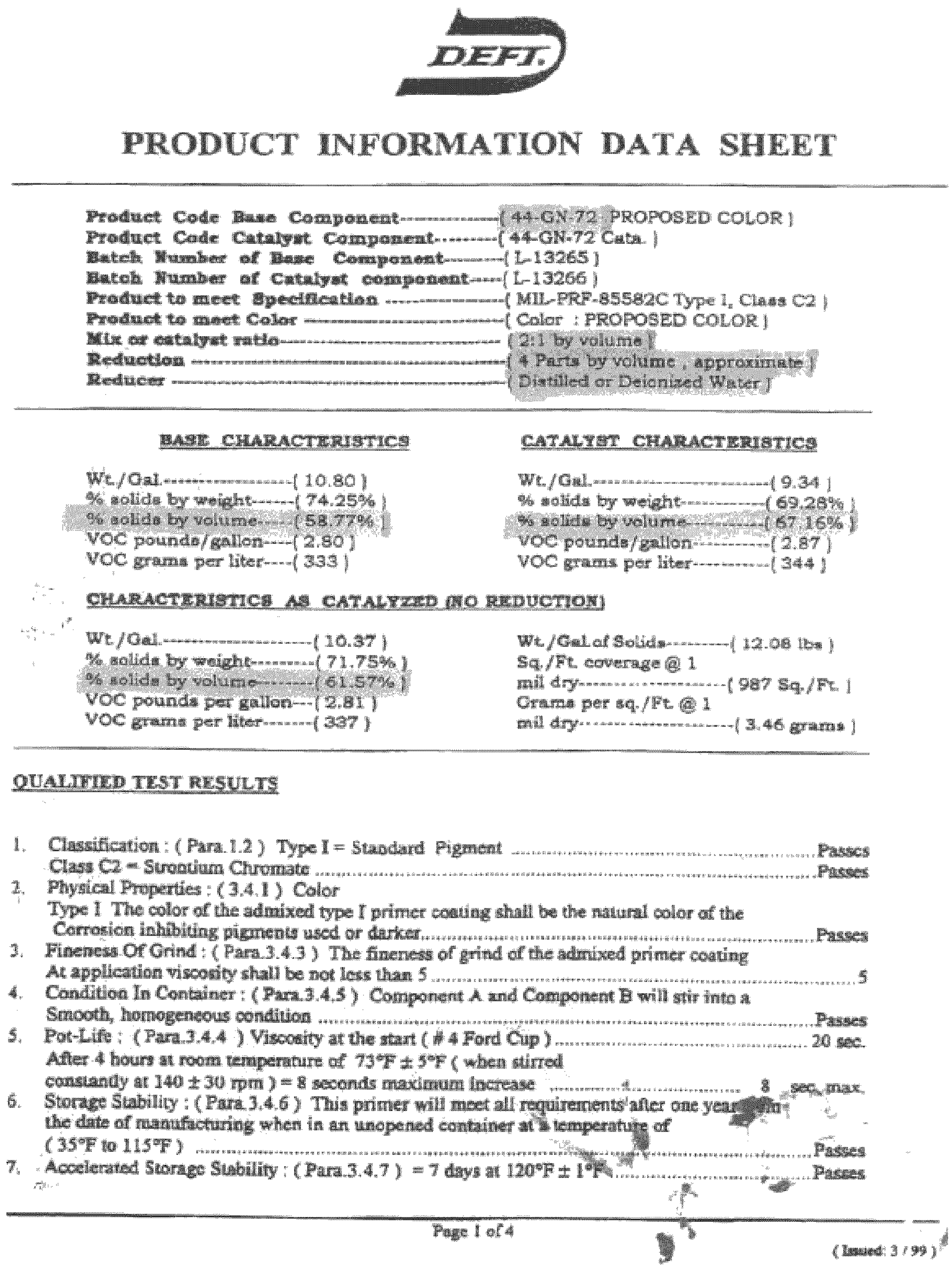
SKIN AND EYE CONTACT: SKIN: Contact with the skin can cause irritation. Symptoms may be swelling, redness, and rash.
EYES: Liquid, areosols, or vapors are irritating and may cause tearing, redness, and swelling accompanied by a stinging sensation.

SKIN ABSORPTION: Prolonged or repeated contact can cause moderate irritation, drying, and defatting of the skin which can cause the skin to crack.

INGESTION: Acute: Can result in irritation and possible corrosive action in the mouth, stomach tissue and digestive tract. Vomiting may cause aspiration of the solvent, resulting in chemical pneumonitis.

HEALTH HAZARDS (ACUTE AND CHRONIC)
ACUTE: Vapors are irritating to eyes, nose, and throat. Inhalation may cause headaches, difficult breathing and loss of consciousness.

Appendix B-5: Deft® Water Epoxy Primer Product Information Data Sheet



DEFT.

PRODUCT INFORMATION DATA SHEET

Product Code Base Component------------(44-GN-72 PROPOSED COLOR)
Product Code Catalyst Component--------(44-GN-72 Cata.)
Batch Number of Base Component---------(L-13265)
Batch Number of Catalyst component----(L-13266)
Product to meet Specification ----------------(MIL-PRF-85582C Type I, Class C2)
Product to meet Color --------------------------(Color : PROPOSED COLOR)
Mix or catalyst ratio---------------------------(2:1 by volume)
Reduction ---(4 Parts by volume , approximate)
Reducer ---(Distilled or Deionized Water)

BASE CHARACTERISTICS		CATALYST CHARACTERISTICS	
Wt./Gal.	(10.80)	Wt./Gal.	(9.34)
% solids by weight	(74.25%)	% solids by weight	(69.28%)
% solids by volume	(58.77%)	% solids by volume	(67.16%)
VOC pounds/gallon	(2.80)	VOC pounds/gallon	(2.87)
VOC grams per liter	(333)	VOC grams per liter	(344)

CHARACTERISTICS AS CATALYZED (NO REDUCTION)

Wt./Gal.---------------------(10.37)
% solids by weight---------(71.75%)
% solids by volume---------(61.57%)
VOC pounds per gallon---(2.81)
VOC grams per liter--------(337)

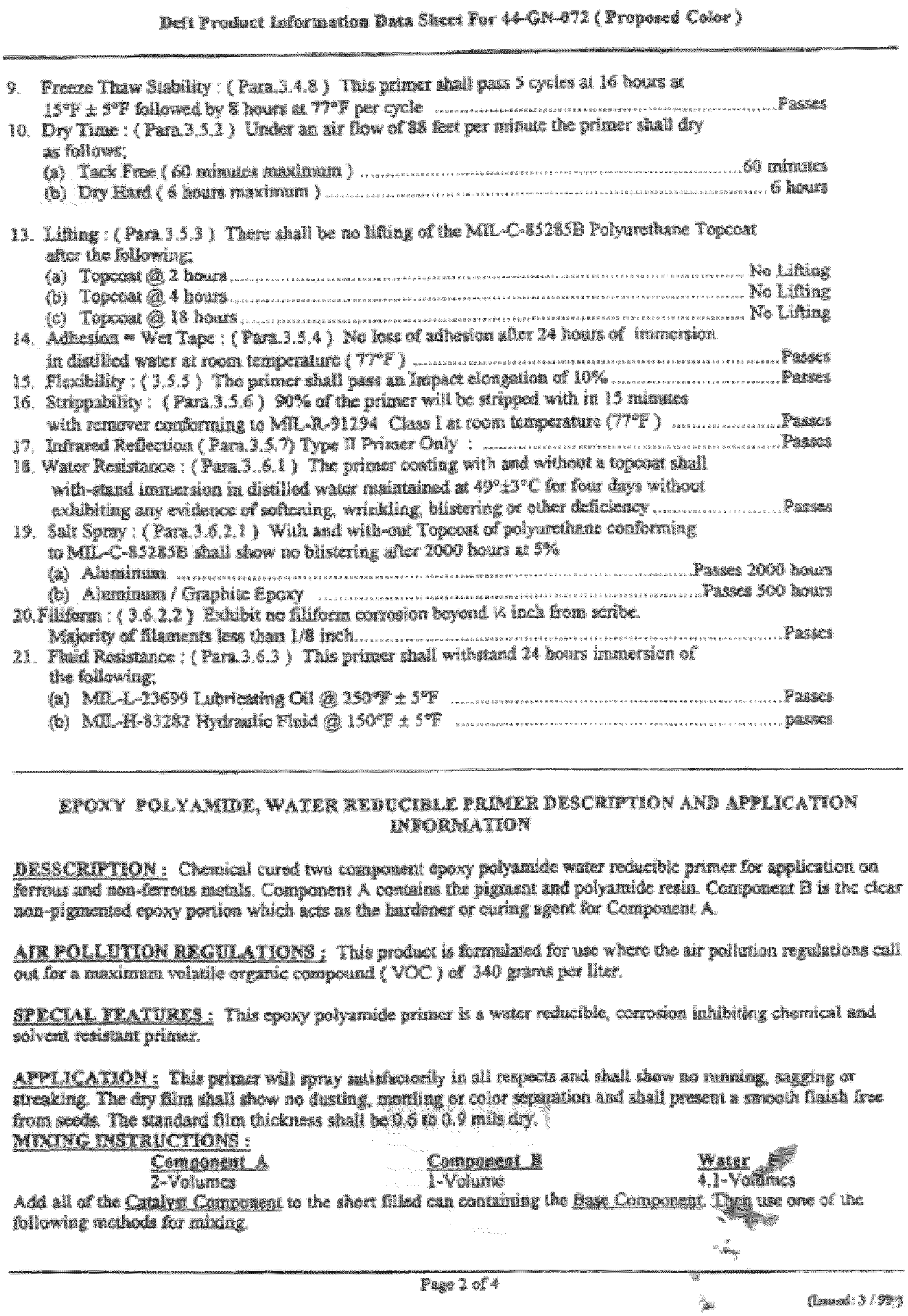
Wt./Gal. of Solids-----------(12.08 lbs)
Sq./Ft. coverage @ 1
mil dry-------------------------(987 Sq./Ft.)
Grams per sq./Ft. @ 1
mil dry-------------------------(3.46 grams)

QUALIFIED TEST RESULTS

1. Classification : (Para.1.2) Type I = Standard Pigment .... Passes
   Class C2 = Strontium Chromate .... Passes
2. Physical Properties : (3.4.1) Color
   Type I The color of the admixed type I primer coating shall be the natural color of the Corrosion inhibiting pigments used or darker.. Passes
3. Fineness Of Grind : (Para.3.4.3) The fineness of grind of the admixed primer coating At application viscosity shall be not less than 5 5
4. Condition In Container : (Para.3.4.5) Component A and Component B will stir into a Smooth, homogeneous condition .... Passes
5. Pot-Life : (Para.3.4.4) Viscosity at the start (# 4 Ford Cup) .... 20 sec.
   After 4 hours at room temperature of 73°F ± 5°F (when stirred constantly at 140 ± 30 rpm) = 8 seconds maximum increase .... 8 sec. max.
6. Storage Stability : (Para.3.4.6) This primer will meet all requirements after one year [illegible] the date of manufacturing when in an unopened container at a temperature of (35°F to 115°F) .... Passes
7. Accelerated Storage Stability : (Para.3.4.7) = 7 days at 120°F ± 1°F.. Passes

Page 1 of 4

(Issued: 3 / 99)



9. Freeze Thaw Stability : (Para.3.4.8) This primer shall pass 5 cycles at 16 hours at
   15°F ± 5°F followed by 8 hours at 77°F per cycle .... Passes
10. Dry Time : (Para.3.5.2) Under an air flow of 88 feet per minute the primer shall dry
    as follows;
    (a) Tack Free (60 minutes maximum) .... 60 minutes
    (b) Dry Hard (6 hours maximum) .... 6 hours

13. Lifting : (Para.3.5.3) There shall be no lifting of the MIL-C-85285B Polyurethane Topcoat
    after the following;
    (a) Topcoat @ 2 hours .... No Lifting
    (b) Topcoat @ 4 hours .... No Lifting
    (c) Topcoat @ 18 hours .... No Lifting
14. Adhesion = Wet Tape : (Para.3.5.4) No loss of adhesion after 24 hours of immersion
    in distilled water at room temperature (77°F) .... Passes
15. Flexibility : (3.5.5) The primer shall pass an Impact elongation of 10% .... Passes
16. Strippability : (Para.3.5.6) 90% of the primer will be stripped with in 15 minutes
    with remover conforming to MIL-R-91294 Class I at room temperature (77°F) .... Passes
17. Infrared Reflection (Para.3.5.7) Type II Primer Only : .... Passes
18. Water Resistance : (Para.3..6.1) The primer coating with and without a topcoat shall
    with-stand immersion in distilled water maintained at 49°±3°C for four days without
    exhibiting any evidence of softening, wrinkling, blistering or other deficiency .... Passes
19. Salt Spray : (Para.3.6.2.1) With and with-out Topcoat of polyurethane conforming
    to MIL-C-85285B shall show no blistering after 2000 hours at 5%
    (a) Aluminum .... Passes 2000 hours
    (b) Aluminum / Graphite Epoxy .... Passes 500 hours
20. Filiform : (3.6.2.2) Exhibit no filiform corrosion beyond ¼ inch from scribe.
    Majority of filaments less than 1/8 inch........ Passes
21. Fluid Resistance : (Para.3.6.3) This primer shall withstand 24 hours immersion of
    the following;
    (a) MIL-L-23699 Lubricating Oil @ 250°F ± 5°F .... Passes
    (b) MIL-H-83282 Hydraulic Fluid @ 150°F ± 5°F .... passes

EPOXY POLYAMIDE, WATER REDUCIBLE PRIMER DESCRIPTION AND APPLICATION INFORMATION

DESSCRIPTION : Chemical cured two component epoxy polyamide water reducible primer for application on ferrous and non-ferrous metals. Component A contains the pigment and polyamide resin. Component B is the clear non-pigmented epoxy portion which acts as the hardener or curing agent for Component A.

AIR POLLUTION REGULATIONS ; This product is formulated for use where the air pollution regulations call out for a maximum volatile organic compound (VOC) of 340 grams per liter.

SPECIAL FEATURES : This epoxy polyamide primer is a water reducible, corrosion inhibiting chemical and solvent resistant primer.

APPLICATION : This primer will spray satisfactorily in all respects and shall show no running, sagging or streaking. The dry film shall show no dusting, mottling or color separation and shall present a smooth finish free from seeds. The standard film thickness shall be 0.6 to 0.9 mils dry.

MIXING INSTRUCTIONS :

Component A	Component B	Water
2-Volumes	1-Volume	4.1-Volumes

Add all of the Catalyst Component to the short filled can containing the Base Component. Then use one of the following methods for mixing.

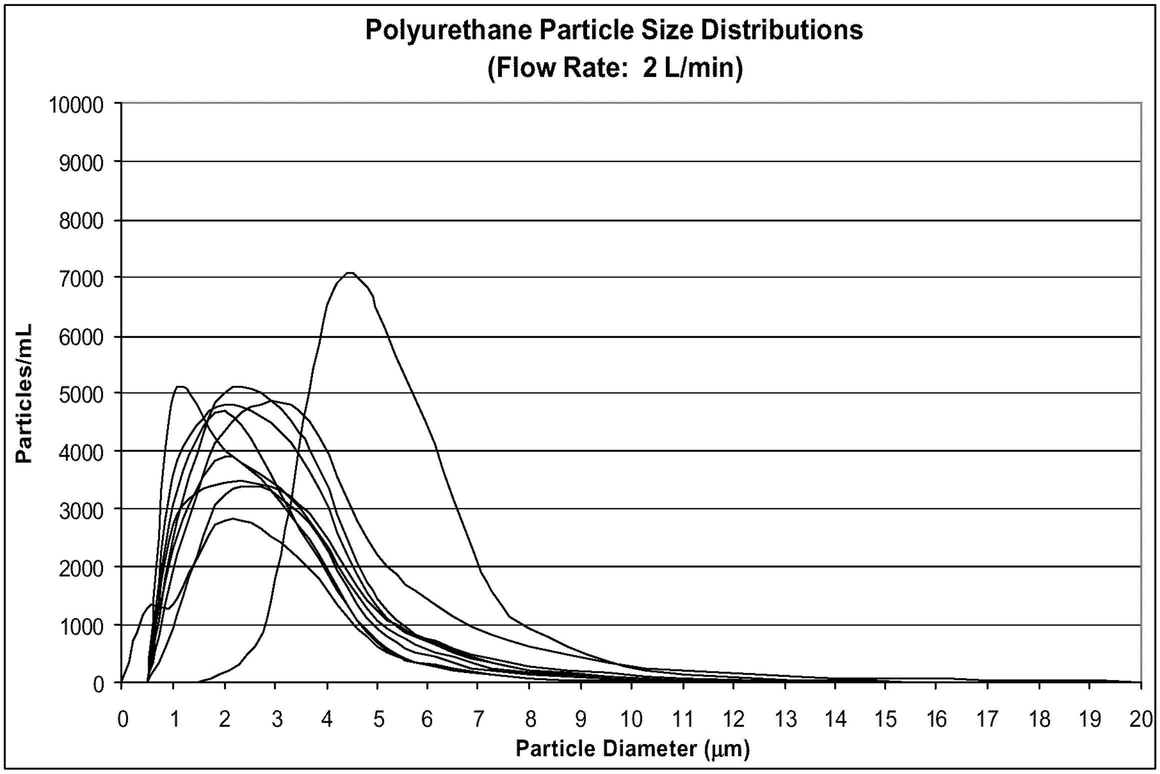
Appendix C:

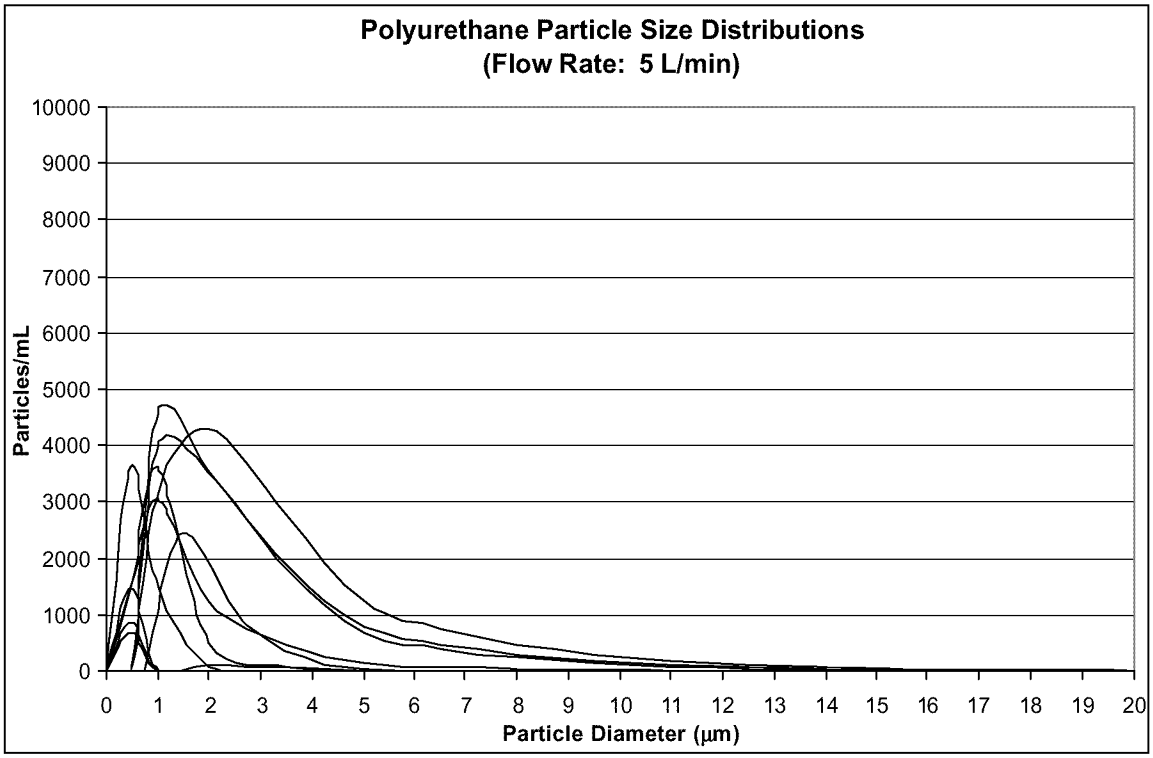
Deft® 09-Y-2 Elastomeric Polyurethane Primer (TT-P-2760A)

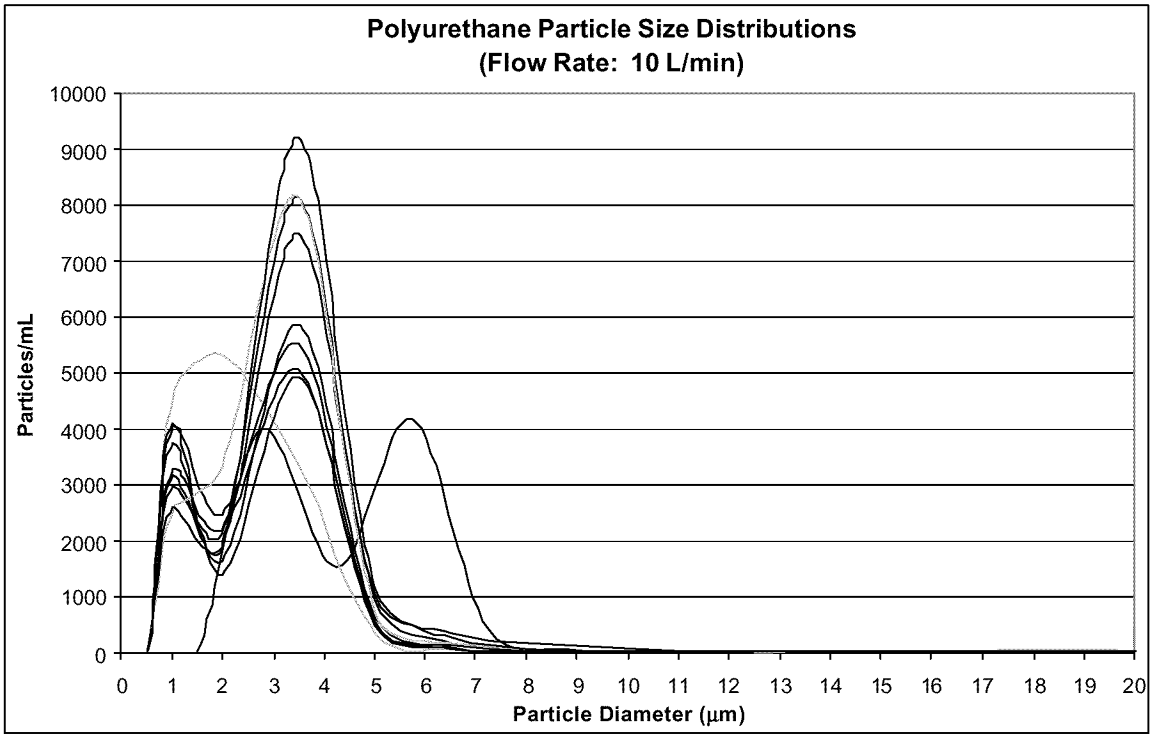
Appendix C-1: Polyurethane Data Summary

Flow Rate (L/min)	Particle Number Concentrations Particle Size Bins (μm)																					
	0.5	1.0	2.0	3.5	5.0	6.5	8.0	9.5	11.0	12.5	14.0	15.5	17.0	18.5	≥20	ΣN_i	$[Cr]_P$ (μg/L)	$[Cr]_{NP1}$ (μg/L)	f_1	$[Cr]_{NP24}$ (μg/L)	f_{24}	Δf_t
2	0	859	6,898	4,911	1,559	620	221	87	28	9	1	0	0	0	0	15,193	1,027	994	97%	918	89%	-7%
2	0	2,319	3,902	2,671	667	214	59	17	5	0	0	0	0	0	0	9,854	547	461	84%	474	87%	2%
2	1,269	1,313	2,802	2,128	608	237	72	28	8	0	0	0	0	0	0	8,465	454	463	102%	506	111%	9%
2	0	3,047	4,695	2,660	713	223	75	21	7	1	0	0	0	0	0	11,441	565	479	85%	511	90%	6%
2	0	920	3,242	2,925	937	355	118	47	14	2	0	0	0	0	0	8,559	689	620	90%	666	97%	7%
2	0	4,925	4,000	3,037	1,068	426	157	58	27	8	5	2	1	1	3	13,718	1,210	1,216	101%	1,278	106%	5%
2	0	1,902	4,365	4,698	2,210	1,147	609	329	184	115	67	47	29	22	39	15,762	2,406	2,229	93%	2,357	98%	5%
2	0	2,454	5,009	4,327	1,455	557	201	86	38	16	7	2	1	1	0	14,156	1,679	1,704	101%	1,684	100%	-1%
2	0	2,725	3,445	3,088	1,239	587	280	141	62	36	16	10	6	3	5	11,643	1,945	1,897	98%	1,864	96%	-2%
2	0	3,583	4,793	3,923	1,302	530	209	90	38	19	7	6	3	2	0	14,505	1,506	1,509	100%	1,486	99%	-2%
5	2,441	828	114	11	3	0	0	0	0	0	0	0	0	0	0	3,397	1,000	952	95%	902	90%	-5%
5	883	0	110	51	11	8	3	2	1	0	0	1	1	0	2	1,072	1,067	979	92%	1,144	107%	15%
5	3,619	1,497	81	0	0	0	0	0	0	0	0	0	0	0	0	5,197	1,160	1,168	101%	1,149	99%	-2%
5	1,479	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1,480	624	652	104%	609	98%	-7%
5	1,469	3,606	526	80	13	4	2	0	0	0	0	0	0	0	0	5,699	1,170	1,204	103%	1,203	103%	0%
5	691	0	0	0	0	0	0	0	0	0	0	0	0	0	15	706	308	317	103%	312	101%	-1%
5	0	4,586	3,552	1,868	782	486	307	196	112	63	41	27	17	11	32	12,078	1,217	1,129	93%	1,205	99%	6%
5	0	4,005	3,538	1,805	701	405	245	144	78	43	28	16	8	7	14	11,036	1,923	1,918	100%	1,847	96%	-4%
5	0	3,163	4,311	2,766	1,221	759	491	287	176	110	64	42	29	20	76	13,515	1,252	1,223	98%	1,218	97%	0%
5	1,500	3,053	1,236	485	156	86	45	21	11	4	4	1	1	0	8	6,611	1,710	1,712	100%	1,689	99%	-1%
10	0	4,017	1,545	4,149	437	83	14	5	10	17	18	27	29	35	193	10,580	1,248	1,605	129%	1,235	99%	-30%
10	0	4,503	5,331	3,342	363	74	19	7	10	12	21	20	26	26	149	13,901	1,091	739	68%	906	83%	15%
10	0	3,720	1,654	5,867	652	125	22	6	14	21	28	32	38	42	277	12,499	796	780	98%	788	99%	1%
10	0	2,969	2,137	8,128	967	202	44	19	21	29	35	44	56	60	415	15,126	952	909	95%	929	98%	2%
10	0	4,106	1,418	4,928	584	100	22	8	14	20	28	32	37	39	237	11,572	1,020	970	95%	975	96%	0%
10	0	4,024	2,492	5,509	567	107	25	11	13	26	36	38	46	52	328	13,275	920	914	99%	872	95%	-5%
10	0	3,148	1,920	7,487	1,080	371	169	101	70	59	59	59	58	67	423	15,073	2,396	1,971	82%	2,075	87%	4%
10	0	2,521	3,323	8,163	758	210	92	51	37	40	47	53	60	73	490	15,919	1,692	1,510	89%	1,424	84%	-5%
10	0	3,228	2,186	5,065	529	138	53	39	34	29	36	38	44	51	300	11,771	1,348	1,114	83%	1,162	86%	4%
10	0	2,613	1,890	9,184	1,196	285	94	44	36	37	45	49	61	72	485	16,092	1,285	1,307	102%	1,240	96%	-5%
d_p	0.750	1.5	2.75	4.25	5.75	7.25	8.75	10.3	11.8	13.3	14.8	16.3	17.8	19.3	≥20.8							
d_{ae}	0.766	1.54	2.85	4.46	6.08	7.68	9.28	10.86	12.32	13.97	15.59	17.19	18.76	20.34	≥21.9							
v_{Cr}	0.04%	0.09%	0.18%	0.29%	0.39%	0.41%	0.42%	0.41%	0.30%	0.35%	0.38%	0.39%	0.38%	0.38%	0.37%							

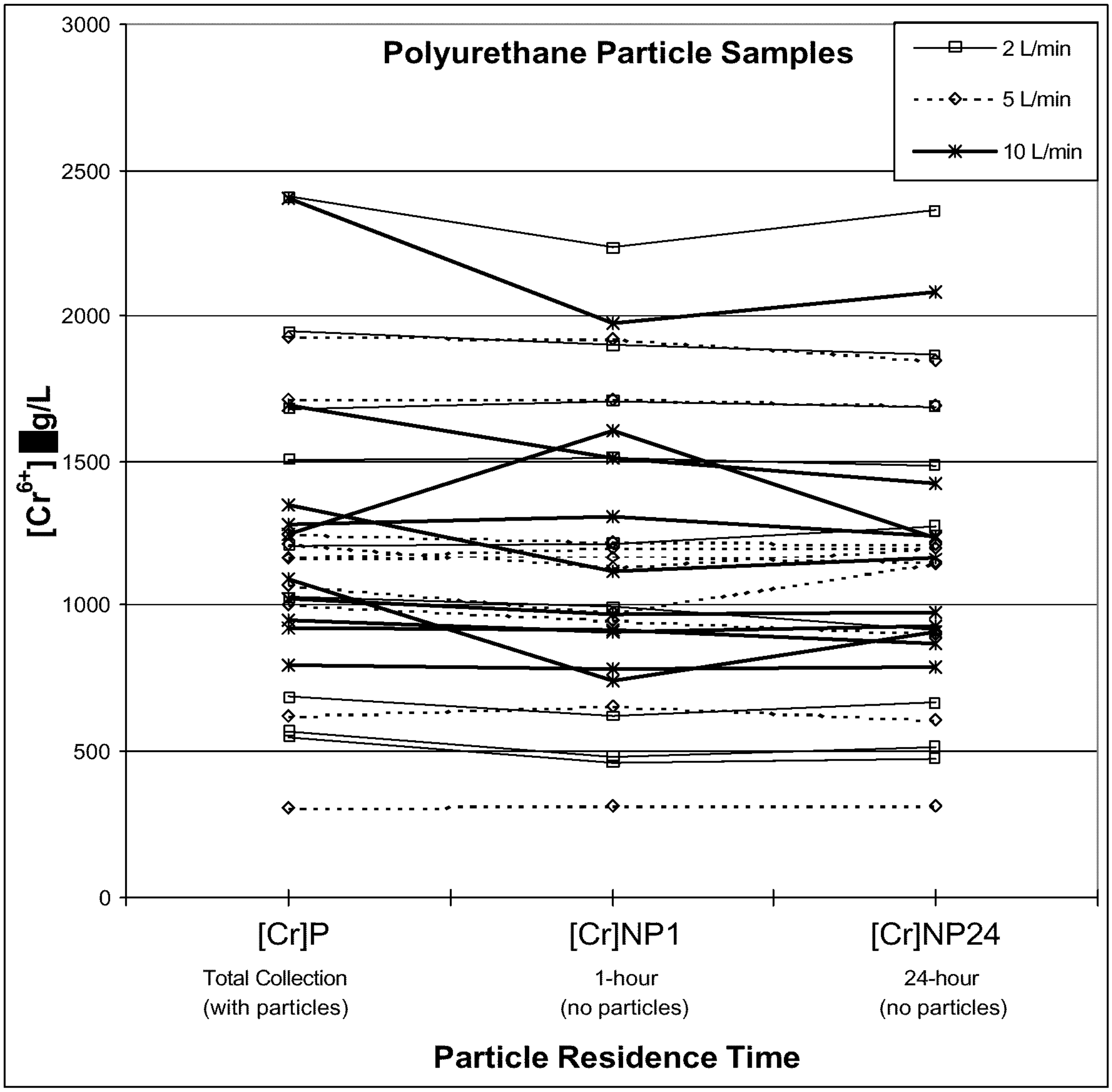
Appendix C-2: Polyurethane Particle Size Distributions by Flow Rate





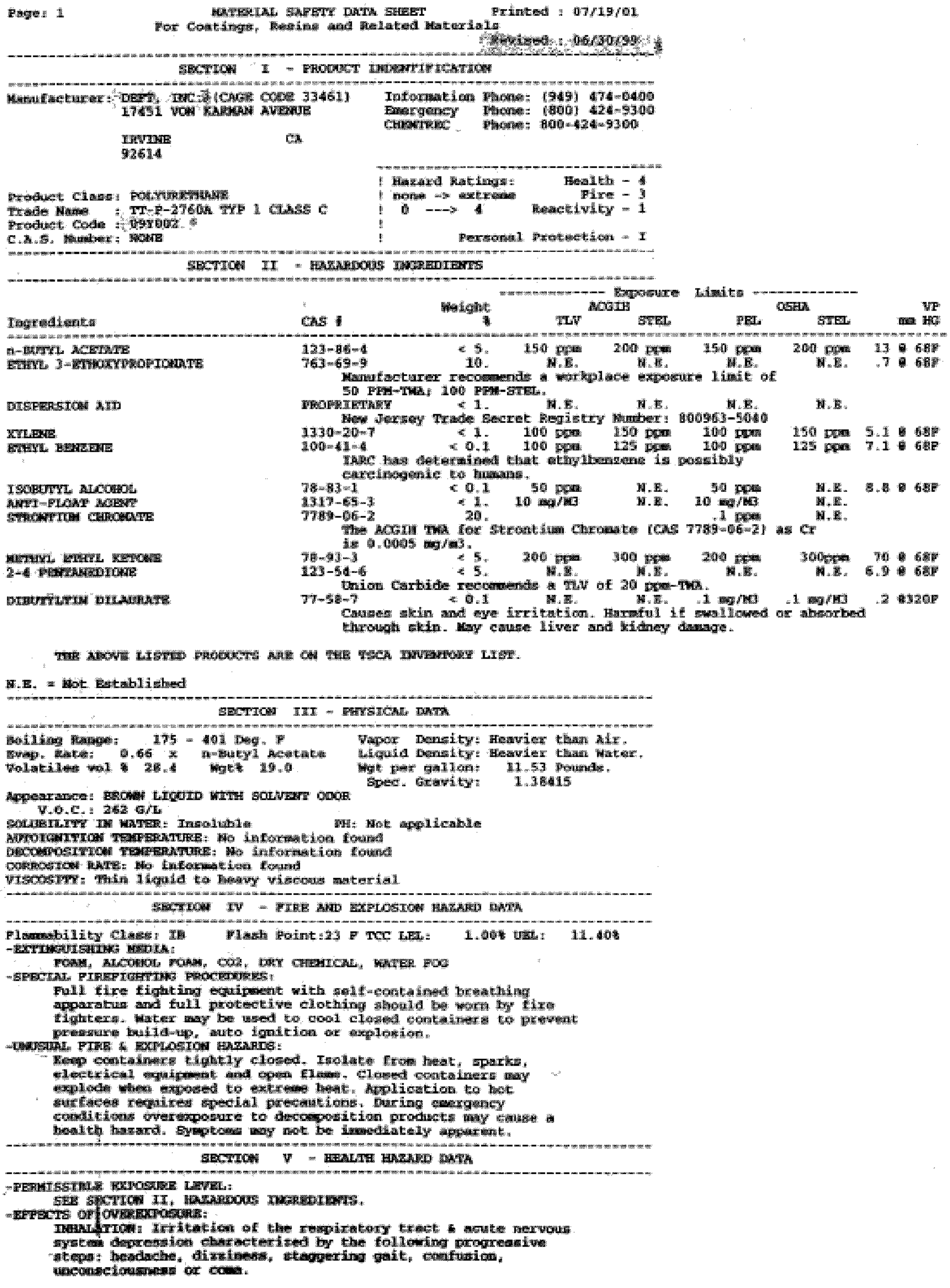

Polyurethane Particle Size Distributions
(Flow Rate: 10 L/min)
Particles/mL
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
Particle Diameter (μm)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

Appendix C-3: Polyurethane Particle Sample DI [Cr^{6+}] vs. Time



The chart above depicts the Cr^{6+} concentration data from the data summary table (Appendix C-1). Lines connect [Cr]P, the concentration of total Cr^{6+} collected (including that in particles) in each sample, to that sample's 1-hour ([Cr]NP1) and 24-hour ([Cr]NP24) concentration from dissociated Cr^{6+} (i.e. with particles removed).

Appendix C-4a: Deft® Polyurethane Primer (Base) MSDS Excerpt



Page: 1 MATERIAL SAFETY DATA SHEET Printed : 07/19/01

For Coatings, Resins and Related Materials

Revised : 06/30/99

SECTION I - PRODUCT INDENTIFICATION

Manufacturer: DEFT, INC. (CAGE CODE 33461)
17451 VON KARMAN AVENUE

IRVINE CA
92614

Information Phone: (949) 474-0400
Emergency Phone: (800) 424-9300
CHEMTREC Phone: 800-424-9300

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

			Exposure Limits				
		Weight	ACGIH		OSHA		VP
Ingredients	CAS #	%	TLV	STEL	PEL	STEL	mm HG
n-BUTYL ACETATE	123-86-4	< 5.	150 ppm	200 ppm	150 ppm	200 ppm	13 @ 68F
ETHYL 3-ETHOXYPROPIONATE	763-69-9	10.	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	< 1.	N.E.	N.E.	N.E.	N.E.	
	New Jersey Trade Secret Registry Number: 800963-5040						
XYLENE	1330-20-7	< 1.	100 ppm	150 ppm	100 ppm	150 ppm	5.1 @ 68F
ETHYL BENZENE	100-41-4	< 0.1	100 ppm	125 ppm	100 ppm	125 ppm	7.1 @ 68F
	IARC has determined that ethylbenzene is possibly carcinogenic to humans.						
ISOBUTYL ALCOHOL	78-83-1	< 0.1	50 ppm	N.E.	50 ppm	N.E.	8.8 @ 68F
ANTI-FLOAT AGENT	1317-65-3	< 1.	10 mg/M3	N.E.	10 mg/M3	N.E.	
STRONTIUM CHROMATE	7789-06-2	20.			.1 ppm	N.E.	
	The ACGIH TWA for Strontium Chromate (CAS 7789-06-2) as Cr is 0.0005 mg/m3.						
METHYL ETHYL KETONE	78-93-3	< 5.	200 ppm	300 ppm	200 ppm	300ppm	70 @ 68F
2-4 PENTANEDIONE	123-54-6	< 5.	N.E.	N.E.	N.E.	N.E.	6.9 @ 68F
	Union Carbide recommends a TLV of 20 ppm-TWA.						
DIBUTYLTIN DILAURATE	77-58-7	< 0.1	N.E.	N.E.	.1 mg/M3	.1 mg/M3	.2 @320F
	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
Evap. Rate: 0.66 x n-Butyl Acetate
Volatiles vol % 28.4 Wgt% 19.0
Vapor Density: Heavier than Air.
Liquid Density: Heavier than Water.
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 IV - FIRE AND EXPLOSION HAZARD DATA

Flammability Class: IB Flash Point:23 F TCC LEL: 1.00% UEL: 11.40%

-EXTINGUISHING MEDIA:
FOAM, ALCOHOL FOAM, CO2, DRY CHEMICAL, WATER FOG

-SPECIAL FIREFIGHTING PROCEDURES:
Full fire fighting equipment with self-contained breathing apparatus and full protective clothing should be worn by fire fighters. Water may be used to cool closed containers to prevent pressure build-up, auto ignition or explosion.

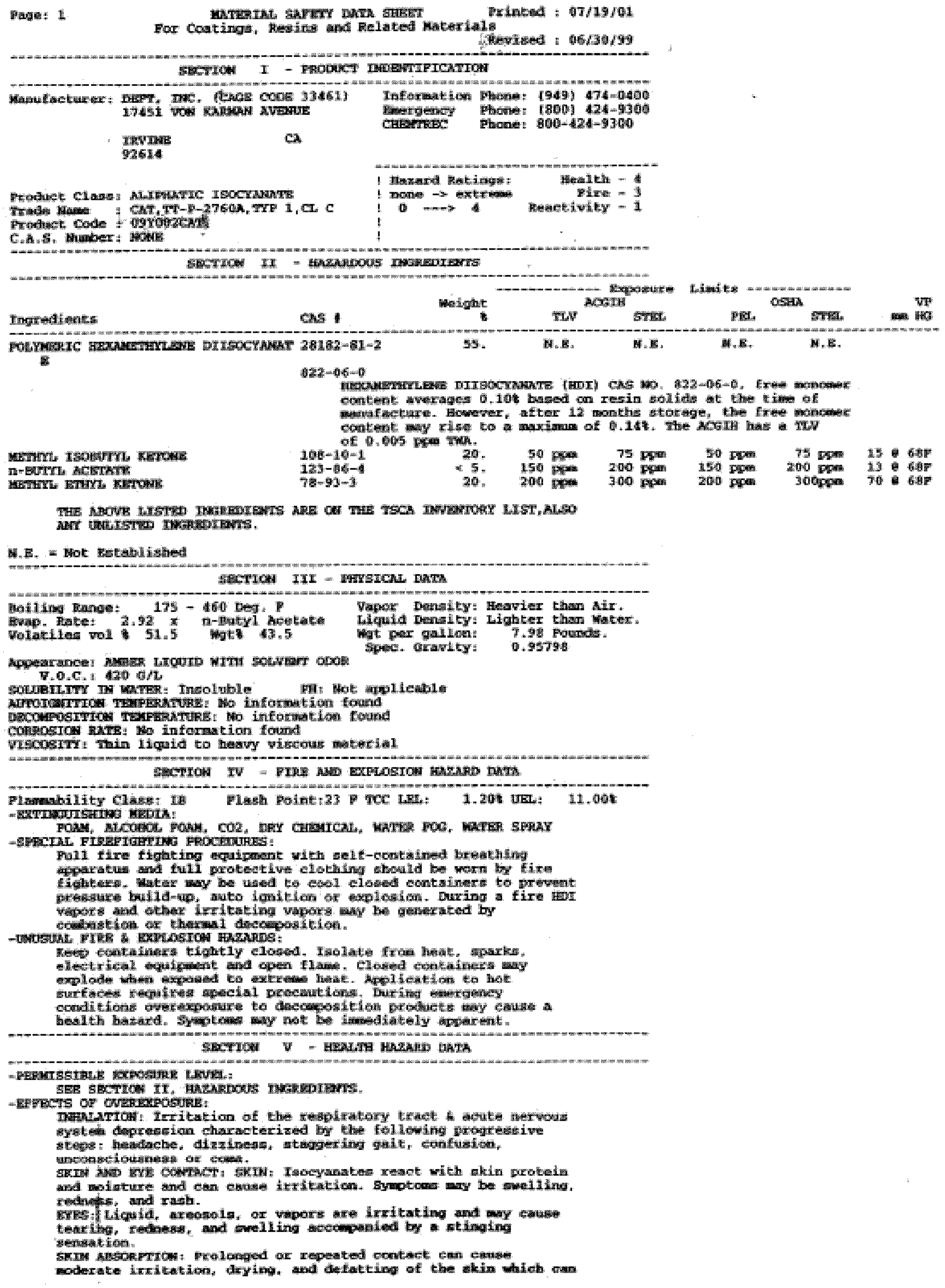
-UNUSUAL FIRE & EXPLOSION HAZARDS:
Keep containers tightly closed. Isolate from heat, sparks, electrical equipment and open flame. Closed containers may explode when exposed to extreme heat. Application to hot surfaces requires special precautions. During emergency conditions overexposure to decomposition products may cause a health hazard. Symptoms may not be immediately apparent.

SECTION V - HEALTH HAZARD DATA

-PERMISSIBLE EXPOSURE LEVEL:
SEE SECTION II, HAZARDOUS INGREDIENTS.

-EFFECTS OF OVEREXPOSURE:
INHALATION: Irritation of the respiratory tract & acute nervous system depression characterized by the following progressive steps: headache, dizziness, staggering gait, confusion, unconsciousness or coma.

Appendix C-4b: Deft® Polyurethane Primer (Catalyst) MSDS Excerpt



Page: 1 MATERIAL SAFETY DATA SHEET Printed : 07/19/01
For Coatings, Resins and Related Materials
Revised : 06/30/99

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: DEFT, INC. (CAGE CODE 33461)
17451 VON KARMAN AVENUE
IRVINE CA
92614

Information Phone: (949) 474-0400
Emergency Phone: (800) 424-9300
CHEMTREC Phone: 800-424-9300

Product Class: ALIPHATIC ISOCYANATE
Trade Name : CAT,TT-P-2760A,TYP 1,CL C
Product Code : 09Y002CAT
C.A.S. Number: NONE

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

SECTION II - HAZARDOUS INGREDIENTS

			Exposure Limits				
		Weight	ACGIH		OSHA		VP
Ingredients	CAS #	%	TLV	STEL	PEL	STEL	mm HG
POLYMERIC HEXAMETHYLENE DIISOCYANATE	28182-81-2	55.	N.E.	N.E.	N.E.	N.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	20.	50 ppm	75 ppm	50 ppm	75 ppm	15 @ 68F
n-BUTYL ACETATE	123-86-4	< 5.	150 ppm	200 ppm	150 ppm	200 ppm	13 @ 68F
METHYL ETHYL KETONE	78-93-3	20.	200 ppm	300 ppm	200 ppm	300ppm	70 @ 68F

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
Evap. Rate: 2.92 x n-Butyl Acetate
Volatiles vol % 51.5 Wgt% 43.5
Vapor Density: Heavier than Air.
Liquid Density: Lighter than Water.
Wgt per gallon: 7.98 Pounds.
Spec. Gravity: 0.95798

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

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

Flammability Class: IB Flash Point:23 F TCC LEL: 1.20% UEL: 11.00%

-EXTINGUISHING MEDIA:
FOAM, ALCOHOL FOAM, CO2, DRY CHEMICAL, WATER FOG, WATER SPRAY

-SPECIAL FIREFIGHTING PROCEDURES:
Full fire fighting equipment with self-contained breathing apparatus and full protective clothing should be worn by fire fighters. Water may be used to cool closed containers to prevent pressure build-up, auto ignition or explosion. During a fire HDI vapors and other irritating vapors may be generated by combustion or thermal decomposition.

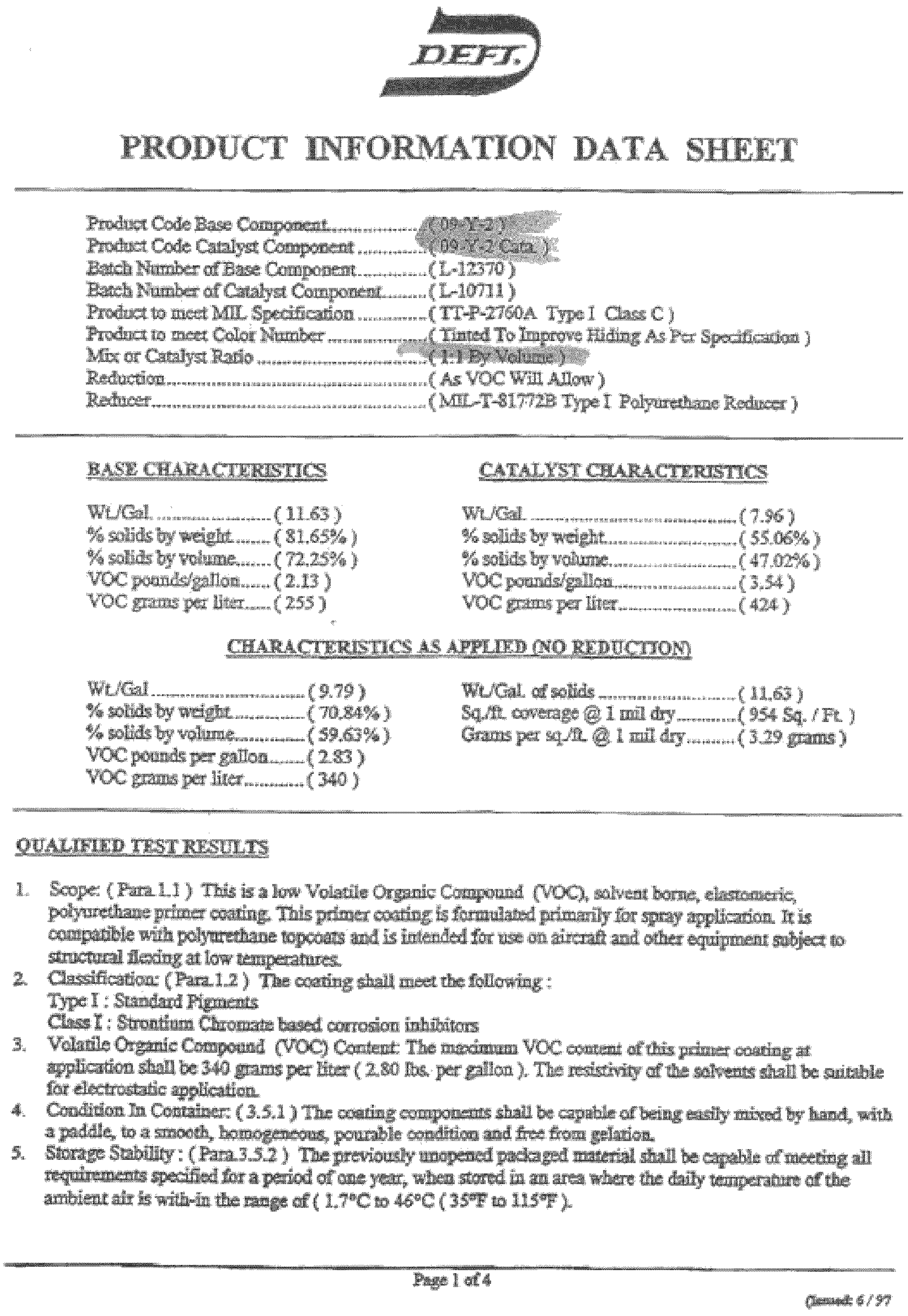
-UNUSUAL FIRE & EXPLOSION HAZARDS:
Keep containers tightly closed. Isolate from heat, sparks, electrical equipment and open flame. Closed containers may explode when exposed to extreme heat. Application to hot surfaces requires special precautions. During emergency conditions overexposure to decomposition products may cause a health hazard. Symptoms may not be immediately apparent.

SECTION V - HEALTH HAZARD DATA

-PERMISSIBLE EXPOSURE LEVEL:
SEE SECTION II, HAZARDOUS INGREDIENTS.

-EFFECTS OF OVEREXPOSURE:
INHALATION: Irritation of the respiratory tract & acute nervous system depression characterized by the following progressive steps: headache, dizziness, staggering gait, confusion, unconsciousness or coma.
SKIN AND EYE CONTACT: SKIN: Isocyanates react with skin protein and moisture and can cause irritation. Symptoms may be swelling, redness, and rash.
EYES: Liquid, areosols, or vapors are irritating and may cause tearing, redness, and swelling accompanied by a stinging sensation.
SKIN ABSORPTION: Prolonged or repeated contact can cause moderate irritation, drying, and defatting of the skin which can

Appendix C-5: Deft® Polyurethane Primer Product Information Data Sheet



DEFT.

PRODUCT INFORMATION DATA SHEET

Product Code Base Component.................(09-Y-2)
Product Code Catalyst Component ....(09-Y-2 Cata.)
Batch Number of Base Component..............(L-12370)
Batch Number of Catalyst Component.........(L-10711)
Product to meet MIL Specification ....(TT-P-2760A Type I Class C)
Product to meet Color Number ....(Tinted To Improve Hiding As Per Specification)
Mix or Catalyst Ratio ....(1:1 By Volume)
Reduction...(As VOC Will Allow)
Reducer..(MIL-T-81772B Type I Polyurethane Reducer)

BASE CHARACTERISTICS		CATALYST CHARACTERISTICS	
Wt./Gal.	(11.63)	Wt./Gal.	(7.96)
% solids by weight	(81.65%)	% solids by weight	(55.06%)
% solids by volume	(72.25%)	% solids by volume	(47.02%)
VOC pounds/gallon	(2.13)	VOC pounds/gallon	(3.54)
VOC grams per liter	(255)	VOC grams per liter	(424)

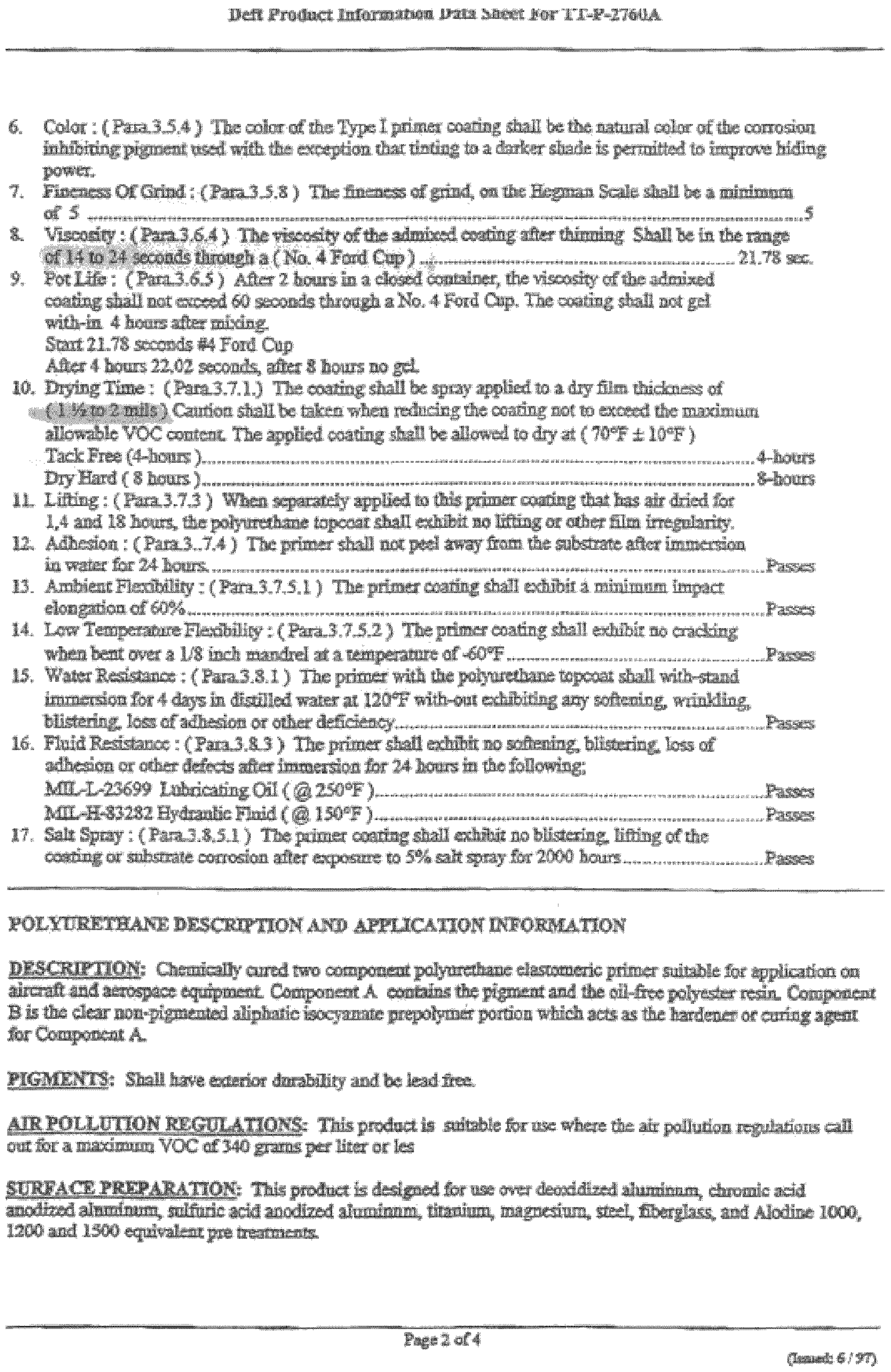
CHARACTERISTICS AS APPLIED (NO REDUCTION)

Wt./Gal	(9.79)	Wt./Gal. of solids	(11.63)
% solids by weight	(70.84%)	Sq./ft. coverage @ 1 mil dry	(954 Sq. / Ft.)
% solids by volume	(59.63%)	Grams per sq./ft. @ 1 mil dry	(3.29 grams)
VOC pounds per gallon	(2.83)		
VOC grams per liter	(340)		

QUALIFIED TEST RESULTS

1. Scope: (Para.1.1) This is a low Volatile Organic Compound (VOC), solvent borne, elastomeric, polyurethane primer coating. This primer coating is formulated primarily for spray application. It is compatible with polyurethane topcoats and is intended for use on aircraft and other equipment subject to structural flexing at low temperatures.
2. Classification: (Para.1.2) The coating shall meet the following :
   Type I : Standard Pigments
   Class I : Strontium Chromate based corrosion inhibitors
3. Volatile Organic Compound (VOC) Content: The maximum VOC content of this primer coating at application shall be 340 grams per liter (2.80 lbs. per gallon). The resistivity of the solvents shall be suitable for electrostatic application.
4. Condition In Container: (3.5.1) The coating components shall be capable of being easily mixed by hand, with a paddle, to a smooth, homogeneous, pourable condition and free from gelation.
5. Storage Stability : (Para.3.5.2) The previously unopened packaged material shall be capable of meeting all requirements specified for a period of one year, when stored in an area where the daily temperature of the ambient air is with-in the range of (1.7°C to 46°C (35°F to 115°F).

(Issued: 6 / 97)



6. Color : (Para.3.5.4) The color of the Type I primer coating shall be the natural color of the corrosion inhibiting pigment used with the exception that tinting to a darker shade is permitted to improve hiding power.
7. Fineness Of Grind : (Para.3.5.8) The fineness of grind, on the Hegman Scale shall be a minimum of 5 5
8. Viscosity : (Para.3.6.4) The viscosity of the admixed coating after thinning Shall be in the range of 14 to 24 seconds through a (No. 4 Ford Cup) .... 21.78 sec.
9. Pot Life : (Para.3.6.5) After 2 hours in a closed container, the viscosity of the admixed coating shall not exceed 60 seconds through a No. 4 Ford Cup. The coating shall not gel with-in 4 hours after mixing.
   Start 21.78 seconds #4 Ford Cup
   After 4 hours 22.02 seconds, after 8 hours no gel.
10. Drying Time : (Para.3.7.1.) The coating shall be spray applied to a dry film thickness of (1 ½ to 2 mils) Caution shall be taken when reducing the coating not to exceed the maximum allowable VOC content. The applied coating shall be allowed to dry at (70°F ± 10°F)
    Tack Free (4-hours) 4-hours
    Dry Hard (8 hours) 8-hours
11. Lifting : (Para.3.7.3) When separately applied to this primer coating that has air dried for 1,4 and 18 hours, the polyurethane topcoat shall exhibit no lifting or other film irregularity.
12. Adhesion : (Para.3..7.4) The primer shall not peel away from the substrate after immersion in water for 24 hours. .... Passes
13. Ambient Flexibility : (Para.3.7.5.1) The primer coating shall exhibit a minimum impact elongation of 60% .... Passes
14. Low Temperature Flexibility : (Para.3.7.5.2) The primer coating shall exhibit no cracking when bent over a 1/8 inch mandrel at a temperature of -60°F .... Passes
15. Water Resistance : (Para.3.8.1) The primer with the polyurethane topcoat shall with-stand immersion for 4 days in distilled water at 120°F with-out exhibiting any softening, wrinkling, blistering, loss of adhesion or other deficiency .... Passes
16. Fluid Resistance : (Para.3.8.3) The primer shall exhibit no softening, blistering, loss of adhesion or other defects after immersion for 24 hours in the following;
    MIL-L-23699 Lubricating Oil (@ 250°F) .... Passes
    MIL-H-83282 Hydraulic Fluid (@ 150°F) .... Passes
17. Salt Spray : (Para.3.8.5.1) The primer coating shall exhibit no blistering, lifting of the coating or substrate corrosion after exposure to 5% salt spray for 2000 hours .... Passes

POLYURETHANE DESCRIPTION AND APPLICATION INFORMATION

DESCRIPTION: Chemically cured two component polyurethane elastomeric primer suitable for application on aircraft and aerospace equipment. Component A contains the pigment and the oil-free polyester resin. Component B is the clear non-pigmented aliphatic isocyanate prepolymer portion which acts as the hardener or curing agent for Component A.

PIGMENTS: Shall have exterior durability and be lead free.

AIR POLLUTION REGULATIONS: This product is suitable for use where the air pollution regulations call out for a maximum VOC of 340 grams per liter or les

SURFACE PREPARATION: This product is designed for use over deoxidized aluminum, chromic acid anodized aluminum, sulfuric acid anodized aluminum, titanium, magnesium, steel, fiberglass, and Alodine 1000, 1200 and 1500 equivalent pre treatments.

Appendix D: Particle Distribution Smoothing

The assumptions that all particles collected in the ≥ 20 µm bin (i.e. all particles collected in the range ≥ 20 µm < 125 µm) had a particle diameter of 20 µm or that the bin had a midpoint of (125 µm - 20 µm)/2 were deemed inaccurate. As a result, extrapolation of particles counted in the 20 µm bin was chosen as the method to smooth the solvent- and water-borne epoxy particle size distributions. This was accomplished using "virtual" bins in 1.5 µm bin size increments (the same increment used in the actual particle counts). Extrapolations are based on the percentage change of particle numbers in the last three bins prior to the ≥ 20 µm bin. More specifically, the trend in the difference (Δ) between successive bin particle number concentrations (N_i's), beginning with the 15.5 µm (N_{12}) bin, was used to weight the decrease for each succeeding bin as in equation A-1. N_i's were computed starting with the 20 µm bin (N_{15}), and extrapolation ceased once the number of particles in the pre-extrapolation 20 µm bin was exhausted.

$$N_i = N_{i-1} - \left(\frac{(N_{i-3} - N_{i-2}) - (N_{i-2} - N_{i-1})}{N_{i-3} - N_{i-2}} \right) \cdot \left(N_{i-2} - N_{i-1} \right) \qquad \text{(A-1)}$$

where: i = the discrete bin number such that i - 1 is the previous bin and i - 2 the bin before that, etc.

For example, given a set of collected particle counts and the differences (ΔN_i) beginning with bin 12 (as shown in the table below):

	Actual LPC Counts/mL				Extrapolated Counts/mL→	
Bin # (i)	**12**	**13**	**14**	**15**	**15**	**16**
N_i	200	150	110	300	?	?
ΔN_i		50	40	?	?	

The first extrapolation is performed for bin 15 as follows:

$$N_{15} = N_{14} - \left(\frac{(N_{12} - N_{13}) - (N_{13} - N_{14})}{N_{12} - N_{13}} \right) \cdot (N_{13} - N_{14}) = 110 - \left(\frac{(50) - (40)}{(50)} \right) \cdot (40) = 78$$

This is continued for bins 16 and higher until the 300 particles/mL counted in the original bin 15 (≥ 20 μm) are exhausted, so that the resulting table looks like:

<table>
<tr><td></td><td colspan="7">Actual LPC Counts/mL</td><td colspan="4">Extrapolated Counts/mL→</td></tr>
<tr><td>Bin # (i)</td><td colspan="2">12</td><td colspan="2">13</td><td colspan="2">14</td><td>15</td><td colspan="2">15</td><td colspan="2">16</td></tr>
<tr><td>N_i</td><td colspan="2">200</td><td colspan="2">150</td><td colspan="2">110</td><td>300</td><td colspan="2">78</td><td colspan="2">52</td></tr>
<tr><td>ΔN_i</td><td></td><td colspan="2">50</td><td colspan="2">40</td><td colspan="3">32</td><td colspan="2">26</td><td></td></tr>
</table>

Note: counts/mL are rounded

Many of the polyurethane samples showed either an upward or incoherent trend in bins > 11 μm. For these distributions, extrapolations assumed the 20 μm bin to have the same N as the 18.5 μm bin and then a linear decrease was applied to determine the remaining N_i's.

Appendix E: Aerodynamic Diameter and Cr^{6+} Volume Calculations

Converting bin midpoint d_p, (denoted as the bold $\mathbf{d_p}$), to an equivalent d_{ae}, and determining the Cr^{6+} % volume for each particle size first required computation of ρ_p, (denoted as the bold $\boldsymbol{\rho}_\mathbf{p}$) the density specific to each $\mathbf{d_p}$. The steps used in the calculations are shown below (1-3 correspond with the conceptual diagram in Chapter 4). Examples calculations are shown for the solvent-borne epoxy 8 µm particle size bin (midpoint 8.75 µm).

Step 1

Using Table 16, linearly interpolate the mass fraction of Cr (mean % Cr) in a *dry* paint particle for the bin midpoint size, $\mathbf{d_p}$, using effective cutoff diameter (ECD) as an estimate of $\mathbf{d_p}$.

$$m_{Cr,d_p} = \left(\frac{\mathbf{d_p} - ECD_1}{ECD_2 - ECD_1} \right) \cdot (\%Cr_2 - \%Cr_1) + \%Cr_1 \qquad \text{(E-1)}$$

where: $m_{Cr,\mathbf{d_p}}$ = (mass of Cr)/(mass of *dry* paint) in a particle of size $\mathbf{d_p}$ [Table 16]
$\mathbf{d_p}$ = particle size bin midpoint diameter
ECD_1 = closest ECD (from Table 16) to $\mathbf{d_p}$ that is smaller than $\mathbf{d_p}$
ECD_2 = closest ECD (from Table 16) to $\mathbf{d_p}$ that is larger than $\mathbf{d_p}$
$\%Cr_1$ = (mass of Cr)/(mass of *dry* paint) corresponding to ECD_1 [Table 16]
$\%Cr_2$ = (mass of Cr)/(mass of *dry* paint) corresponding to ECD_2 [Table 16]

Example 1

$$m_{Cr,\mathbf{8.75\mu m}} = \left(\frac{8.75\mu m - 7.0\mu m}{9.5\mu m - 7.0\mu m} \right) \cdot (5.3\% - 4.6\%) + 4.6\% = 5.09\% \cong .0509$$

Step 2a

Convert the mass fraction of Cr in a *dry* paint particle of size $\mathbf{d_p}$, interpolated from Table 16, to the mass fraction of Cr in a *wet* droplet (particle) of size $\mathbf{d_p}$.

$$M_{Cr,\mathbf{d}_p} = m_{Cr,\mathbf{d}_p} \cdot v_{solids} \cdot \left(\frac{?_{dry}}{?_{wet}} \right) \tag{E-2a}$$

where: $M_{Cr,\mathbf{d_p}}$ = (mass of Cr)/(mass of *wet* paint) in a particle of size $\mathbf{d_p}$
$m_{Cr,\mathbf{d_p}}$ = (mass of Cr)/(mass of *dry* paint) in a particle of size $\mathbf{d_p}$ [Table 16]
v_{solids} = (Vol. of dry paint)/(Vol. of wet paint) [Table 15]
ρ_{dry} = density of dry paint ≅ solids density (g/L) [Table 15]
ρ_{wet} = density of the total wet paint mixture (g/L) [Table 15]

Example 2a

$$M_{Cr,\mathbf{8}.75\mu m} = 0.0509 \frac{\text{g Cr}}{\text{g dry paint}} \cdot .5855 \frac{\text{L solids}}{\text{L paint}} \cdot \left(\frac{1539.8 \frac{\text{g}}{\text{L dry paint}}}{1240.2 \frac{\text{g}}{\text{L wet paint}}} \right) = 0.0370 \frac{\text{g Cr}}{\text{g wet paint}}$$

Step 2b

Convert the mass fraction of Cr in a *wet* particle of size $\mathbf{d_p}$ to a mass fraction of $SrCrO_4$ in a *wet* particle of size $\mathbf{d_p}$.

$$m_{SrCrO_4,\mathbf{d}_p} = M_{Cr,\mathbf{d}_p} \cdot \left(\frac{MW_{SrCrO_4}}{MW_{Cr}} \right) \tag{E-2b}$$

where: $m_{SrCrO4,\mathbf{d_p}}$ = (mass of $SrCrO_4$)/(mass of wet paint) in a particle of size $\mathbf{d_p}$
MW_{SrCrO4} = molecular weight of $SrCrO_4$ (204 g/mol)
MW_{Cr} = molecular weight of Cr (52 g/mol)

Example 2b

$$m_{SrCrO_4,\mathbf{8}.75\mu m} = 0.0370 \frac{\text{g Cr}}{\text{g wet paint}} \cdot \left(\frac{204 \text{ g/mol}}{52 \text{ g/mol}} \right) = 0.1452 \frac{\text{g SrCrO}_4}{\text{g wet paint}}$$

Step 3

Convert the mass fraction of $SrCrO_4$ in a *wet* particle of size $\mathbf{d_p}$ to a *volume* fraction of $SrCrO_4$ in a *wet* particle of size $\mathbf{d_p}$.

$$v_{SrCrO_4,\mathbf{d_p}} = m_{SrCrO_4,\mathbf{d_p}} \cdot \left(\frac{\rho_{wet}}{\rho_{SrCrO_4}} \right) \qquad \text{(E-3)}$$

where: $v_{SrCrO4,\mathbf{dp}}$ = (Vol. of $SrCrO_4$)/(Vol. of wet paint) in a particle of size $\mathbf{d_p}$

ρ_{SrCrO4} = density of $SrCrO_4$ (3900 g/L)

Example 3

$$v_{SrCrO4,\mathbf{8.75\mu m}} = 0.1452 \frac{\text{g SrCrO}_4}{\text{g wet paint}} \cdot \left(\frac{1240.2 \frac{\text{g}}{\text{L wet paint}}}{3900 \frac{\text{g}}{\text{L SrCrO}_4}} \right) = 0.04616 \frac{\text{L SrCrO}_4}{\text{L wet paint}}$$

Step 4

Calculate $\boldsymbol{\rho_p}$, the density of a wet paint particle of size $\mathbf{d_p}$.

$$\rho_p = [v_{SrCrO_4,\mathbf{d_p}}] \cdot \rho_{SrCrO_4} + [1 - v_{SrCrO_4,\mathbf{d_p}}] \cdot \rho_{non-SrCrO_4} \qquad \text{(E-4)}$$

where: $\rho_{non\text{-}SrCrO4}$ = the combined density of all the non-$SrCrO_4$ paint constituents in the paint mixture, such that:

$\rho_{non\text{-}SrCrO4} = \rho_{wet}$ – (ρ_{SrCrO4} □ vol. fraction of $SrCrO_4$ in the total, homogenous, paint mixture)

Example 4

$$\rho_{\mathbf{8.75\mu m}} = \left[0.04616 \frac{\text{L SrCrO}_4}{\text{L wet paint}} \right] \cdot 3900 \frac{\text{g}}{\text{L SrCrO}_4} + \left[1 - 0.04616 \frac{\text{L SrCrO}_4}{\text{L wet paint}} \right] \cdot 988.3 \frac{\text{g}}{\text{L non - SrCrO}_4}$$

$$= 1123 \frac{\text{g}}{\text{L}}$$

Step 5

Calculate a terminal settling velocity (v_t) for the wet droplet of size $\mathbf{d_p}$ by applying $\boldsymbol{\rho_p}$ to the Stokes equation.

$$v_t = \frac{C_c \mathbf{?_p d_p^2}}{18\cdot\mu}\cdot g \qquad \text{(E-5)}$$

where: C_c = Cunningham Slip Correction factor (unitless) [diameter-dependent]; values ranged from 1.326 to 1.008 for collected particle sizes

μ = dynamic viscosity of air (g/cm·s) [temperature-dependent]

g = acceleration due to gravity (cm/s^2)

Example 5

$$v_t = \frac{(1.02)\cdot\left(1123\frac{g}{L}\right)\cdot(8.75\,\mu m)^2\cdot\left(\frac{L}{1000\,cm^3}\right)\cdot\left(\frac{cm^2}{1\cdot 10^8\mu m^2}\right)}{18\cdot\left(1.85\cdot 10^{-4}\frac{g}{cm\cdot s}\right)}\cdot\left(980\frac{cm}{s^2}\right)$$

$$= .2581\frac{cm}{s} = 2581\frac{\mu m}{s}$$

Step 6

Calculate d_{ae} by solving for diameter given the computed v_t and ρ_p = 1 g/cm^3 (unit density).

$$d_{ae} = \sqrt{\frac{v_t\cdot(18\cdot\mu)}{C_c\cdot ?_p\cdot g}} \qquad \text{(E-6)}$$

Example 6

$$d_{ae} = \sqrt{\frac{\left(2581\frac{\mu m}{s}\right)\cdot 18\cdot\left(1.85\cdot 10^{-4}\frac{g}{cm\cdot s}\right)\cdot\left(\frac{cm}{1\cdot 10^4\,\mu m}\right)}{(1.02)\cdot\left(1\frac{g}{cm^3}\right)\cdot\left(980\frac{cm}{s^2}\right)\cdot\left(\frac{cm^3}{1\cdot 10^{12}\mu m^3}\right)\cdot\left(\frac{1\cdot 10^4\mu m}{cm}\right)}} = 9.3\,\mu m$$

Step 7

Calculate the volume fraction of Cr^{6+} (as a % volume) in a wet particle of size $\mathbf{d_p}$ by applying $\boldsymbol{\rho}_{\mathbf{p}}$.

$$v_{Cr,\mathbf{d_p}} = m_{SrCrO_4,\mathbf{d_p}} \cdot \left(\frac{MW_{Cr}}{MW_{SrCrO_4}}\right) \cdot \left(\frac{?_{\mathbf{p}}}{?_{Cr}}\right) \times 100\% \qquad \text{(E-7)}$$

where: $v_{Cr,\mathbf{d_p}}$ = (Vol. of Cr)/(Vol. of wet paint) in a particle of size $\mathbf{d_p}$ (as a % vol.)

ρ_{Cr} = density of Cr (7190 g/L)

Example 7

$$v_{Cr,\mathbf{8.75\mu m}} = 0.1452 \frac{\text{g } SrCrO_4}{\text{g wet paint}} \cdot \left(\frac{52 \text{ g/mol}}{204 \text{ g/mol}}\right) \cdot \left(\frac{1123 \frac{g}{L}}{7190 \frac{g}{L}}\right) \times 100\% = 0.58\% \leftarrow \frac{\text{Cr Volume}}{\text{Particle Volume}}$$

BIBLIOGRAPHY

Cited

Agency for Toxic Substance and Disease Registry (ATSDR). "Chromium Toxicity". 1-21 (June 1990).

Alexander, B. H., H. Checkoway, L. Wechsler, N. J. Heyer, J. M. Muhm, and T. P. O'Keeffe. "Lung Cancer in Chromate-Exposed Aerospace Workers," *Journal of Occupational and Environmental Medicine*, 38 (12): 1253-1258 (1996).

American Conference of Governmental Industrial Hygienists (ACGIH): Industrial Ventilation, A Manual of Recommended Practices. Cincinnati OH, 1995.

American Conference of Governmental Industrial Hygienists (ACGIH) Worldwide. *2001 TLV's and BEI's: Threshold Limit Values for Chemical Substances and Physical Agents, & Biological Exposure Indices.* (2001).

Aw, T. C. "Clinical and Epidemiological Data on Lung Cancer at a Chromate Plant," *Regulatory Toxicology and Pharmacology*, 26: S8-S12 (1997).

Axelsson, G., Rylander, R., and A. Schmidt. "Mortality and Incidence of Tumours Among Ferrochromium Workers," *British Journal of Industrial Medicine*, 37, 121-127 (1980).

Bayvel, L. and Z. Orzechowski. *Liquid Atomization*. Washington DC, Taylor and Francis, 1993.

Bidstrup, P. L. and J. M. Davies. "Epidemiology: Update to 1985" In *Proceedings Chromium Symposium 1986: An Update* (D. M. Serrone, Ed.), 192-209, Pittsburgh PA, Industrial Health Foundation, 1986.

Carlton, G. N. and M. R. Flynn. "A Model to Estimate Worker Exposure to Spray Paint Mists." *Applied Occupational Environmental Hygiene,* 12(5): 375-382 (1997a).

Carlton, G. N. and M. R. Flynn. "Influence of Spray Painting Parameters on Breathing Zone Particle Size Distributions." *Applied Occupational Environmental Hygiene,* 12(11): 744-750 (1997b).

Casarett, L. J. *Casarett and Doull's Toxicology: the basic science of poisons.* 3d ed. Eds. Amdur, M. O., Doull, J., and C. D. Klaassen. New York: MacMillan Publishing Co., 1986.

Chan, T. L., and M. Lippmann. "Experimental Measurements and Empirical Modeling of the Regional Deposition of Inhaled Particles in Humans," *American Industrial Hygiene Association Journal*, 41: 399-408 (1980).

Clark, M. M. *Transport Modeling for Environmental Engineers and Scientists.* New York: John Wiley & Sons, 1996.

Connett P. H., and K. E. Wetterhahn. "Metabolism of the Carcinogen Chromate by Cellular Constituents," *Structure and Bonding*, 54: 93-124 (1983).

Connett P. H., and K. E. Wetterhahn. "In-vitro Reaction of the Carcinogen Chromate with Cellular Thiols and Carboxylic Acids," *Journal of the American Chemical Society*, 107: 4282-4288 (1985).

Dalager, N. A., T. J. Mason, J. F. Fraumeni, R. Hoover and W. W. Payne. "Cancer Mortality among Workers Exposed to Zinc Chromate Paints," *Journal of Occupational Medicine*, 22 (1): 25-29 (1980).

DeFlora, S., G. S. Badolati, D. Serra, A. Picciotto, M. R. Magnolia, and V. Savarino. "Circadian Reduction of Chromium in the Gastric Environment," *Mutation Research*, 192: 169-174 (1987).

Deft Incorporated. (2000). Deft® 02-Y-40 and 02-Y-40 Catalyst Product Information Data Sheet. Base Batch number L-12441, Catalyst Batch number L-12393.

Deft Incorporated. (1999). Deft® 44-GN-72 and 44-GN-72 Catalyst Product Information Data Sheet. Base Batch number L-13265, Catalyst Batch number L-13266.

Deft Incorporated. (1997). Deft® 09-Y-2 and 09-Y-2 Catalyst Product Information Data Sheet. Base Batch number L-12370, Catalyst Batch number L-10711.

Devore, J. L. *Probability and Statistics for Engineering and the Sciences*. 5th ed. Pacific Grove CA: Duxbury, 2000.

Fisher, D. R., and J. K. Briant. "Assessment of Accidental Intakes of Uranyl Acetylacetonate (UAA)," *Radiation Protection Dosimetry*, 53 (1-4): 263-267 (1994).

Fox, S. I. *Human Physiology*. 6th ed. Boston MA: The McGraw-Hill Companies, 1999.

Gad, S. C. "Acute and Chronic Systemic Chromium Toxicity," *The Science of the Total Environment*, 86: 149-157 (1989).

Gibb, H. J., and C. W. Chen. "Evaluation of Issues Relating to the Carcinogen Risk Assessment of Chromium," *The Science of the Total Environment*, 86: 181-186 (1989).

Godish, T. *Air Quality*. 3rd ed. Boca Raton FL: Lewis Publishers, 1997.

Hathaway, J. A. "Role of Epidemiologic Studies in Evaluating the Carcinogenicity of Chromium Compounds," *The Science of the Total Environment* 86: 169-179 (1989).

Health Effects Institute. *Atmospheric Observations: Helping Build the Scientific Basis for Decisions Related To Airborne Particulate Matter*, Report of the PM Measurements Research Workshop. Cambridge: 1998.

Hinds, W. C. *Aerosol Technology: properties, behavior, and measurement of airborne particles*. New York: John Wiley & Sons, 1982.

International Agency for Research on Cancer (IARC) *Monographs on the Evaluation of Carcinogenic Risks to Humans. Chromium, Nickel and Welding*, Vol 49. United Kingdom: World Health Organization, (1990).

Ishikawa, Y., K. Nakagawa, Y. Satoh, T. Kitagawa, H. Sugano, T. Hirano, and E. Tsuchiya. "Characteristics of Chromate Workers' Cancers, Chromium Lung Deposition and Precancerous Bronchial Lesions: an autopsy study," *British Journal of Cancer* 70: 160-166 (1994).

Jones, R. E. "Hexavalent Chrome: Threshold Concept for Carcinogenicity," *Biomedical and Environmental Sciences* 3: 20-34 (1990).

Kano, K., M. Horikawa, T. Utsunomiya, M. Tati, K. Satoh, S. Yamaguchi. "Lung Cancer Mortality Among a Cohort of Male Chromate Pigment Workers in Japan," *International Journal of Epidemiology* 22 (1):16-22 (1993).

Kauth, D.A. *Dissolution of Chromium From Inhalable Primer Paint Particles Into a Simulated Lung Fluid*. MS thesis, AFIT/GEE/ENV/01M-07. School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, March 2001 (AD-A390877) .

Korallus, U., Lange, H., Ness, A., Wuestefeld, E., and T. Zwingers. "Relationships Between Precautionary Measures and Bronchial Carcinoma Mortality in the Chromate-Producing Industry," *Arbeitsmed. Socialmed. Preventivmed.* 17 (7): 159-167.

Langard, S. "Chromium Carcinogenicity; a review of experimental animal data," *Science of the Total Environment* 71: 341-350 (1988).

Langard, S. "One Hundred Years of Chromium and Cancer: A review of epidemiological evidence and selected case reports," *American Journal of Industrial Medicine* 17:189-215 (1990).

Langard, S., Andersen, A., and Ravnestad, J. "Incidence of Cancer Among Ferrochromium and Ferrosilicon Workers: an extended observation period," *British Journal of Industrial Medicine* 47: 14-19 (1990).

LaPuma, P. T., J. M. Fox, and E. C. Kimmel. "Chromate Concentration Bias in Primer Paint Particles," *Regulatory Toxicology and Pharmacology*, 33: 343-349 (2001).

Levy, L. S., P. A. Martin, and P. L. Bidstrup. "Investigation of the Potential Carcinogenicity of a Range of Chromium Containing Materials on Rat Lung," *British Journal of Industrial Medicine*, 43: 243-256 (1986).

Lippmann, M., and R. E. Albert. "The Effect of Particle Size on the Regional Deposition of Inhaled Aerosols in the Human Respiratory Tract," *American Industrial Hygiene Journal*, 30: 257-275 (1969).

Lippman M., and R. Altschuler. "Regional Deposition of Aerosols," in *Air Pollution and the Lung*, E. F. Aharonsom, A. Ben David, and M. A. Klingberg (Eds.). Proceedings of the Twentieth Annual OHOLO Biological Conference, Maalot, Israel, New York: Wiley, 1976.

Lippman, M. "Regional Deposition of Particles in the Human Respiratory Tract," in *Handbook of Physiology,* D. H. K. Lee, H. L. Falk, and S. D. Murphy (Eds.). Section 9: Reaction to Environmental Agents, Bethesda MD: American Psychology Society, 1977.

Mancuso, T. F. "Consideration of Chromium as an Industrial Carcinogen," *International Conference on Heavy Metals in the Environm*ent, Toronto, Ontario, Canada, 343-356, 1975.

Mancuso, T. F. "Chromium as an Industrial Carcinogen: Part I," *American Journal of Industrial Medicine*, 31: 129-139 (1997).

Miller, F. J., D. E. Gardner, J. A. Graham, R. E. Lee, W. E. Wilson, Jr., J. D. Bachmann. "Size Considerations for Establishing a Standard for Inhalable Particles," *Journal of the Air Pollution Control Association,* 29: 610-615 (1979).

Miller, R. N. "Corrosion-inhibitive Sealants and Primers," in *Corrosion Control by Coatings*. Ed. Henry Leidheiser, Jr. Princeton: Science Press, 1979.

Morgan, T. J. R. *Chromate Dissociation From Primer Paint in Simulated Lung Fluid.* MS thesis, AFIT/GEE/ENV/00M-14. School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, March 2000.

Munger, C. G. *Corrosion Prevention by Protective Coatings*. Houston: National Association of Corrosion Engineers, 1984.

National Defense Center for Environmental Excellence (NDCEE). Engineering and Technical Services for Joint Group on Acquisition Pollution Prevention (JG-APP) Pilot Projects. "Potential Alternatives Report TI-A-1-1 for Alternatives to High-Volatile Organic Compound Primers and Topcoats Containing Methyl Ethyl Ketone, Toluene, and Xylene," Contract No. DAAA21-93-C-0046, Task No N.072, CDRL No. A004. February 5, 1998a.

National Defense Center for Environmental Excellence (NDCEE). Engineering and Technical Services for Joint Group on Acquisition Pollution Prevention (JG-APP) Pilot Projects. "Joint Test Report MD-R-1-1 for Laboratory Validation (Testing) of Alternatives to Chromate-Containing Primer Coatings for Aircraft Exterior Mold Line Skins," Contract No. DAAA21-93-C-0046, Task No N.072, CDRL No. A006. February 24, 1998b.

National Institute of Occupational Safety and Health (NIOSH). *NIOSH Pocket Guide to Chemical Hazards.* U.S. Department of Health and Human Services. Public Health Service. Center for Disease Control and Prevention (CDC), June 1997.

Nettesheim, P., M. G. Hanna, D. G. Doherty, R. F. Newell, and A. Hellman. "Effect of Calcium Chromate Dust, Influenza Virus, and 100R Whole Body X Radiation on Lung Tumor Incidence in Mice." *Journal of the National Cancer Institute* 47:1129-1138 (1971).

Newman, D. "A Case of Adeno-Carcinoma of the Left Inferior Turbinated Body, and Perforation of the Nasal Septum, in the Person of a Worker in Chrome Pigments," *Glasgow Medical Journal,* 33: 469-470 (1890).

Novy, D.B. *Chromate Content Bias as a Function of Particle Size in Aircraft Primer Paint Overspray*. MS thesis, AFIT/GEE/ENV/01M-12. School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, March 2001 (AD-A389222).

Occupational Safety and Health Administration Federal Register (Federal Register). "Occupational Exposure to Hexavalent Chromium (Preventing Occupational Illness: Chromium)." 61: 62748-62788 sequence 2240, November 1996.

Occupational Safety and Health Administration Federal Register (Federal Register). "Occupational Exposure to Hexavalent Chromium (Preventing Occupational Illness: Chromium)". 65:74107-74123 sequence 2247, November 2000.

O'Flaherty, J. O., and M. J. Radike. "Pharmacokinetic Modeling of Trivalent and Hexavalent Chromium Based on Ingestion and Inhalation of Soluble Chromium Compounds." College of Medicine, University of Cincinnati. Final report for the period June 1990 through December 1991 to Armstrong Aerospace Medical Research Laboratory, Wright-Patterson AFB OH, December 1991 (AD-A256238).

Petrilli, F. L., and S. DeFlora, 1998, "Metabolic Reduction of Chromium as a Threshold Mechanism limiting its in vivo activity," *Science of the Total Environment* 71: 357-364 (1988).

Phalen, R. F. *Inhalation Studies: Foundations and Techniques*. Boca Raton FL: CRC Press, 1984.

Rhodes, B. S. *Chromate Content Bias Versus Overspray Particle Size in Three Aircraft Primer Paints.* MS thesis, AFIT/GEE/ENV/01M-11. School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, March 2002.

Seinfeld, J. H. *Atmospheric Chemistry and Physics of Air Pollution*. New York: John Wiley & Sons, 1986.

SKC Incorporated, "The SKC BioSampler®." Product pamphlet. [On-line]. n. pag. Available: http//www.skcgc.com/main/products/biosampler.htm. 1 June 2001.

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*, 41: 385-398, 1980.

Steinhoff, D., S. C. Gad, G. K. Hatfield, and U. Mohr. "Carcinogenicity Studies with Sodium Dichromate in Animals," *Experimental Pathology,* 30: 129-141 (1986).

Sugden, K.D., and D. M. Stearns. "The Role of Chromium(V) in the Mechanism of Chromate-Induced Oxidative DNA Damage and Cancer," *Journal of Environmental Pathology, Toxicology, and Oncology* 19(3): 215-230 (2000).

United States Air Force (USAF), Technical Manual. *Application and Removal of Organic Coatings, Aerospace and Non-Aerospace Equipment* (TO-1-1-8), 23 April 2001.

United States Environmental Protection Agency (USEPA). (2000). *National Air Pollutant Emission Trends, 1900-1998* (United States Office of Air Quality Report No. EPA-454/R-00-002). Research Triangle Park NC: S. V. Nizich, A. A. Pope, L. M. Driver, & Pechan-Avanti Group.

United States Navy (USN), Technical Manual. *Aircraft Weapons Systems Cleaning and Corrosion Control* (NAVAIR 01-1A-509, T.O. 1-1-691, TM 1-1500-344-23), 1 May 2001.

Visek, W. J., Whitney, I. B., Kuhn, U. S. G., III, and C. L. Comer. "Metabolism of Cr-51 by animals as influenced by chemical state," *Proceedings for the Society for Experimental Biology and Medicine* 84: 610-615 (1953).

Willard, H. H., Merritt, L. L., Dean, J. A., and F. A. Settle. *Instrumental Methods of Analysis*. 7th ed. Belmont CA: Wadsworth Publishing Company, 1988.

Uncited

Ballantyne, Bryan, Timothy Marrs, and Paul Turner. *General and Applied Toxicology*. New York: Stockton Press, 1995.

Brain, Joseph D., John Godleski, Wolfgang Kreyling. "*In Vivo* Evaluation of Chemical Biopersistence of Nonfibrous Inorganic Particles," *Environmental Health Perspectives*, 102 Suppl 5: 119-125 (October 1994).

Finlayson-Pitts, B. J., and J. N. Pitts, *Atmospheric Chemistry: fundamentals and experimental techniques*. New York: John Wiley & Sons, 1986.

Fox, J. M. *Chromium Concentration Bias in the Particle Size Distribution of Primer Overspray*. MS thesis, AFIT/GEE/ENV/00M-06. School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, March 2000 (AD-A376614).

Gibson H., D. Mark, and J. H. Vincent. "A Personal Inspirable Dust Spectrometer for Applications in Occupational Hygiene Research," *Annals of Occupational Hygiene*, 31: 463-479 (1987).

Spear, T. M., M. A. Werner., J. Bootland, E. Murray, G. Ramachandran, and J. H. Vincent. "Assessment of Particle Size Distributions of Health-relevant Aerosol Exposures of Primary Lead Smelter Workers," *Annals of Occupational Hygiene*, 42(2): 73-80 (1998).

Vita

Captain Richard A. Schilke was born in Elyria, Ohio and graduated from Elyria Catholic High School in June 1988. On 26 May 1993 he graduated from the U. S. Naval Academy, receiving a Bachelor of Science degree in Oceanography and a commission as a 2nd Lt. in the U. S. Marine Corps (USMC). After training at The Basic School, Marine Corps Base (MCB) Quantico, Virgina, he reported to Naval Air Station Pensacola, Florida for Naval Flight Officer training. In April 1996, 1st Lt. Schilke received his wings of gold and proceeded to Marine Corps Air Station (MCAS) El Toro, California to train in the F/A-18D Hornet as a Weapons and Sensors Officer (WSO). In April 1997, he reported to Marine All-Weather Fighter Attack Squadron 332 [VMFA(AW)-332], MCAS Beaufort, South Carolina. There he served as the Naval Aviation Training and Operating Procedures Standardization Officer and was promoted to Captain in July 1997. In July 1998, Captain Schilke joined VMFA(AW)-533. From August 1998 to March 1999 he deployed to the Western Pacific with VMFA(AW)-533 and served as the squadron Maintenance Training Division Officer. There he participated in joint and combined exercises, and earned qualification as a squadron Air Combat Tactics Instructor. In May 1999, his squadron deployed to Taszar Air Base, Hungary as part of Combined Joint Task Force Noble Anvil. There he flew combat missions into Serbia and Kosovo in support of Operation Allied Force. Captain Schilke remained in VMFA(AW)-533 until August 2000, serving as the Current and Future Operations Officer and graduating from the U. S. Navy Fighter Weapons School (TopGun). In August 2000, he entered the Graduate School of Engineering and Management, Air Force Institute of Technology and upon graduation will be assigned as the Deputy, Natural Resources and Environmental Affairs Branch, Facilities Division, MCB Quantico, Virginia. Captain Schilke's personal awards include the Strike Flight Air Medal and the Navy and Marine Corps Commendation Medal with Combat V.

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 074-0188*

1. REPORT DATE *(DD-MM-YYYY)* 26-03-2002	**2. REPORT TYPE** **Master's Thesis**	**3. DATES COVERED** *(From – To)* Jun 2001 – Mar 2002

4. TITLE AND SUBTITLE

HEXAVALENT CHROMIUM DISSOCIATION FROM OVERSPRAY PARTICLES INTO FLUID FOR THREE AIRCRAFT PRIMERS

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Schilke, Richard A., Captain, USMC

5d. PROJECT NUMBER
01-180

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(S)

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2950 P Street, Building 640
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8. PERFORMING ORGANIZATION REPORT NUMBER

AFIT/GEE/ENV/02M-12

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/MLQL & HQ AFMC/CEVQ

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

DOD and industry use chromate-containing primers extensively to inhibit corrosion on metal assets. Chromate contains Cr^{6+}, a human carcinogen, but there is little epidemiological evidence of increased lung cancer among spray painters. Using bio-aerosol impingers, overspray particles from three primers (solvent-borne epoxy, water-borne epoxy, and solvent-borne polyurethane) were collected into water to test the hypothesis that the paint matrix inhibits Cr^{6+} release into water, under the premise that this simulates Cr^{6+} release from particles into lung fluid. Particles were allowed to reside in water for 1 or 24 hours, then separated from the water by centrifugation, and the water tested for $[Cr^{6+}]$. The mean fractions of Cr^{6+} released into the water after 1 and 24 hours for each primer (95% confidence) were: 70 ± 5% and 85 ± 5% (solvent epoxy), 74 ± 4% and 84 ± 4% (water epoxy), and 94 ± 3% and 95 ± 2% (polyurethane). Solvent and water epoxy primer 24-hour Cr^{6+} release ranged from 100% dissociation to 33% and 48%, respectively. Correlations between Cr^{6+} distribution with particle size and % Cr^{6+} dissociated from each sample indicate that particles $< 5\ \mu m$ release a larger fraction of Cr^{6+} during the first 24 hours vs. particles $> 5\ \mu m$.

15. SUBJECT TERMS

Chromates, Chromium Compounds, Hexavalent Chromium, Cr^{6+}, Anti-corrosive paints, Inhalation, Exposure (physiology), Aerosols, Particle size, Epoxy coatings, Polyurethane coatings, Lung cancer, Cr^{6+} bioavailability, Spray painting, Overspray

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			LaPuma, Peter T., Major , USAF (ENV)
U	U	U	UU	126	**19b. TELEPHONE NUMBER** *(Include area code)* (937) 255-6565, ext 4319; e-mail: Peter.Lapuma@afit.edu