Spray painters are potentially exposed to aerosols containing hexavalent chromium [Cr(VI)] via inhalation of chromate-based paint sprays. Evaluating the particle size distribution of a paint spray aerosol, and the variables that may affect this distribution, is necessary to determine the site and degree of respiratory deposition and the damage that may result from inhaled Cr(VI)-containing paint particles. This study examined the effect of spray gun atomization pressure, aerosol generation source and aerosol aging on the size distribution of chromate-based paint overspray aerosols generated in a bench-scale paint spray booth. The study also determined the effect of particle bounce inside a Marple personal cascade impactor on measured size distributions of paint spray aerosols. Marple personal cascade impactors with a modified inlet were used for sample collection. The data indicated that paint particle bounce did not occur inside the cascade impactors sufficiently to affect size distribution when using uncoated stainless steel or PVC substrate sampling media. A decrease in paint aerosol mass median aerodynamic diameter (MMAD) from 8.2 to 7.0 μm was observed as gun atomization pressure increased from 6 to 10 psi. Overspray aerosols were sampled at two locations in the spray booth. A downstream sampling position simulated the exposure of a worker standing between the painted surface and exhaust, a situation encountered in booths with multiple workers. The measured mean MMAD was 7.2 μm. The distance between the painted surface and sampler was varied to sample oversprays of varying ages between 2.8 and 7.7 s. Age was not a significant factor for determining MMAD. Overspray was sampled at a 90° position to simulate a worker standing in front of the surface being painted with air flowing to the worker’s side, a common situation in field applications. The resulting overspray MMAD averaged 5.9 μm. Direct-spray aerosols were sampled at ages from 5.3 to 11.7 s. Overspray and direct-spray results indicated that most of the change in aerosol size distribution occurred between the time the paint aerosol impacted the painted surface and the time the overspray became 2.8 s old. The overall mean MMAD of overspray in the study was 6.4 μm and may have been underestimated due to sampling efficiency biases. If inhaled by a worker, the overspray aerosols evaluated in this study would mostly deposit in the head airways region of the respiratory tract. Paint overspray aerosols contained Cr primarily in the Cr(VI) state.

Keywords: cascade impactor; chromium; overspray; paint aerosol; particle bounce; size distribution; spray booth

INTRODUCTION

The International Agency for Research on Cancer (IARC) has classified hexavalent chromium [Cr(VI)] as a human carcinogen (IARC, 1990). Cr(VI) is found in chromate-based paint sprays. Chromate-based paints are applied as a first-coat primer onto metal to protect the metal from corrosion damage. In the aerospace industry, chromate-based paints are widely used for priming aircraft fuselage and other aircraft parts. Typically, the primer is sprayed onto the aircraft metal parts. Workers spraying chromate-based paints are potentially exposed to Cr(VI) via inhalation of paint spray aerosols.

When evaluating the potential health effects that may result from exposure to Cr(VI)-containing paint aerosols there are five important toxicokinetic
issues: (i) respiratory deposition of the aerosol; (ii) bioavailability of Cr(VI) from the epoxy-based particle; (iii) knowledge of Cr(VI) absorption by the epithelial tissue of the respiratory system; (iv) the rate of Cr(VI) clearance from the lung and (v) the rate of reduction of Cr(VI) to trivalent chromium [Cr(III)].

Evaluating the particle size distribution of a paint spray aerosol is necessary to determine the site and degree of respiratory deposition and the damage that may result from inhaled Cr(VI)-containing paint particles. The site of deposition and the quantity of particles deposited there is greatly affected by the aerodynamic diameter of particles (ACGIH, 1985). The damage caused by an inhaled aerosol depends on its site of deposition within the respiratory system because clearance mechanisms in various lung compartments differ in effectiveness and rate of action (Lippmann et al., 1980; Petrilli and De Flora, 1988; De Flora et al., 1997). For instance, larger particles (>10 μm) tend to deposit in the head airways while much smaller particles tend to deposit in the tracheobronchial and alveolar regions of the lungs (Gorner and Fabries, 1996).

High-volume low-pressure (HVLP) spray guns have largely replaced conventional spray guns in paint spray applications. HVLP spray-painting guns have transfer efficiencies of 65–75%, more efficient than conventional spray guns (Heitbrink et al., 1996; Hund, 1997). A paint-spray-gun transfer efficiency of at least 65% is required in some parts of the United States to minimize the amount of paint used and the emission of volatile organic pollutants into the atmosphere (SCAQMD, 1991). The National Institute of Occupational Safety and Health (NIOSH) recommends the use of HVLP guns because of their higher transfer efficiencies (NIOSH, 1996).

Several variables may affect the aerosol size distribution generated during spray painting operations. These variables include gun atomization pressure, aging of the spray aerosol and generation source of the spray aerosol. Knowledge of how these variables affect size distribution may provide useful information to base recommendations about control strategies that would reduce worker exposures to the inhalation of harmful paint aerosol particles.

The overall objective of this study was to determine the effect of the different variables on the size distribution of chromate-based paint spray aerosols generated in a bench-scale spray booth. Specific objectives of this study were: (i) to determine if particle bounce inside a Marple personal cascade impactor is sufficient to adversely affect the measured size distribution of paint spray aerosols; (ii) to assess the effect of gun atomization pressure on the size distribution of paint spray aerosols; (iii) to compare the size distribution of paint aerosols generated by direct-spray paint and overspray paint; and (iv) to study the effect of aerosol aging on the size distribution of direct-spray and overspray paint aerosols.

**METHODS**

Experiments were carried out in a laboratory setting to study the effects of different variables on the size distribution of chromate-based paint spray aerosols. Paint was prepared, sprayed and sampled in a bench-scale spray booth.

**Paint preparation**

The paint selected for this study was a water-reducible and chromate-containing epoxy primer (product 44GN011, Deft Incorporated, Irvine, CA, USA) widely used by the aerospace industry for priming commercial and military airplanes. The epoxy primer is a two-component coating consisting of a base and a catalyst. The base reacts with amines and polyamides in the catalyst to form cross-links and chains that provide the coating with its characteristics of toughness and flexibility (Kroschwitz, 1994). To achieve inter-experiment consistency, the manufacturer provided custom-made chromate-free paint, which was spiked in the laboratory with 99.99% pure strontium chromate (SrCrO₄) powder (GFS Chemicals Incorporated, Columbus, OH, USA) to achieve 10.6% by weight SrCrO₄ composition, the same as that used in aerospace applications. The base component and the SrCrO₄ powder were placed in a 500 mL acid-washed Wheaton bottle and mixed in an enclosed rotating shaker for 5 min. The shaker rotated at a speed of about 1300 r.p.m in a temperature-controlled environment of 24–27°C. The paint catalyst was then added to the chromate-containing base component and mixed in the shaker for 5 min. Water was then added and mixed in the shaker for at least 15 min until the paint mix appeared homogeneous. Milli-Q ultrapure water of 18 mΩ resistivity (Millipore Corporation, Bedford, MA, USA) was used. The ratio of base:catalyst:water was 2:1:4.5, as recommended by the manufacturer.

**Bench-scale spray booth**

A bench-scale spray booth was built to study the characteristics of chromate-based paints in a controlled laboratory setting in which the paint can be sprayed and sampled. It consisted of a 3.5 m (11.5 ft) long steel sheet metal duct, 0.4 m (16 in.) in diameter, connected to the sidewall of a chemical fume hood at one end and to a spray box (a five-sided wooden box) at the other end (Fig. 1). The draft from the chemical fume hood pulled air into and through the spray box and the duct. Disposable air filters (Filtration Group, Joliet, IL, USA) were placed at the end of the duct to remove more than 95% of airborne particulates from the paint mist leaving the duct and entering the fume...
hood. The air velocity inside the duct was controlled by a sliding damper in the duct as well as by the position of the front sash of the chemical fume hood. Paint was sprayed with a paint gun positioned inside the spray box. The spray system consisted of a one-quart HVLP gun (model 98-1130 Mach 1, Binks Manufacturing Company, Franklin Park, IL, USA) connected to a 2.5 hp portable air compressor (model 4B229, Campbell Hausfeld, Harrison, OH, USA). An oil and water extractor (model 96-945, Binks Manufacturing Company), was placed in line between the air compressor and the spray gun to supply water-free and oil-free air to the gun. The extractor included a regulator (model 85-225, Binks Manufacturing Company) to control the air pressure to the spray gun.

Sampling equipment

Paint aerosol was sampled using eight-stage Marple personal cascade impactors (Model 298, Graseby Andersen Samplers, Inc., Atlanta, GA, USA) and constant flow rate pumps (model 224-PCXR4, SKC Inc., Eighty Four, PA, USA). Pumps were calibrated in-line, before and after sampling at a flow rate of 2 liters per minute (L/min), using a minibuck calibrator (model M-5, A.P. Buck Inc., Orlando, FL, USA). Sample collection media consisted of 35 mm stainless steel metal substrates (Graseby Andersen Samplers, Inc., Atlanta, GA, USA) or 35 mm PVC filters with 5.0 µm pore size (Graseby Andersen Samplers, Inc.). Stainless steel substrates with pre-cut slots were supplied by the manufacturer. A die was custom made in the laboratory to cut slots in PVC filters since these were supplied by the manufacturer without slots. Ten filters with slots and a backup filter were used in each cascade impactor. The backup filter was a PVC filter without slots.

Paint aerosol sampling and analysis

Effect of particle bounce. Paint samples were collected on three different types of substrates in the bench-scale spray booth to determine whether particle bounce in the impactor affects the size distribution of the paint spray aerosol samples in this study.

Sample collection and analysis: Three to four minute paint aerosol samples were collected. Six samples were collected using cascade impactors outfitted with stainless steel metal substrates coated with a thin coat of silicon oil (Fluid Products Group, Saint Louis, MO, USA). Six samples were collected on uncoated stainless steel metal substrates. Four samples were collected on PVC filters.

Isokinetic sampling was necessary to ensure that a representative sample of the paint aerosol enters the inlet of the sampling device. Sampling is considered isokinetic when the sampler inlet is aligned with the direction of the approaching gas flow and the average sample flow velocity entering the sampler inlet is equal to the gas flow velocity approaching the sampler (Hinds, 1999). The cascade impactor sampler was placed on a wooden stand inside the duct, along the centerline of the duct and 10.5 ft downstream from the spray gun. The cowl of the cascade impactor was replaced with a custom-made inlet (Fig. 2) that was in alignment with the gas flow in the duct during sampling. The custom-made inlet
consisted of an 89 mm (3.5 in.) long stainless steel thin-walled tube 11 mm (0.43 in.) in diameter connected to a cylindrical stainless steel section 30 mm (1.2 in.) long and 28 mm (1.1 in.) in diameter. The wall of the cylindrical section was lined with plaster (Custom Building Products, Seal Beach, CA, USA) to produce a conical path for the gas going into the cascade impactor sampler. The conical path allowed for a smooth gradual expansion of the path through which the sampled gas passed as it traveled from the sampler inlet 11 mm (0.43 in.) in diameter to the first cascade impactor stage which was 28 mm (1.1 in.) in diameter. A smooth gas expansion in the cascade impactor inlet minimized gas turbulence inside the sampler inlet and was therefore assumed to minimize sample losses to the walls of the sampler inlet. The new sampler inlet of diameter 1 mm (0.43 in.) allowed for an airflow velocity of 0.36 m/s (70 ft/min) inside the inlet. During paint sampling, the air velocity in the duct was maintained equal to the air velocity inside the cascade impactor inlet at 0.37 m/s (72 ft/min). Duct velocity was equivalent to the airflow requirement of 0.045 m³/s (100 ft³/min) per 0.09 m² (1 ft²) for a large paint booth (ACGIH, 1988).

Substrates were weighed before sampling and 16–20 h after sampling on a Cahn 25 automatic electrobalance (Orion Research Inc., Boston, MA, USA) to determine the aerosol mass collected on each cascade impactor stage and backup filter.

Effect of gun atomization pressure. This experiment sought to determine the effect of different gun atomization pressures on the size distribution of paint spray aerosols.

Sample collection and analysis: The nozzle of the spray gun used in this study was outfitted with a pressure gauge to measure its atomization pressure. HVLP spray guns are supposed to operate at atomization pressures no greater than 10 psi (Hund, 1997). The effect of atomization pressures 6, 8, 9 and 10 psi on paint aerosol size distribution was evaluated in this study. Paint spray samples were collected inside the spray duct using cascade impactors with stainless steel substrates. The cascade impactor inlet was 0.2 m (8 in.) away from the duct walls and 2.7 m (9 ft) downstream from the spray gun nozzle during sampling. The sampling inlet was aligned parallel to the aerosol flow streamlines in the duct. However, anisokinetic sampling conditions prevailed in this experiment with the air velocity in the chamber duct at 0.77 m/s (150 ft/min) and the air velocity inside the sampler inlet at 0.37 m/s (72 ft/min). Duct velocity was equivalent to the airflow requirement of 0.045 m³/s (100 ft³/min) per 0.09 m² (1 ft²) for a large paint booth (ACGIH, 1988).

Samples were analyzed gravimetrically. All samples in the study were analyzed similarly to samples in the particle bounce study.

Effect of aerosol generation source—direct-spray aerosol. Direct-spray aerosols of different ages were collected in the bench-scale spray booth in order to study the effect of aerosol aging on the size distribution of direct-spray paint aerosols.

Sample collection and analysis: The air velocity inside the duct was kept constant at 0.36 m/s throughout the sampling. Varying the distance between the spray gun and the sampler inlet results in a time differential between release from the gun nozzle
and sample collection. This time differential is referred to as the age of the aerosol. Cascade impactor stages with stainless steel substrates were used. Samples were collected along the centerline of the duct under isokinetic sampling conditions. The distances between the sampling inlet and spray gun nozzle were 1.9, 2.4, 3.0, 3.6 and 4.2 m (6.1, 8.0, 9.8, 11.9 and 13.7 ft) and produced aerosols aged 5.3, 6.9, 8.4, 10.2 and 11.7 s. The atomization pressure of the spray gun was maintained at 10 psi. Samples were analyzed gravimetrically.

Effect of aerosol generation source—overspray aerosol. The size distribution of overspray paint aerosols was determined.

Sample collection and analysis: Cascade impactors with stainless steel substrates were used to collect samples. Atomization pressure of the spray gun was maintained at 10 psi. Samples were analyzed gravimetrically. Overspray was sampled at two different locations in the paint booth, downstream and at a 90° position.

Downstream position: Overspray paint aerosol was generated in the spray box and sampled inside the duct (Fig. 3a). A flat 0.5 m × 0.5 m (20 in. × 20 in.) piece of sheet metal was sprayed. The sampler was positioned inside the booth such that the direction of overspray paint traveling from the metal plate to the sampler was parallel to the airflow in the paint booth. Samples were collected isokinetically along the

Fig. 3. Schematic illustration of the experimental setup for sampling overspray: (a) overspray sampled downstream and (b) overspray sampled at a 90° position.
centerline of the duct with a gas flow rate of 0.36 m/s (70 ft/min) inside the duct and the sampler inlet. Guidelines recommend a spray gun to object distance of 15 cm (6 in.) to 20 cm (8 in.) (Hund, 1997). The distance between the paint gun nozzle and the metal surface to be painted in this experiment was maintained at 20 cm (8 in.) to simulate spray-painting operations in field operations. The sampler was placed inside the duct at different distances away from the metal surface to be painted. The paint left the spray gun at an estimated velocity of 0.85 m/s (≈170 ft/min) (see Appendix 1 for calculation) and traveled for about 0.2 s before reaching the metal surface. The distances between the metal surface and the sampler inlet were 0.9, 2.0 and 2.6 m (3, 6.8, and 8.7 ft). The paint aerosol traveled between the metal and the sampler at a velocity of 0.3 m/s (70 ft/min), the gas velocity in the duct. Therefore, the overspray aerosol sampled in this experiment was 2.8, 6.0 and 7.7 s old by the time it was sampled.

90° position: A cascade impactor was placed next to the paint spray gun, inside the spray box (Fig. 3b). A flat 0.5 m × 0.5 m piece of sheet metal was sprayed. The sampler and the spray gun were placed side by side, 13 cm (5 in.) apart. The direction of overspray traveling from the metal plate to the sampler was perpendicular to the direction of air flow in the paint booth. The distance between the gun nozzle and the metal surface to be painted was maintained at 0.2 m (8 in.). Three to 6 min samples were collected. A complex flow field of turbulence was present in the area between the spray gun, the target and the sampler.

Data analysis

The aerosol mass of particles collected on each impactor stage and backup filter was used to determine the cumulative mass distribution of particles in each aerosol sample to define the particle size distribution of the paint aerosol. The particle size fractions were corrected for anisokinetic sampling in the gun atomization pressure experiments using the Belyaev and Levin (1974) equation for sampling inlet efficiency. The cumulative mass fractions were averaged across each size range and plotted on log-probability graphs to determine aerosol size distributions for all samples. The median of each distribution defined the mass median aerodynamic diameter (MMAD). The ratio between the median size MMAD and the size associated with a cumulative mass of 16% represented the geometric standard deviation (GSD) of the aerosol size distribution (Hinds, 1999). The GSD was determined from the lognormally distributed portion of the graphs.

A one-way analysis of variance (ANOVA) test was conducted to determine the effects of: (i) using coated metal, uncoated metal or PVC substrates; (ii) spray gun atomization pressure; (iii) aerosol aging in direct-spray aerosol; (iv) aerosol aging in overspray aerosol sampled downstream from the item being painted; (v) aerosol generation source on aerosol MMAD. The Kolmogorov–Smirnov test was used to test data groups for normal distribution. Variability about data group means was determined. The data were analyzed using the nonparametric Kruskal–Wallis ANOVA on Ranks test when either the normality test or the equal variance test failed.

RESULTS AND DISCUSSION

This study examined the effects of particle bounce in a Marple cascade impactor, spray gun atomization pressure, aerosol aging and aerosol generation source (direct versus overspray) on the size distribution of chromate-based paint spray aerosols in a bench-scale spray booth.

Effect of particle bounce

Cascade impactors were the collection devices used in the study to determine the size distribution of chromate-based paint spray aerosols. Particle bounce inside a cascade impactor may result in biased size distributions and can be avoided by coating impaction substrates with silicon grease or other similar material (Dzubay et al., 1976; Rao and Whitby, 1978a,b; Esmen and Lee, 1980; Lawson, 1980, Chan and Lawson, 1981; Hinds et al., 1985). A study of paint spray aerosol size distribution by Chan et al. (1986) used cascade impactors for sample collection but did not describe the impaction substrates. Another study of paint aerosol size distribution that used cascade impactors did not coat the collection substrates (Kalman et al., 1984). Carlton and Flynn (1997) measured the breathing zone particle size distribution of a paint aerosol sampled with uncoated polycarbonate filter. PVC filters are used for impaction surfaces when certain chemical analysis is needed, such as analysis for Cr(VI).

Table 1 gives the mean MMAD and standard deviation (SD) of paint spray aerosols sampled on three impaction surfaces: uncoated metal, coated metal and PVC. The differences between the average MMADs of laboratory-generated paint aerosols sampled using uncoated metal, coated metal or PVC substrates were not statistically significant (P = 0.464). There was an absence of significant bounce for paint aerosols

Table 1. Mean MMAD and SD of paint spray aerosols by impaction surface

<table>
<thead>
<tr>
<th>Impaction surface</th>
<th>Mean MMAD (μm)</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated metal (n = 6)</td>
<td>10.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Coated metal (n = 6)</td>
<td>9.7</td>
<td>0.6</td>
</tr>
<tr>
<td>PVC (n = 4)</td>
<td>9.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Coated with a thin coat of silicon oil.
Effect of gun atomization pressure

A study objective was to evaluate the effect of atomization pressure on the size distribution of paint spray aerosols generated in a laboratory setting. Table 2 gives the range, mean MMAD and mean GSD of paint aerosols at different atomization pressures. About 90% of the aerosol mass consisted of particles larger than 2 μm and can be represented by a lognormal distribution. The mean MMAD ranged from 8.2 μm (mean GSD = 2.4) for a paint aerosol generated by a spray gun with an atomization pressure of 6 psi to 7.0 μm (mean GSD = 3.1 μm) for an atomization pressure of 10 psi. There was a decreasing trend in mean MMAD as atomization pressure increased. The differences in mean MMADs between paint aerosols generated at various atomization pressures were not statistically significant (P = 0.659). Although not statistically significant, the observed trend was consistent with those published by others. Chan et al. (1986) evaluated the effect of atomization pressure on the size distribution of high-solids paint overspray aerosols in a paint booth. As atomization pressure to the spray gun increased from 30 to 65 psi, the particle MMAD decreased from 6.6 to 4.7 μm. The difference between the MMADs reported by Chan et al. and the larger mean MMADs observed in this study may be attributed to the type of spray gun used. Conventional spray guns operate at much higher atomization pressures than HVLP guns and generate smaller paint aerosol droplets. Carlton and Flynn (1997) evaluated the effect of atomization pressure on breathing zone particle size distribution of paint spray in a laboratory setting and in the field. They evaluated nozzle atomization pressures of 30–50 psi in a conventional spray gun. They found that the mean GSD of paint aerosol decreased significantly, from 11.2 to 10.6 μm, as nozzle pressure increased from 30 to 50 psi. This finding was observed in a laboratory spray booth when a mannequin was positioned with the air stream flowing towards the mannequin’s back. The mean diameters of paint aerosol particles reported by Carlton and Flynn are much larger than those measured in this study and the one by Chan et al.

High gun nozzle pressures result in paint aerosols with smaller size distributions. Smaller paint droplets do not transfer efficiently to the surface being painted and are likely to be carried by air movements to the spray painter’s breathing zone. Using the minimum gun nozzle pressure possible to achieve a spray paint job is recommended to reduce worker exposures to paint aerosol.

Size distribution of overspray aerosol

Overspray may be a source of exposure to workers as a result of paint not contacting the surface being painted and being carried back into the breathing zone of a worker by moving air.

Overspray aerosol is potentially a major source of worker exposure to paint spray aerosol in field applications. Two overspray sampling positions were evaluated: a downstream position and a 90° position. Direct-spray aerosol was also evaluated for comparison purposes. Fig. 4 shows the size distribution of direct-spray and overspray aerosols sampled at downstream and 90° positions. The size distribution of overspray aerosols was lognormally distributed for only about 60% of the aerosol mass, particles from 2 to 10 μm. Others (Kim and Marshall, 1971; Ackley, 1980; Kwok, 1991) had reported size distributions of paint spray aerosol that did not follow the logarithmic distribution function.

Overspray sampled downstream. The overspray paint aerosol sampled downstream was considered representative of the exposure of a worker positioned between the item being painted and the exhaust in a paint booth. The distance between the painted surface and the sampler evaluated in these experiments ranged from 0.9 to 2.6 m (3–8.7 ft) and resulted in a mean MMAD of 7.2 μm (±2.1 μm). Although it is not common for workers to position themselves between the painted surface and the exhaust, they do occasionally. For example, this has been reported in field applications where the worker walked into a paint booth equipped with a backwall exhaust ventilation system, as he sprayed large metal parts arranged on tables (Sabty-Daily et al., 2004).

Overspray sampled at 90°. The overspray paint aerosol sampled at the 90° position was considered representative of a worker’s exposure when the worker is spraying a surface such that the spray direction is perpendicular to the airflow in a paint booth and the worker’s breathing zone is 0.2 m (8 in.) away from the painted surface. This position of a worker in a paint booth is quite common in field applications (Heitbrink et al., 1995; Carlton and Flynn, 1997;
Sabty-Daily et al. (2004) and resulted in a mean MMAD of 5.9 μm (±1.6 μm) (Fig. 4).

Carlton and Flynn (1997) reported average MMADs of 18.9 μm in the field and 22 μm in the laboratory for size distributions of HVLP-generated paint aerosols sampled at the breathing zone of a worker spraying with a paint gun 0.2 m (8 in.) away from a metal surface and with the direction of spray perpendicular to that of booth airflow. In a similar setup, our study of overspray sampled at 90° measured a mean MMAD of 5.9 μm. The sampled aerosol is representative of exposure in the breathing zone of a spray painter located 0.2 m from a surface being painted with air flowing across his side. A complex turbulent airflow field was created between the spray gun nozzle, the painted metal plate and the sampler during sampling. The effect that possible anisokinetic sampling conditions may have had on the measured size distributions cannot be quantitatively assessed due to the complex and turbulent nature of the airflow field around the sampler inlet.

The difference between the size distributions reported by Carlton and Flynn and the ones measured here for overspray sampled at 90° may be attributed to several factors. In our study, some solvent had evaporated from the paint aerosol droplets as they traveled from the spray gun to the sampler inlet, while Carlton and Flynn measured particle size distribution directly to minimize bias from solvent evaporation. Paint particles were somewhere between 100 and 63% of their original aerodynamic size at the time they impacted inside the cascade impactors of our study (Appendix 2). Therefore, evaporation alone cannot explain the difference in MMADs observed in the two studies. Biases in the efficiency of sampling devices used for sampling larger particles may explain part of the results. Carlton and Flynn used 37 mm closed-face filter cassettes while cascade impactors were used in this study. Cascade impactors have been shown to undersample larger particles (Rubow et al., 1987). Rubow et al. (1987) evaluated the sampling efficiency of cascade impactors; sampling effectiveness was 84% for 10 μm particles and decreased to about 60% for 20 μm particles.

Whether overspray was sampled downstream or at 90° had no significant effect on its MMAD (P < 0.05).

Comparison to direct-spray aerosol. The size distribution of direct-spray aerosol was assessed for comparison purposes. It is uncommon for a worker to be exposed to direct-spray paint in field applications since paint spray is typically directed towards a surface to be painted and not the worker himself. The MMAD of direct-spray paint aerosol ranged from 7.2 to 10.2 μm with an average of 9.2 μm (mean GSD = 2.1) (Fig. 4).

A comparison of overspray to direct-spray aerosol indicated that differences in mean MMADs between
direct-spray aerosol and overspray aerosols were statistically significant ($P < 0.010$). A Tukey test for pairwise multiple comparisons indicated the difference between mean MMADs of direct-spray and overspray sampled either downstream or at $90^\circ$ was statistically significant ($P \leq 0.007$). The data showed that overspray aerosol consisted of particles smaller in diameter than direct spray paint particles. Larger paint aerosol particles appear to have adhered to the painted surface or deposited on the chamber walls leaving the small particles to be carried by air movement into the sampler inlet.

Measured size distributions represented the size distributions of paint spray aerosol at specific sampling locations within the bench-scale spray booth. Droplets of paint leaving the spray gun were composed of solid Cr-containing particles surrounded by resin and solvent. Atomizing air transported paint droplets from the spray gun nozzle to the workpiece surface. During the transport process, some solvents evaporated. Paint droplet size decreased as solvents evaporated. The size distribution of paint spray aerosol reached a steady size distribution only after the evaporation of solvents was complete. Cascade impactors captured paint spray at specific locations inside the spray booth. Resulting size distributions characterized paint aerosols at these locations but did not represent size distributions of paint spray aerosols at the spray gun nozzle. The assumption was made that all droplets reduce in size by the same factor as solvents evaporate. Thus, solvent evaporation prior to sampling, while the paint aerosol travels from spray gun to sampler inlet, had no effect on the width of the size distributions measured at the locations specified in this study. The mass of solids was measured on each impactor stage 16–20 h after sampling. Solvent evaporation from all captured particles was assumed to be complete at the time of weighing. Therefore, solvent evaporation after sample collection did not affect size distribution measurements significantly. During sampling, particles impacted on different stages of the cascade impactor based on their aerodynamic size as they traveled through the impactor. Evaporation of solvents may have occurred during sample collection, as the paint aerosol traveled through the cascade impactor. This evaporation would have significantly changed the measured size distribution of the aerosol traveling through the impactor only if sufficient time elapsed between the time a particle entered the impactor inlet and the time it reached an impactor stage. Maximum evaporation during sampling occurred for particles traveling the maximum distance in the cascade impactor, i.e. to the last impactor stage. The time it took a particle to travel this maximum distance was estimated to be 0.4 s (Appendix 3). Most of the Cr mass in the paint aerosols evaluated in this study that deposited on the upper 2 or 3 stages of the cascade impactor was in larger particle size ranges. The MMAD of the studied aerosols traveled only about 0.2 s before depositing on these stages of the impactor. Sampled paint particles lost less than the maximum of 37% (Appendix 2) of their original aerodynamic diameter due to solvent evaporation as they traveled a short amount of time in the impactor before depositing, because paint droplets were still wet and sticky when they deposited in the cascade impactor. Sampled particles were observed stuck together and to the sampling substrates. Therefore, it is reasonable to assume that evaporation of solvent from paint aerosol droplets during passage through the impactor had no significant effect on the measured size distributions reported in this study.

Effect of aerosol aging

**Direct-spray aerosol.** The direct-spray paint aerosol was evaluated at different distances from the spray gun nozzle to determine its size distribution 5.3–11.7 s after it was released by the spray gun nozzle. Fig. 5 shows the log probability graph of particle diameter versus percentage of particles less than a given size. The graph illustrates the size distribution of the direct spray aerosol at different aerosol ages. The graph indicates the size distributions of the direct spray aerosol for the portion of the size distribution 2–15 μm to be approximately lognormally distributed, for all studied aerosol ages. About 75% of the aerosol mass consisted of particles 2–15 μm and can be represented by a lognormal distribution. The mean GSD was estimated for the lognormally distributed portion of the aerosol. The mean MMADs were 9.0 μm (mean GSD = 2.1), 9.4 μm (mean GSD = 2.2), 8.9 μm (mean GSD = 2.2), 9.1 μm (mean GSD = 2.1) and 9.6 μm (mean GSD = 2.1) for aerosols 5.3, 6.9, 8.4, 10.2 and 11.7 s old. Time was not a significant factor in determining the MMAD of direct-spray aerosols after 5.3 s ($P = 0.877$).

**Overspray aerosol.** Figure 6 is a log probability graph of particle diameter versus percentage of particles less than a given size for overspray aerosol sampled downstream at different aerosol ages. About 50–70% of the aerosol mass consisted of particles smaller than 10 μm and can be represented by a lognormal distribution. The mean GSD of the lognormally distributed portion of the size distribution was estimated. Mean MMADs were 7.5 μm (mean GSD = 2.8 μm), 5.4 μm (mean GSD = 5.5 μm) and 8.8 μm (mean GSD = 3.0 μm) for aerosols 2.8, 6.0 and 7.7 s old.

Overspray sampled downstream traveled 2.8–7.7 s from spray gun nozzle to sampler inlet and 0.9–2.6 m (3.0–8.7 ft) from the painted surface to sampler inlet. This time differential had no significant effect on
aerosol MMAD ($P = 0.200$). Most of the change in aerosol size distribution, due to impaction onto the painted surface, deposition on the walls and/or solvent evaporation, appears to have occurred sometime between the time the paint aerosol impacted the painted surface and the time it became 2.8 s old. The data suggest that a worker positioned between the painted surface and the exhaust or exposed to air...
contaminated with overspray that has traveled 2.8–7.7 s from the time it left the spray gun may be exposed to inhalation of paint aerosols with mean MMAD of 7 μm. Workers in the field may be exposed to such an overspray when in proximity to a spray painting operation. This was reported in split-level booths where two painters stand on two separate platforms in a spray booth and overspray may travel to the breathing zone of a worker as it flows towards the exhaust (Sabty-Daily et al., 2004).

Health risk implications

To evaluate the potential health effects that may result from exposure to Cr(VI)-containing overspray paint aerosols three issues need to be determined: (i) deposition of the aerosol; (ii) the uptake of Cr(VI) by lung tissues and cells; (iii) the clearance of Cr(VI) from the lung. In this study we attempted to measure the size distribution of paint overspray aerosols in the laboratory. The measured overspray size distributions were representative of a worker’s exposure to overspray that found its way to the worker’s breathing zone up to 7.7 s after paint spray was generated at the nozzle. Size distribution influences the site and degree of respiratory deposition and damage that may result from inhaled Cr(VI)-containing paint particles. The overall mean MMAD of overspray was 7 μm in this study. The fraction of aerosol mass expected to deposit in the head airways, tracheobronchial and alveolar regions of the respiratory tract was estimated to deposit in the head airways region. Only 3 and 4% of the mass is expected to deposit in the tracheobronchial and alveolar regions, respectively. Since MMADs reported in this study are expected to be underestimated due to bias from the cascade impactor sampling inlet efficiency, the fraction of overspray aerosol mass expected to deposit in the head airways region may even be >88%. Sabty-Daily et al. (2004) conducted a field study that determined the particle size distribution and valence state of Cr at the breathing zone of workers spraying paint. The size distributions reported in the field study were based on the analysis of 30 cascade impactor samples. They were consistent with the ones reported here. They suggested most of the paint aerosol reaching the breathing zone of a spray painter will most likely deposit in the head airways region of the respiratory system.

APPENDIX 1

Based on fluid dynamic laws, the mass flow rate \( m \) of a liquid passing through a controlled orifice of fixed size and shape is a function of the liquid density \( \rho \), the area of the orifice \( A \) and the average liquid velocity \( V \) through the orifice (Wark, 1983):

\[
m = \rho A V
\]

\[
V = m p^{-1} A^{-1}
\]

Based on the authors’ experience in the laboratory, the paint mass flow rate averaged 20 g/min out of the paint spray gun. The density of the paint was 1.16 g/ml. The area of the spray gun nozzle orifice was 3.4 \( \times \) 10\(^{-3} \) cm\(^2\). Therefore, the velocity of paint spray at the spray gun nozzle was:

\[
V = (20 \text{ g min}^{-1}) \times (1.16 \text{ g ml}^{-1})^{-1} \times (3.4 \times 10^{-3} \text{ cm}^2)^{-1} = 5.07 \times 10^3 \text{ cm min}^{-1} = (5.07 \times 10^3 \text{ cm min}^{-1}) \times (10^{-2} \text{ m cm}^{-1}) \times (60^{-1} \text{ min s}^{-1}) = 0.85 \text{ m/s}
\]

APPENDIX 2

Bulk paint products used in the booths evaluated in this study had a maximum solvent content of 75% by volume. Therefore, if all the solvent evaporated from a paint droplet, the relationship between its initial volume \( V_1 \) and its volume after total evaporation \( V_2 \) would have been:

\[
V_2 = 0.25 \times V_1
\]

Given the following relationship between volume \( V \) and diameter \( D \):

\[
D \propto V^{1/3}
\]

The diameter of a paint droplet \( D_1 \) would have reduced to a minimum diameter \( D_2 \) after total evaporation of solvents as follows:

\[
D_2 = D_1 \times (0.25)^{1/3} = 0.63 \times D_1
\]

or

\[
D \propto (0.25)^{1/3}
\]

For example, 20 and 10 μm particles exiting the paint spray gun will have diameters of 12.6 and 6.3 μm, respectively, after complete evaporation of all solvents.
APPENDIX 3

Maximum solvent evaporation from paint droplets during sampling occurred for droplets traveling the maximum distance in the cascade impactor to the last impactor stage. To calculate the time it took a particle to travel this maximum distance at a sampling flow rate of 2 L/min, the air space volume \( V_{\text{air}} \) between the first and last stage of the cascade impactor was estimated as follows.

The volume of the aluminum in the cascade impactor stack of stages 1–8 based on its actual mass \( (M) \) and the density of aluminum \( (\rho_{\text{Al}}) \) is:

\[
V_1 = \frac{M}{\rho_{\text{Al}}} = \frac{125.7 \text{ g}}{2.7 \text{ g cm}^{-3}} = 46.6 \text{ cm}^3
\]

The volume of the cascade impactor stack of stages 1–8 based on its physical dimensions is:

\[
V_2 = 59.6 \text{ cm}^3
\]

Therefore,

\[
V_{\text{air}} = V_2 - V_1 = 59.6 \text{ cm}^3 - 46.6 \text{ cm}^3 = 13.0 \text{ cm}^3
\]

The time \( (t) \) it took a droplet to travel the maximum distance from first to last cascade impactor stage was:

\[
t = \frac{V_{\text{air}}}{Q}, \text{ where } Q \text{ is the gas flow rate inside the cascade impactor}
\]

\[
= \frac{13.0 \text{ cm}^3/(2 \text{ L min}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1} \times 60 \text{ s}^{-1})}{0.4 \text{ s}}
\]

Acknowledgements—We sincerely thank the management of the Aircraft Division of Northrop Grumman Corporation in Hawthorne, CA, particularly Ms. Scotty Butler and Ms Jackie Lucas, who allowed us to observe workers in primer spray painting operations. Deft Inc., Irvine, CA, supplied paint materials and information. Mr Richard Albers with Deft Inc. provided technical assistance. Dr Yoram Cohen and Dr Wen Chen Liu provided helpful discussions and suggestions. Mr Gustavo Cordero, Mr stavro Pilafas, Ms Kanugnig Thirakomen and Ms Wendy Way provided valuable laboratory technical assistance. Partial funding was received from the NIOSH grant U60 CCU902286, the Toxic Substances Research and Teaching Program of the University of California, the Center for Occupational and Environmental Health of the University of California in Los Angeles, the Public Health Trust grant 543A 8802 G1298 and the NIOSH Education and Research Center grant 742/CCT918726. The study was supported by the National Institute of Environmental Health Sciences grant 5 P30 ES07048-06.

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