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Exposure to airborne nano-titanium dioxide during airless spray painting and sanding

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ABSTRACT

The objectives of the study were to measure and characterize exposure to airborne nanoscale titanium dioxide during airless spraying and sanding of a nano-enabled paint, and to evaluate the effectiveness of dust capture methods in reducing airborne nanoparticle concentrations. A tradesperson performed the work activities in an environmentally controlled chamber. Samples were collected in the tradesperson's breathing zone and in surrounding areas to assess bystander exposure. Filter-based samples were analyzed using gravimetric methods, scanning electron microscopy, and energy dispersive spectroscopy. Differential particle count data were obtained by means of a scanning mobility particle sizer. Local exhaust ventilation provided statistically significant reductions of airborne nanoparticle concentrations during sanding. Sanding the paint after drying with a handheld power sander generated relatively low levels of airborne titanium dioxide. In contrast, task-based exposure measurements collected during the initial airless spray application of the nano-enabled paint suggested a potential for occupational exposures to exceed the time-weighted average exposure limit for ultrafine titanium dioxide recommended by the National Institute for Occupational Safety and Health. Painters applying nano-enabled coatings may have little recourse but to rely, in some instances, on lower tiers of the hierarchy of controls, such as personal protective equipment. In light of these findings, employers and industrial hygienists should characterize exposures and implement the hierarchy of controls to ensure painters are sufficiently protected.

KEYWORDS

Construction; engineering controls; inhalation; local exhaust ventilation; nano-enabled; nanomaterials

Introduction

Advances in science, technology, and engineering at the nanoscale (~1–100 nm) have led to the development of nano-enhanced and nano-enabled products (NEP). Examples of commercially available NEPs in the construction industry include a range of paints and coatings, such as anticorrosive coatings enriched with carbon nanotubes and self-cleaning nanoscale films applied to glass windows.[1] Among the types of NEPs used by construction workers, paints and coatings are currently the most widely available.[2] Manufactured nano-objects and their agglomerates and aggregates (NOAA) can be added to paints for improved performance, and nanoscale titanium dioxide (TiO_2) is a commonly used additive for this purpose.

Whether occupational exposure to TiO_2 can cause adverse health effects has been the subject of research since the 1980s. The National Institute for Occupational Safety and Health (NIOSH) evaluated this body of literature, conducted a quantitative risk assessment, and recommended an occupational exposure limit 8 times lower for ultrafine TiO_2 ($0.3\,mg/m^3$) compared to fine TiO_2 ($2.4\,mg/m^3$). These Recommended Exposure Limits (RELs) were established as time-weighted average concentrations for up to 10 hr per day during a 40-hr workweek.[3] Ultrafine TiO_2, which includes engineered nanoscale TiO_2, was also classified as a potential occupational carcinogen, whereas larger-sized fine TiO_2 was not, due to insufficient evidence.

Far more studies have been published on the intrinsic hazards of nanomaterials (83%) as opposed to exposure assessment (16%) and release of nanomaterials from solid composites (<1%), according to a review of the nanotechnology environmental health and safety literature.[4] Only a relatively small number of studies have examined release of nano-TiO_2 from construction materials and potential for occupational exposure. Most of these studies investigated sanding

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Figure 1. Photographs of the tradesperson in the test chamber performing airless spray painting (left image) and power sanding with local exhaust ventilation (right image).

of paints or coatings,[5–9] while others examined initial spray application of coatings or machining of cementitious materials.[10–13] Results from these studies are mostly encouraging with regard to worker health, but further research is needed to bolster the current understanding of exposure risk among construction workers handling NEPs, an area of knowledge that remains fairly limited.

Objectives of the current study were to examine potential release of unbound nanoscale TiO_2 and to measure exposure to TiO_2 NOAA during airless spray painting and subsequent sanding of a commercially available paint plus primer containing nanoscale TiO_2. The study also sought to evaluate dust capture methods during sanding with regard to airborne nanoparticle concentrations.

Methods

Overview

An experienced tradesperson performed the spray painting and sanding activities in an enclosed space to avoid measurement of nano-sized atmospheric particles, such as those found in vehicle exhaust. Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) was used to ascertain chemical identity, morphology, and size of particles added to the paint as well as those generated during work activities. Particle size distributions and particle number concentrations were obtained via real-time particle counters. Mass-based measures of exposure were made using gravimetric filter-based sampling techniques. The Center for Construction Research and Training's (CPWR) Institutional Review Board (FWA 00000608, IRB 00001202) approved the sampling activities described below.

Bulk sample analysis

A 1-gallon can of a nano-enabled paint purchased from a major hardware chain was stirred with a wooden paint stirring stick for approximately 10 min, and a 50 mL aliquot was submitted to the microscopy laboratory (Maxxam Analytics, Kennesaw, GA). Particle size and morphology were determined via on-screen observation and micrograph analysis. A Tescan scanning electron microscope equipped with a Gresham light element detector and an IXRF digital imaging system capable of providing EDS was used for elemental identification of particles. For comparison, the same analyses were performed on a one-gallon can of the same brand of paint, for which there was no claim of nanomaterial additives. Beyond the bulk characterization, no further analyses were performed using the conventional paint of the same brand.

Sampling environment

Sampling was conducted inside an environmentally-controlled chamber in Columbia, Maryland (Figure 1). Smoking was not allowed in or around the chamber or prior to working in the chamber. A HEPA-filtered ventilation unit (Abatement Technologies, HEPA AIRE H1000V, Suwanee, GA) was used to evacuate air from the 2,900 ft^3 (82 m^3) chamber at a rate of approximately two air changes per hour (ACH) and to maintain negative pressure relative to outside. Make-up air was directed into the chamber with a variable speed HEPA-filtered supply ventilation unit (Bluedri Air Shield 550 HEPA, Irwindale, CA) affixed to the wall of the chamber (Figure 2). Negative pressure was maintained in the chamber throughout the study and was monitored using a magnehelic gauge mounted on the chamber wall. Personal air samples were collected to assess exposure to the tradesperson during spraying and sanding, and static area samples were collected to assess bystander exposure. Temperature was measured inside the chamber and consistently maintained throughout the study; relative humidity was measured and varied slightly during testing.

Entry into and exit from the study chamber were controlled through a segregated airlock attached to the testing chamber. All tools, sampling media, and personal protective equipment, i.e., respirator and Tyvek suit, were kept in the airlock between trials. The door from the chamber exterior to the airlock was sealed using duct tape during and between each trial.

After each trial, the chamber was wet wiped followed by accelerated air purging using both HEPA-filtered machines. Negative air pressure was maintained in the chamber during the purging process. Airborne particle counts were measured while purging to observe the decrease in airborne particle concentrations, returning the chamber to a baseline condition prior to each subsequent trial. In terms of mass concentration, no measurements above the limit of detection were reported for total dust background samples collected just before the start of a trial.

Sampling protocol

Five spray painting trials were conducted, each lasting 12–15 min. For each trial, the tradesperson used an airless sprayer (Graco Magnum X5, Minneapolis, MN) to spray paint vertically-mounted plywood (11/32” BC Sanded 4 X 8 ft Plytanium sheathing) at a rate of approximately 0.2 gallons per min for 4–6 min. The spray pump was kept in the sealed airlock to prevent any particles generated by the motor from entering the chamber. Boards designated for sanding received a second coating after drying as would typically be done by painters in the field.

Twelve sanding trials were conducted, consisting of four exposure scenarios examined in triplicate. Either coated or uncoated boards were sanded with either local exhaust ventilation (LEV) supplied by a HEPA-filtered vacuum (VC40-U, Hilti Corporation, Schaan, Liechtenstein) or a dust collection bag connected to a 5-in, 12,000 orbits per minute random orbital sander (Ridgid, Pickens, SC). The LEV equipment was also kept in the sealed airlock separate from the test chamber. A new 100-grit ceramic-based sanding pad was used for each trial, during which the tradesperson continuously sanded the entire surface of the vertically mounted plywood for 10 min.

The tradesperson who performed all of the work wore an MSA Ultra Elite full-face mask connected to an OptimAir powered air-purifying respirator (Mine Safety Appliances Company, Inc., Cranberry Township, PA), a Tyvek suit with hood, and nitrile or latex gloves during the spraying operation (Figure 1). The tradesperson had decades of construction experience and prior to sampling received safety training and technical guidance from an apprenticeship instructor from the International Union of Painters and Allied Trades.

Real-time measurements of particle diameter and count were collected once per minute with a Scanning Mobility Particle Sizer, a TSI NanoScan SMPS Nanoparticle Sizer Model 3910 (TSI Incorporated, Shoreview, MN) at the SMPS station during and between all spraying and sanding. The Model 3910 cyclonically removes particles above 550 nm. The unit creates a charge on the remaining particles that are then sized with a Radial Differential Mobility Analyzer and counted with a Condensation Particle Counter. Together, the NanoScan SMPS and Optical Particle Sizer (OPS) (TSI Model 3330) can measure particles from 10 nm to 10 μm.

During spraying and sanding, four personal sampling pumps worn by the tradesperson were connected by Tygon tubing to a sampling device affixed in his breathing zone. Three GilAir 5 personal air samplers (Sensidyne Inc., USA) and one Escort Elf personal air sampler (Zefon International Inc., Ocala, FL) were used. The first personal sample pulled air at 3.0 liters per minute (LPM) through a 37 mm, 5-micron porosity, pre-weighed polyvinyl chloride (PVC) filter cassette. The second personal sample pulled air at 4.2 LPM through an aluminum GK2.69 (BGI by Mesa Labs, Inc., Butler, NJ) respirable dust cyclone holding a 37 mm, 5-micron porosity, pre-weighed PVC filter. The third personal sample pulled air at 2.5 LPM through an aluminum SKC respirable dust cyclone holding a 37 mm, 0.4-micron porosity polycarbonate (PC) filter (Maxxam Analytics, Novi, MI). The fourth personal sample pulled air at 3.0 LPM through an open-faced 37 mm, 0.4-micron porosity PC filter.

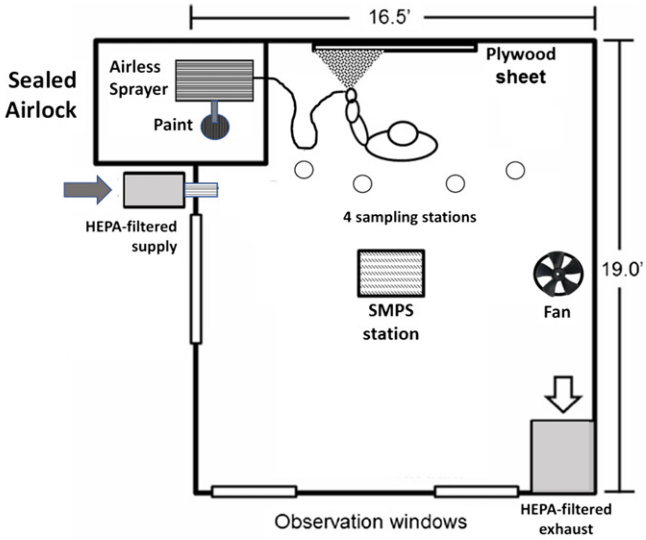

Figure 2. Diagram of the sampling chamber during spray application.

The two personal air samples collected on PC filter membranes, one for total particulate collection (open-faced) and one for respirable particulate (cyclone), underwent SEM/EDS analysis to identify, photograph, and determine the elemental composition of deposited airborne particles encountered on the air sampling medium. One personal sample collected on a pre-weighed PVC filter membrane was analyzed for total dust by NIOSH Method 0500 and for titanium by NIOSH Method 7300 (modified). The other personal sample was collected on a PVC filter membrane using the cyclone and analyzed by NIOSH 0600 for respirable dust and NIOSH Method 7300 for titanium. All pumps were calibrated before and after sampling using an electronic dry piston primary flow meter (DryCal DC-Lite; Bios International Corp., Butler, NJ).

Four sampling stations, positioned in a static arc around the work station (Figure 2), consisted of two types of sampling media: two 37-mm diameter, closed-face cassettes containing 5-micron porosity, pre-weighed PVC filters and two 37-mm diameter, open-face cassettes containing 0.4-micron porosity PC. Cassettes were placed at breathing zone height (1.5 m) on sampling stands approximately 1.2 m from the work and attached by Tygon tubing to high volume samplers (Reliance Electric, Gallipolis, OH) calibrated to draw between 5.8 and 6.0 LPM. These cassettes were analyzed for total dust by NIOSH Method 0500 and for titanium by NIOSH Method 7300 (modified) (PVC); and SEM/EDS characterization (PC).

A direct preparation for SEM analyses was used, which involved cutting a representative portion from each filter, placing it onto an SEM stub and evaporating a surface coat of carbon to provide electrical conductivity for analysis. Sizing and elemental identification of particles and structures on the sample filters were performed using a Tescan scanning electron microscope equipped with a Gresham light element detector and an IXRF digital imaging system capable of providing EDS.

Data analysis

Descriptive statistics for mass-based measurements were derived using univariate methods. Particle count data obtained by the OPS and SMPS were merged and fitted using TSI Inc. software (NanoScan Manager, Aerosol Instrument Manager, and Multi Instrument Manager). Normalized particle number concentrations (*dN/dlogDp*) were used to account for differences in resolution between the two instruments, where *dN* = particle number concentration and *dlogDp* = the difference in the log of the channel width. A representative particle size distribution is presented for each exposure scenario, each representing a single experimental trial.

Concentrations were adjusted for background by subtracting background measurements immediately preceding each trial. Background particle number concentrations measured by the SMPS immediately prior to each trial ranged from approximately 430–1,250 #/cm^3. Normalized particle number concentrations in the nanoscale size range were summed for all experimental trials and exported for analysis. Analysis of Variance (ANOVA) was used to determine if airborne nanoparticle number concentrations differed for coated vs. uncoated wood and by method of dust

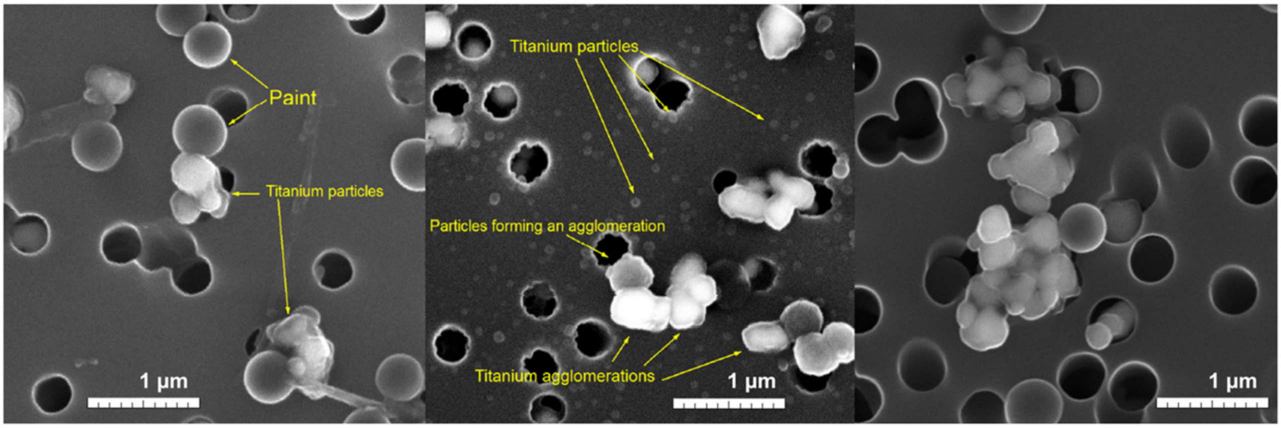

Figure 3. Bulk characterization via SEM showing the nano-enabled paint prepared in water (left), the nano-enabled paint prepared in acetone (middle), and a conventional comparison paint prepared in acetone (right).

capture. Student Newman-Keuls multiple range test was used as a post hoc comparison test for differences in airborne nanoparticle concentrations between sanding conditions. Levene's Test for Homogeneity of Variance, quantile-quantile plots, and Shapiro-Wilk tests were used to verify ANOVA assumptions. Box plots illustrating airborne nanoparticle concentrations during sanding were generated with an open-source R-based application.[14] Hypothesis testing and univariate methods were conducted with SAS 9.4 (SAS Institute Inc., Carey, NC).

Results

Electron microscopy

Bulk characterization of the nano-enabled paint via electron microscopy detected agglomerated nanoscale TiO_2 in the paint. Unbound TiO_2 nanoparticles were not observed in paint samples prepared with water and sonicated, whereas TiO_2 nanoparticles were observed when samples were prepared with acetone and sonicated (Figure 3). Sizing of TiO_2 particles following acetone treatment and sonication revealed that 84% of TiO_2 particles and agglomerates were less than 100 nm, with 46% in the size range of 50–75 nm. TiO_2 nanoparticles were not detected in a conventional paint of the same brand that was prepared with acetone and sonicated.

Unbound nanoparticles were not observed in SEM samples collected during spray application nor sanding. Aerosol captured during spray application consisted of TiO_2 NOAA contained within larger paint globules (see Figure 4). Paint globules ranged in size from approximately 0.5 microns to more than 10 microns. TiO_2 NOAA contained within the paint globules ranged in size from approximately 100–500 nm. TiO_2 NOAA was not detected while sanding unpainted boards, and all sanding conditions appeared to generate airborne copper particles roughly 1 micron in diameter (Figure 5). TiO_2 NOAA was either embedded within or protruding from debris fragments collected during sanding (Figure 6).

Particle counts

For all test conditions, particle size distributions were primarily below 100 nm. Spray application, compared to sanding, generated a higher concentration of particles >100 nm. Peaks in particle number concentrations while spraying were observed at 15 nm, 27 nm, 154 nm, 1 µm, and 2.4 µm (Figure 7).

Particle size distributions during sanding were mostly unaffected by the method of dust capture used and whether the boards were painted or unpainted (Figure 8). The notable exception was a divergence of the particle size distributions around the 100 nm size range; particle counts in this size range were higher when sanding the painted boards compared to the unpainted boards. LEV provided a statistically significant reduction ($p \leq 0.05$) in the number of airborne nanoparticles, and sanding the painted boards generated statistically significantly fewer ($p \leq 0.05$) airborne nanoparticles compared to sanding the unpainted boards (Figure 9).

Mass-based measures of exposure

Spray painting produced considerable levels of airborne particulate and TiO_2 in the test subject's breathing zone (Table 1). Respirable fractions of total aerosol and TiO_2 during spray painting were approximately 5% by weight. The 95% confidence interval for mean exposure to respirable TiO_2 was below the NIOSH REL for fine TiO_2 but greater than the

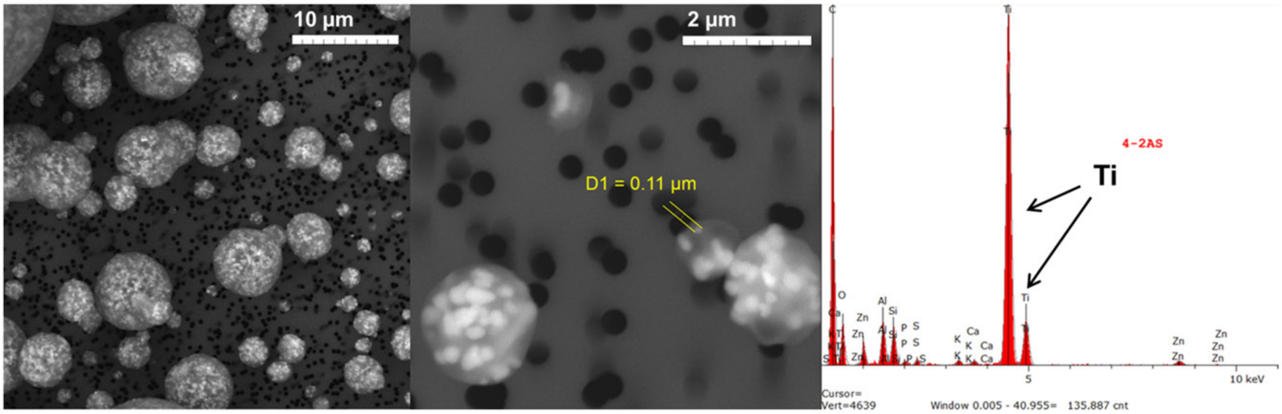

Figure 4. SEM images of aerosol captured during spraying and EDS spectra indicating the presence of titanium.

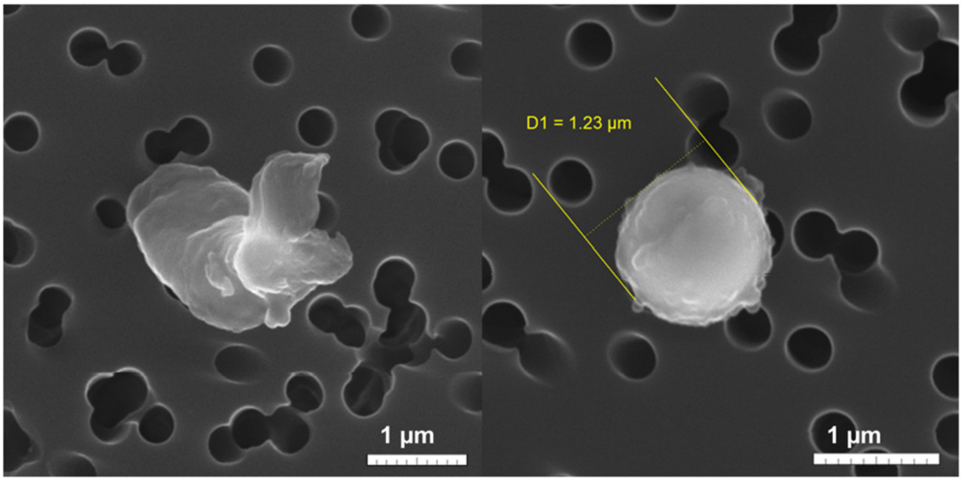

Figure 5. SEM images of sanding debris from unpainted plywood (left) and a copper sphere (right).

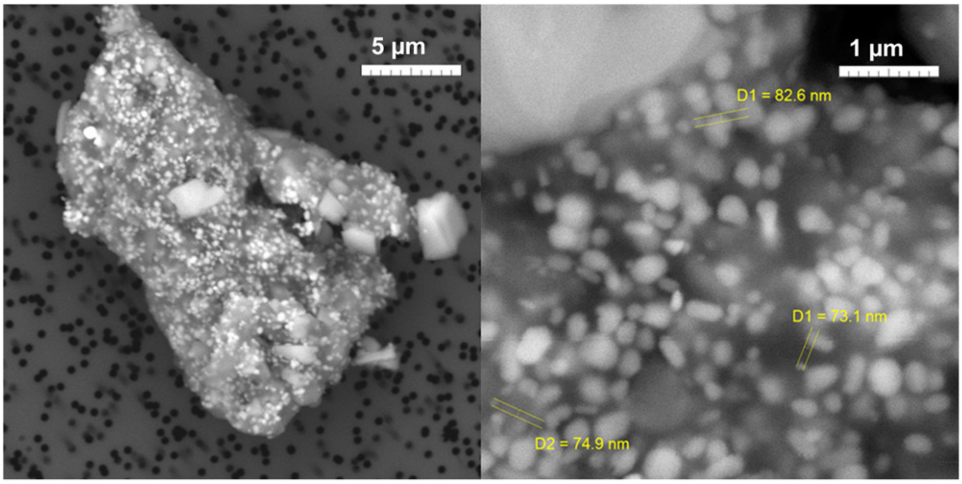

Figure 6. SEM images of sanding debris from plywood painted with the nano-enabled paint.

NIOSH REL for ultrafine TiO_2. TiO_2 represented approximately 38% of the total particulate sampled by weight. Exposure measurements from area samples collected during spraying and sanding as a measure of bystander exposure were similar to exposure measurements obtained from personal samples.

Sanding with either the dust collection bag or LEV produced low levels of dust. The majority of samples were below detectable limits for dust and TiO_2. Peak concentrations in the test subject's breathing zone were 2.9 mg/m^3 for total dust and 1.2 mg/m^3 for respirable dust, well below OSHA's Permissible Exposure

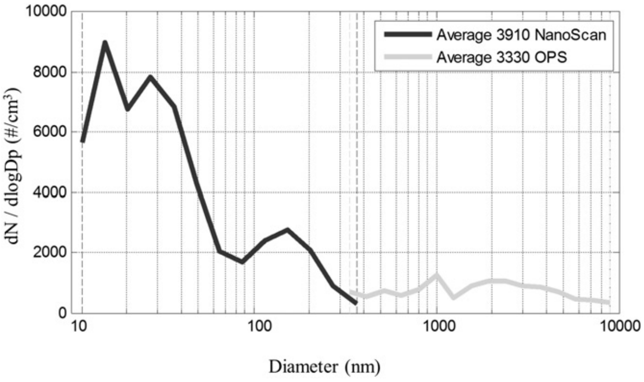

Figure 7. Background adjusted particle size distribution during airless spraying of the nano-enabled paint.

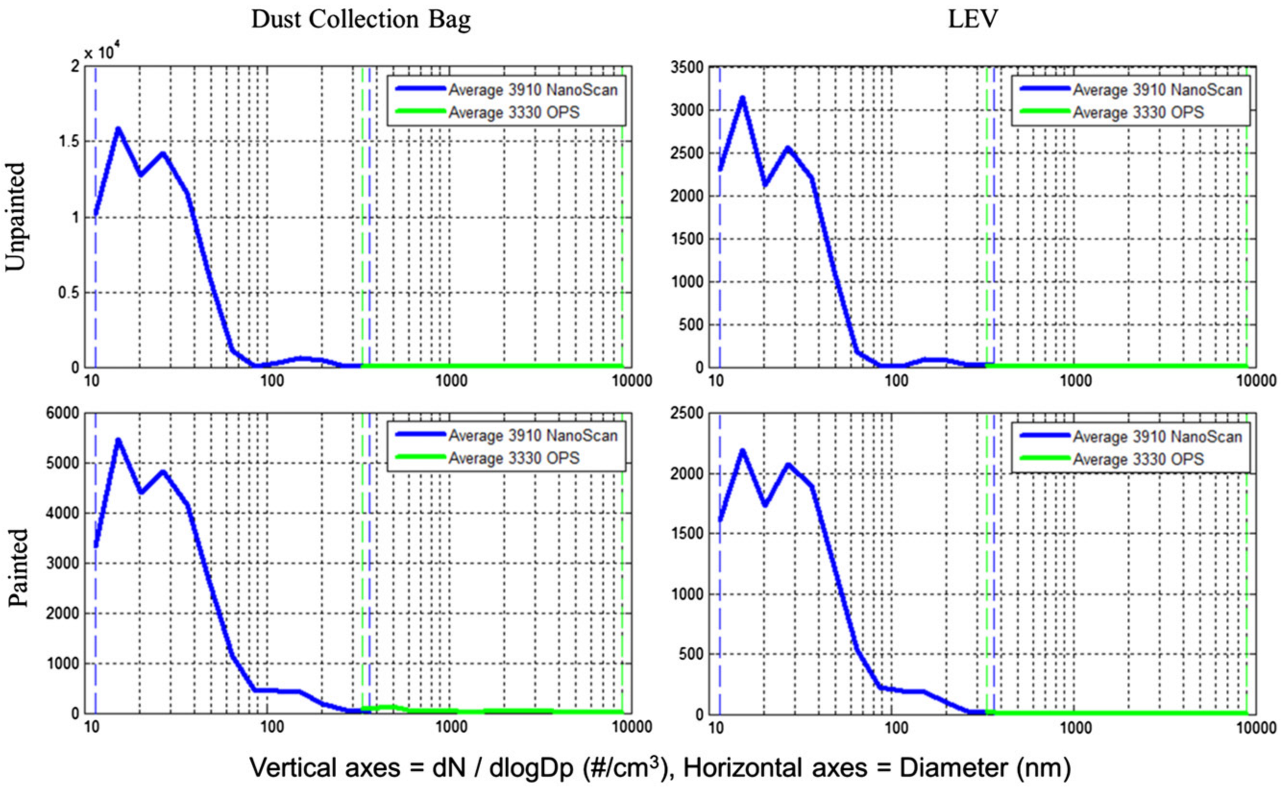

Figure 8. Background adjusted particle size distributions while sanding painted vs. unpainted plywood with the dust collection bag or local exhaust ventilation (LEV).

Table 1. Personal exposure measurements during airless spray painting.

Exposure Agent	N	Mean Conc. (mg/m^3)	Std. Dev.	95% CI
Total Particulate	5	35.8	8.6	25.1–46.5
TiO_2	5	13.6	3.2	9.6–17.6
Respirable Particulate	5	2.1	0.7	1.2–3.0
Respirable TiO_2	5	0.7	0.1	0.5–0.9

Limits.[15] The highest recorded concentration of TiO_2 in the test subject's breathing zone (0.14 mg/m^3) occurred when sanding painted boards with the dust collection bag provided with the sander. No TiO_2 was detected when sanding unpainted boards, and exposures to respirable TiO_2 were below detectable limits for all sanding trials (<0.065 mg/m^3).

Discussion

To accurately measure the size of primary particles forming the TiO_2 agglomerates in the nano-enabled paint, the paint was treated with acetone and sonicated, which caused the agglomerates to break apart into individual nanoparticles in the nano-enabled paint but not in a conventional paint from the same manufacturer. These findings suggest an avenue for future inquiry to determine if construction activities can mimic these effects observed in the lab, thereby increasing the potential for occupational exposure to unbound nanoparticles. Acetone and other ketones are also used as paint thinners in construction, and mechanical paint mixers might similarly disrupt agglomerates by means of physical force. Agglomerates are collections of primary particles held together by weak forces, such as van der Waals forces or simple physical entanglement.[16] Nano-toxicity studies have often examined well dispersed nanomaterials in their initial manufactured state, prior to their inclusion in end-user products; far fewer studies have examined changes to engineered nanomaterials as they are used in products and later released.[17] A recent *in vivo* study showed that gold nanoparticles and widely used surfactants were individually benign but caused a pronounced synergistic toxic effect when combined in a mixture.[18] Surfactants are often combined with nanoparticles in consumer products to aid dispersion. Results presented here suggest it is worth investigating if chemicals commonly used in construction, such as ketone-based paint thinners, can impact the likelihood of exposure to unbound nanomaterials during tasks such as airless spraying of paints.

In the present study, the paint was not treated with acetone prior to application nor was a mechanical paint mixer used. Unbound or "free" nanoparticles were not detected by electron microscopy in air samples collected during spraying and sanding. This finding is consistent with prior research on nanomaterial release from composites, showing that nanomaterials tend to remain bound to the host materials to which they are added.[4] The caveat is that it is difficult to prove the absence of airborne TiO_2 nanoparticles using a highly focused detection method like EM. Although the SMPS measured airborne nanoparticles for all exposure scenarios examined, EM could not confirm the presence of unbound nanoparticles on the sampling media, leaving some uncertainty about the characteristics of the particles measured by the SMPS.

NIOSH researchers have noted that SMPS instruments must rely on indirect methods to create electronic signals when detecting airborne particles, which is markedly different from the direct observations made of individual particles during electron microscopy. Chen and colleagues reported SMPS counts of nanoparticles in the 50 nm size during application of paint from a spray can that could not be corroborated with SEM.[19] They hypothesized the discrepancy may have come from the transient presence of vapor molecules created by the propellant from the spray can. The authors recommended using filter-based measurements with electron microscopy, as was done for the current study, to augment SMPS readings. Notably, the low-VOC (volatile organic compounds) paint applied by the airless sprayer did not contain volatile propellant. Prior research suggests that some of the larger micron-sized particles measured here during spraying were likely a product of the target droplet sizes of the airless sprayer, whereas dried droplets between 100 nm and 200 nm may have resulted from unintended overspray.[20] Peaks below 30 nm during sanding might also have been associated with the formation of pyrogenic aerosols.[21] Regardless of origin and chemical composition, it was clear that LEV was capable of significant reductions in airborne nanoparticle emissions measured by the SMPS.

Results of this study are mostly in accordance with prior sanding studies that did not detect a clear effect on sanding emissions resulting from the addition of engineered nanoparticles to paints.[7,8] In fact, overall nanoparticle emissions in the current study were significantly lower when sanding the painted plywood vs. unpainted plywood and when using LEV versus the dust collection bag, otherwise the particle size distributions were similar. The exception was the deviation in particle size distributions slightly above and below 100 nm; at this size range, elevated particle concentrations were only observed when sanding the painted boards.

Investigators have also shown how nanoparticle emissions can vary as a function of sandpaper grit size and the number of coats of paint.[22] Some researchers have gone beyond examining exposures, providing evidence that dusts from sanding nano-enabled paints are not more toxic *in vivo* than dusts obtained from their conventional counterparts.[23–26] Moreover, exposures to nano-TiO_2 in construction have not yet been shown to exceed existing reference values or exposure limits.[10,12,13,27] Taken together, these research findings are encouraging with regard to occupational safety and health. In 2014, a research institute in Switzerland issued a news release declaring that "After 42 months the EU research project NanoHouse has ended, and the verdict is a cautious 'all clear'—nanoparticles in the paint used on building façades do not represent a particular health risk."[28]

This cautious verdict may be justified in the context of sanding, but there has been comparatively less research on occupational exposure during initial application of nanoparticle-doped paints and coatings. Airless sprayers are often used in construction because they are considerably faster than a brush or a roller,

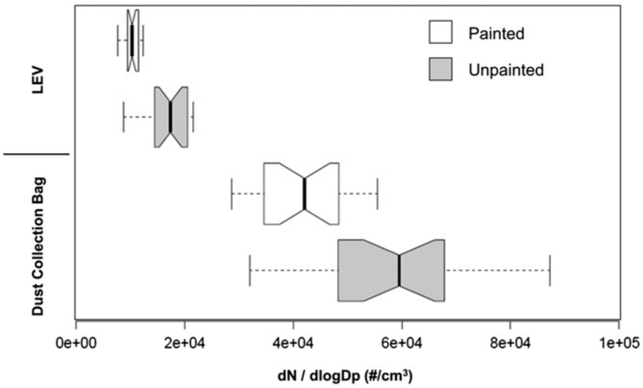

Figure 9. Comparison of background adjusted airborne nanoparticle concentrations while sanding painted or unpainted boards with either the dust collection bag or local exhaust ventilation (LEV): Center lines show the medians; box limits indicate the 25th and 75th percentiles; whiskers extend 1.5 times the interquartile range (IQR); n = 22, 22, 21, 22 sample points. The notches are defined as +/-1.58*IQR/sqrt(n) and represent the 95% confidence interval for each median. Non-overlapping notches give roughly 95% confidence that 2 medians differ.

and a prior study reported higher mass-based exposures to zinc during initial spray application of a wood sealant containing nanoscale zinc oxide, compared to subsequent sanding.[29] Spray painting nano-enabled paint and sanding the paint after it dries both have a high potential for exposure, according to a risk framework and tool designed for categorization of nanomaterials used in consumer products;[30] however, the former involves nanomaterials suspended in liquid, and the latter involves nanomaterials suspended in a solid—differences worth considering from a risk assessment perspective, for example whether nanomaterials suspended in liquids are more bioavailable following inhalation compared to nanomaterials embedded in solid composites. Applicability of the hierarchy of controls is another important factor to consider. Results presented here demonstrate the effectiveness of an engineering control to reduce uncontrolled nanoparticle emissions during sanding, but painters may need to resort to less protective tiers of the hierarchy, such as personal protective equipment, when applying nano-enabled coatings.

This study may be the first to provide evidence suggesting potential for overexposure to nano- TiO_2 during routine construction activity in reference to the NIOSH REL for ultrafine TiO_2 (0.3 mg/m^3 as a 10-hr TWA). Spraying produced a much higher concentration of airborne TiO_2 than sanding the paint after drying. The mean concentration of respirable TiO_2 during spraying (0.7 mg/m^3) was more than double the NIOSH REL, and even the lower end of the 95% confidence interval (0.5 mg/m^3) was nearly twice as high as the NIOSH REL. Granted, applicability of task-based exposure measurements to a TWA-based exposure limit would depend on the hours spent on the task over the course of a day. As such, administrative controls, such as scheduling and work rotations, could represent another tier in the hierarchy to minimize exposures to an acceptable level. The NIOSH REL for ultrafine TiO_2 does not make a distinction between agglomerated and unbound TiO_2; ultrafine is defined as the fraction of respirable particles with a primary particle diameter of $<0.1\,\mu$m.[3] This definition would include respirable agglomerates composed of primary particles <100 nm. An important caveat in the interpretation of these results is that the bulk material analysis indicated that most of the TiO_2 contained in the paint (84%) was agglomerated and consisted of primary particles <100 nm in terms of percentage by number, but the presence of respirable pigment grade TiO_2 in air samples could not be excluded.

This uncertainty illustrates some of the challenges inherent to evaluating exposures to MNMs in construction at this point in time. Despite the use of multiple measurement techniques and instruments, the exact % by weight of nanoscale TiO_2 in the paint was not ascertained. Nor was this information included in the safety data sheet for this product. It is useful in this situation to place some parameters on the exposure data presented. The upper end of the 95% CI for respirable TiO_2 (0.9 mg/m^3) provides a good estimate of the upper limit of exposure to nanoscale TiO_2 while spraying, at three times the level of the NIOSH REL. Given that the mean total particulate concentration during spraying was 35.8 mg/m^3, there would be potential to exceed the NIOSH REL if the % by weight of nanoscale TiO_2 in the aerosol generated was $>$ 0.84%. The gravimetric and metal analyses found that TiO_2 accounted for approximately 38% of the total particulate sampled and one-third of the respirable particulate. As described in greater detail above, bulk analysis via SEM and EDS indicated that a high percentage of TiO_2 primary particles in the paint were $< 100\,\text{nm}$.

The sampling environment can be viewed as both a strength and limitation. Measuring exposures in an environmentally controlled chamber raises the question of generalizability to actual construction work sites. In this particular case, the sampling environment was comparable to spray painting the walls of an interior room within a home. A painter working in a closed environment with less ventilation than the test chamber could be exposed to higher concentrations than those presented here. Sampling on actual jobsites has proven problematic from a research perspective due to confounding measurements of atmospheric and incidental nanoparticles.[27] Sampling in the environmentally-controlled chamber helped to eliminate confounding measurements. Finally, the use of actual construction equipment and a human operator increased the generalizability of the exposure measurements to real-world construction activities, as opposed to glove box experiments using automated equipment, such as Taber Abraders.

Conclusions

This study may be the first to demonstrate potential for overexposure to nano-TiO_2 during a common construction task. Airless spray painting generated levels of respirable TiO_2 above the NIOSH REL for ultrafine TiO_2. Bulk analyses of the material suggested that most of the TiO_2 primary particles contained in the paint were nanoscale. Unbound aerosolized nanoparticles were measured during the work tasks being studied but could not be confirmed by electron microscopy. Compared to sanding the uncoated plywood, sanding the plywood coated with a nano-enabled paint did not increase overall nanoparticle emissions or significantly alter particle size distributions, aside from the increased emissions observed around the 100 nm size range. Exposure to TiO_2 during sanding was below the NIOSH REL. Future research should consider exposure scenarios where chemicals commonly used in construction, such as ketone-based paint thinners, might impact potential for exposure to unbound nanomaterials.

Recommendations

Given the demonstration that airless spray painting can potentially release agglomerated TiO_2 nanoparticles in excess of the NIOSH REL, employers and industrial hygienists should characterize exposures and use the hierarchy of controls to ensure painters are sufficiently protected.

Acknowledgments

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