NIST Technical Note 1843

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ABSTRACT

Polymer and other coatings are commonly used to protect, enhance or decorate wood, plastic and metal products used in homes and other buildings. Nanoparticles (i.e., particles having at least one dimension smaller than 100 nm) are increasingly being added to coating formulations to reduce damage as well as to enhance their performance. Because of their small size and large surface area, nanomaterials may exhibit unique physical, chemical and transport behaviors in the environment and in the human body. Research in recent years has indicated that nanoparticles may be potentially harmful to the environment and to human health. In order to better understand human exposure associated with the airborne release of such particles, material specimens with coatings containing nanoparticles were tested in a small environmental chamber in which coated materials were subjected to surface abrasion intended to simulate normal wear and tear. This report describes the experimental approach and the results obtained, which showed minimal airborne release of the nanoparticles in the tested coatings.

Keywords: abrasion, chamber, coatings, consumer products, nanoparticles, paint

1 BACKGROUND

Polymer and other coatings are commonly used to protect, enhance or decorate wood, plastic and metal products used in homes and other buildings, including flooring finishes and interior paints. However, these coatings are subject to scratching, abrasion and chipping during manufacture, shipping and use. Nanoparticles are increasingly being added to coating formulations to reduce mechanical damage as well as to enhance properties such as mildew resistance [1]. Because of their small size and large surface area, nanomaterials may exhibit unique physical, chemical and transport behaviors in the human body and the environment. Research in recent years has indicated that nanoparticles may be potentially harmful to human health and the environment [2]. Such concerns could potentially inhibit innovation and commercialization of nanotechnology.

Current research on the health effects of nanoparticles is focused on human and environmental exposure during manufacturing [1]. However, the release of nanoparticles from flooring finishes, interior paints and other products over their service life, and the resulting exposure of building occupants, potentially poses greater risks than those encountered during manufacture. This is true because: 1) the population of general building occupants is much larger than those involved only in manufacturing; 2) the amount of surface area of interior walls and floorings in residential and commercial buildings is large, and 3) the human exposure to these particles is potentially continuous over the entire service life of the nanoparticle-containing products. Flooring products are of particular concern for young children who spend more time on the floor and, therefore, may have greater opportunities for exposure. In addition to airborne nanoparticles, nanoparticles that accumulate on surfaces may potentially pose a health hazard associated with resuspension into the air. Despite such potential risks, little information is available on the in-service release, surface accumulation, transport and exposure to nanoparticles from flooring finishes and interior paints. The lack of such data hinders the ability to assess and manage the potential harmful effects of nanoparticle release from these large-volume sources.

In order to better understand human exposure associated with the airborne release of such particles, a series of tests of materials with coatings containing nanoparticles was conducted in a small environmental chamber in which coated materials were subjected to surface abrasion intended to simulate normal wear and tear. This report describes the experimental approach and the results obtained for the materials tested. Based on these results, additional experimental and analysis work is described to build on the work described in this report.

1.1 Previous studies

Previous studies have investigated the generation of particles, specifically associated with nanomaterials, in a variety of experimental settings. Several of those studies are summarized in Table 1. Note that the concentrations in this table are presented in units of particle counts per cm^3, referred to as $\#/cm^3$ in this report. In some cases the original results in the referenced studies had to be converted into these units, which in some cases required the interpretation of some incomplete reporting of results. The first two studies, described in references [3] and [4], employed a Rotary Taber abraser to simulate the effects of mechanical friction on the test sample. In both studies the test sample was a plate or panel coated with a nanoparticle-containing paint. Airborne concentrations were measured over a size range from less than 10 nm to 10 μm or more. In both cases, the air was sampled from a small hood surrounding the location where the abrasion was occurring and the measured concentrations were typically less than 100 $\#/cm^3$ and in many cases only single digits of $\#/cm^3$. The measurements observed no "free" nanoparticles, i.e., nanoparticles not embedded within larger particles of the coating.

Figure 1 Dual specimen Taber rotary abraser with wood flooring specimen on right side

These two studies, as well as the experiments described later in this report, used a Taber rotary abraser as shown in Figure 1. The Taber abraser is widely used to evaluate the abrasion, wear and rubbing resistance of coatings and paints and is specified in various international standards, including ASTM D 4060-95:2007, ISO 5470-1999, and DIN 68861-2-1981. The stress exerted by the Taber test simulates typical mechanical stresses applied to organic coatings and paints, such as walking, chair movement, sanding, polishing actions and rubbing. The Taber abraser consists of two abrasive wheels that abrade the material continuously while the specimen is rotating on a vertical axis at a fixed speed. The abrasion/rubbing action is produced by the friction at the contact line between the material and the sliding rotation of the two wheels. In Figure 1, a sample is installed on the right side of the abraser, with the two abrading wheels shown in contact with the sample.

The next two studies listed in Table 1, [5] and [6], used high speed sanders instead of the less aggressive abrasers used in the previous two studies. In the first sanding study, the airborne particle concentrations were measured in a small chamber surrounding the sanding location, while in the latter study the concentrations were measured in the exhaust airstream of the sander. The use of these more aggressive processes led to much higher measured concentrations than with just the abraser.

The last five studies listed in the table [7-11], the test materials contained nanoparticles throughout the material sample itself, or in one case covering a fabric surface, rather than incorporated into a coating on a plate or panel. The experiments in these studies involved both rotary abrasion and higher speed sanding. The measured concentrations varied over several orders of magnitude starting as low as about 10 #/cm^3.

Much of this work is summarized in a paper by Göhler et al. [12], which notes that most previous studies show that nanoparticles released due to mechanical processes are “firmly embedded" in the released wear particles. These authors state their belief that release of isolated nanoparticles from well-prepared nanocomposites will only take place if there is "a prior chemical or thermal degradation" of the product.

Another observation from these previous studies is that the sampling has been done in close proximity to the spot where the material is abraded, in the exhaust of a chamber surrounding the abrasion or even in the exhaust airstream from a rotary sander. None of these studies involve sampling in a volume designed to represent a ventilation space in a building in terms of air speeds and air change rates.

Study	Material	Abrasion	Collection	Size Range Measured	Measured Concentration
Coatings containing nanoparticles, abrasion					
Golanski (2011)	Paint with TiO_2 nanoparticles on glass	Rotary Taber	Sample tube next to material, 10.6 L/min	7 nm to 10 µm	No free nanoparticles; 10 to 120 #/cm^3 in 300 nm to 1 µm range
Vorbau (2008)	Polyurethane paint with zinc oxide nanoparticles on oak veneer and steel plates	Rotary Taber	Hood covering grinding wheel	6 nm to >10 µm (CPC), 16 nm to 625 nm (SMPS)	~1 #/cm^3 < 100 nm; ~2 #/cm^3 < 625 nm; 3 #/cm^3 to 19 #/cm^3 (CPC),
Coatings containing nanoparticles, high speed sanding					
Gohler (2010)	Polyurethane coating with zinc oxide nanoparticles on steel panels; architectural coating with zinc oxide and iron oxide nanoparticles on fiber cement plates	Miniature sander (5000 rpm to 30000 rpm)	Hood around sanding area, 14 L/min	6 nm to ~3 µm (CPC), 6 nm to 560 nm (FMPS); 0.3 µm to 30 µm (LAP)	15000 #/cm^3 to 250000 #/cm^3
Koponen (2008)	Nanoparticle paint and lacquer on MDF boards	Orbital sander (22000 rpm)	Measurement in chamber connected to sander exhaust	6 nm to 542 nm (FMPS), 0.5 µm to 20 µm (APS)	1000000 #/cm^3, most < 50 nm
Non-coating nanomaterials, abrasion and sanding					
Guiot (2009)	Fabric covered with layer of silica or PVC nanoparticles	Linear Taber	Sample tube next to material, 0.3 L/min	20 nm to 100 nm, 80 nm median	~10 #/cm^3
Schlagenhauf (2012)	Carbon nanotubes in epoxy resin blocks	Rotary Taber	Hood around wheel, high velocity sample tube next to material	13 nm to 573 nm (SMPS), 0.5 µm to 20 µm (APS)	8000#/cm^{-3} to 20000 #/cm^{-3}, mean diameter 100 nm (SMPS), 1000#/cm^3 to 3000 #/cm^3, mean diameter 1 µm (APS)
Wohlleben (2011)	Nanoparticle embedded cement and thermoplastic blocks	Rotary Taber and power sander	Not described	50 nm to 200 nm	500 #/cm^3 to 100000 #/cm^3 (sanding tool), 3700 #/cm^3 to 10000 #/cm^3 (Taber)
Huang (2012)	Epoxy resin sticks embedded with carbon nanotubes	Rotary sander (586 rpm to 2126 rpm)	Sampled from chamber containing sander	10 nm to 1 µm (CPC), 10 nm to 850 nm (SMPS), 0.35 µm to 25 µm (OPC)	Up to 3000 #/cm^3 on order of 10 nm
Bellot (2013)	Carbon nanotubes in polystyrene composites	Microgrinder	Sampled from chamber containing sander	10 nm to 1 µm	Micron-sized particles with protruding fibers (probably CNTs) observed, free-standing CNTs not observed.

Table 1 Summary of previous studies of airborne particle release from abrasion and sanding

1.2 Experimental Objectives

In June 2011, the National Institute of Standards and Technology (NIST) and the Consumer Products Safety Commission (CPSC) entered into an interagency agreement to investigate the release of nanoparticles from consumer products. Under this agreement, NIST is working to develop testing and measurement protocols for determining the quantities and properties of nanoparticles released from flooring finishes and interior paints, as well as their subsequent airborne concentrations. This work is intended to provide methods and data to assess such releases that will assist CPSC in estimating occupant exposure and developing strategies to manage and mitigate these exposures.

A key objective of this work is to characterize the airborne release of these nanoparticles in a chamber configured to represent a ventilated space as a means of quantifying the exposures that might exist in a real building. This report presents the initial results of these chamber tests, which were conducted to demonstrate the chamber test procedure for measuring the airborne concentrations associated with these releases. Specifically, these tests investigated the chamber setup, the instrumentation and the measurement protocol to determine their applicability to measuring airborne nanoparticle concentrations associated with material abrasion.

2 Instrumentation and Experimental Methodology

2.1 Experimental Chamber

During an earlier phase of this effort, a conceptual design was developed for a chamber to perform measurements of airborne nanoparticle release associated with material abrasion. The chamber, in which the material abrasion would occur during the experiments, was designed to mimic airflow conditions and air change rates in a ventilated space intended for human occupancy. Figure 2a shows a schematic of the chamber, containing the Taber abraser, located in a recirculating XPert Nanohood, while Figure 2b is a photograph of the installation. The nanohood is an enclosure intended to protect users from hazardous powders and particulates used during procedures such as nanoparticle manipulation and dry powder chemical handling. During typical use, room air is pulled into the enclosure through the front, flows to the baffle in the back of the hood and passes through a 99.999 % efficient ULPA (ultra low penetration air) exhaust filter before returning to the laboratory.

For these experiments, the chamber needs to be sufficiently airtight such that airflow into and out of the chamber can be controlled, but not necessarily "hermetically sealed." In order to limit the entry of nanoparticles from the volume of the nanohood into the chamber, the system maintains a slight positive pressure in the chamber relative to its surroundings. This is done by supplying the chamber with compressed air from the laboratory supply, which is controlled with an electronic mass flow controller and passing through a HEPA filter. The chamber is vented to the nanohood as well as exhausted using the sampling pump in the particle sampling equipment, but at a rate lower than the supply airflow into the chamber to maintain a slight positive pressure. The chamber was made of stainless steel, except from a plastic door for viewing, to reduce the tendency for airborne particles to deposit on these surfaces.

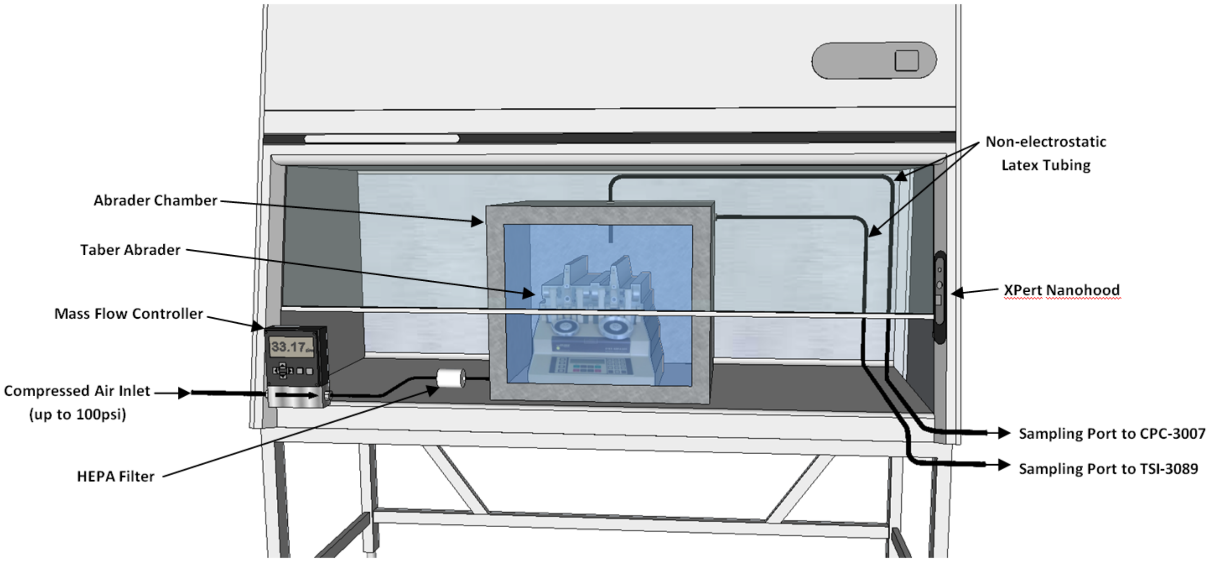

Figure 2a Schematic of Abraser Chamber Installation

Figure 2b Photograph of Abraser Chamber Installation

Figure 3 shows the airflow supply to the chamber, including its filtration and control. The airflow to the chamber is supplied by the laboratory compressed air supply, which passes through a coalescing filter and a HEPA filter before passing through an electronic mass flow controller (MFC). The MFC was sized to achieve chamber air change rates from 0.25 air changes per hour

(h^{-1}) to 1.0 h^{-1}, which correspond to typical ventilation rates in buildings and building rooms. Given the chamber volume of about 200 L, 1 h^{-1} corresponds to about 3.3 L/min. Chamber air is sampled through a port, which can be connected to particle counting instrumentation as described below. The chamber contains a small vent to serve as a relief for any excess supply airflow relative to the sample flow to the particle counter. Note that all of the particles monitoring devices employed have HEPA filters on their outlets, so the air exhausted to the room from these devices are filtered for nanoparticles. The filtered supply air is delivered to the chamber in a manner that does not disrupt the airflow in the vicinity of the sample being abraded and that is consistent with the air speeds in ventilated spaces.

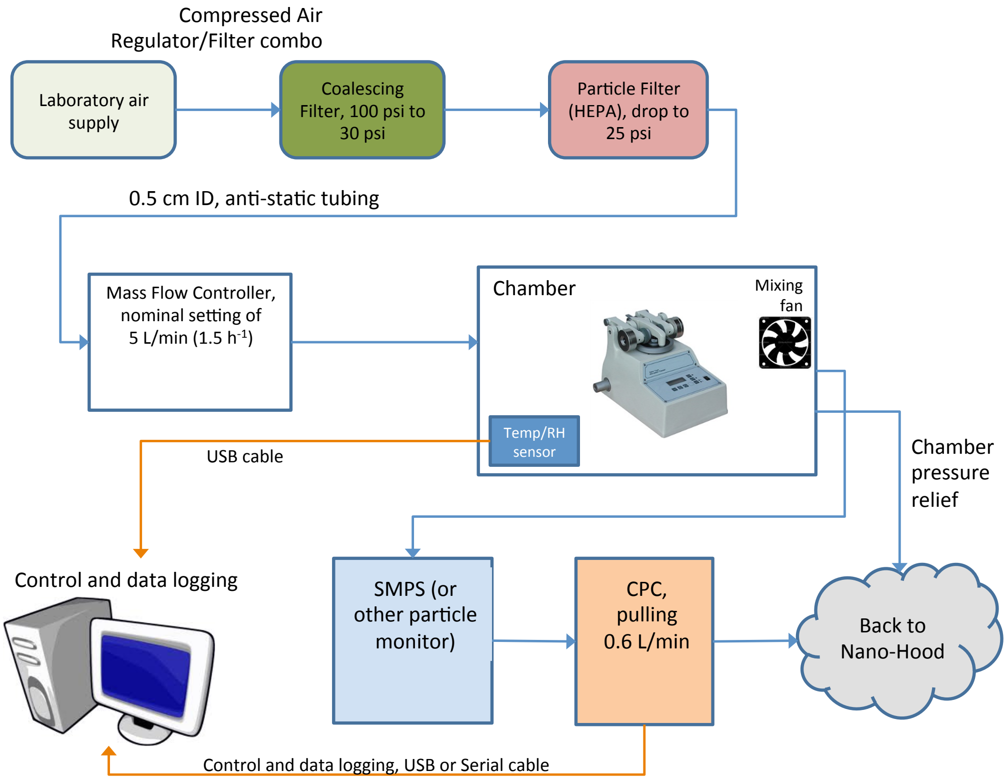

Figure 3 Schematic of Abraser Chamber Airflows

2.2 Particle measuring equipment

Four different devices were used to measure airborne particle levels as described in Table 2. The first three devices are all manufactured by TSI and are supplied with Aerosol Instrument Manager software for instrument control, data collection and export, and data display control. The fourth unit, manufactured by Climet, stores the data internally for subsequent download.

Device	Size range
Handheld condensate particle counter (CPC)	10 nm to > 1 µm
Water based CPC	2.5 nm to 3 µm
SMPS	97 bins, 2.5 nm to 102 nm
Optical particle counter, Climet	6 bins, 0.3 µm to 10 µm

Table 2 Particle measuring equipment employed in experiments

TSI handheld CPC Model 3007

The Model 3007 (Figure 4) is a hand-held portable condensation particle counter (CPC) intended for measuring ultrafine particles for inhalation or exposure studies, as well as a variety of other applications. The unit can be AC or battery powered and has programmable data-logging capabilities. This laminar-flow CPC operates by drawing an aerosol sample continuously through a heated saturator, in which alcohol is vaporized and diffuses into the sample stream. Together, the aerosol sample and alcohol vapor pass into a cooled condenser where the alcohol vapor becomes supersaturated. Particles in the sample stream serve as condensation sites for the alcohol vapor. Once condensation begins, particles grow quickly into larger droplets and pass through an optical detector where they are counted.

Specifications for the Model 3007 include a minimum detectable particle diameter of 10 nm and a maximum detectable diameter of > 1 µm over a concentration range of 0 #/cm^3 to 100 000 #/cm^3. The minimum displayable concentration is 1 #/cm^3, and the device has a stated concentration measurement accuracy of ± 20 %. The CPC temperature operating conditions are from 10 °C to 35 °C, and the instrument has a nominal inlet flow rate of 700 cm^3/min.

Figure 4 TSI CPC Model 3007

TSI N-WCPC Model 3788

The TSI Model 3788 Nano Water-Based Condensation Particle Counter (N-WCPC) (Figure 5) operates on the principle of enlarging small particles using a water condensation technique to form (grow) droplets large enough to be detected optically. An aerosol sample is continuously drawn into the device at a sample flow rate of 0.6 L/min. The Model 3788 N-WCPC detects particles from 2.5 nm in diameter to 3 μm. The manufacturer states that the particle concentration accuracy for particle concentrations up to 400,000 #/cm^3 is 10 %.

Real-time particle concentration, cumulative concentration and operating parameters, as well as a graph of concentration versus time, are all viewable on the front-panel display. Data records are accessible via standard interfaces and include concentration, particle count, sample time, and status information, which can be reported at intervals ranging from 0.1 s to 3600 s.

Figure 5 TSI N-WCPC Model 3788

TSI SMPS System

The Scanning Mobility Particle Sizer (SMPS) (TSI Model 3936) consists of an electrostatic classifier (Model 3080) (Figure 6), a nano-differential mobility analyzer (nano-DMA, Model 3085), and a water-based condensation particle counter (N-WCPC, Model 3788) described above. The SMPS system can be configured to measure particles in multiple size ranges, starting as low as 3 nm up to 100 nm, with a sample flow rate of 0.6 L/m. The measurement uncertainty of the UFP number concentration reported by the manufacturer is estimated to be 12 % based on combining the individual uncertainties in airflow rate, particle charge distribution, voltage adjustment, and particle charge efficiency in quadrature.

Figure 6 TSI Electrostatic Classifier Model 3080

CLIMET CI-500B

The Climet Instruments CI-500B (Figure 7) is a laser diode based aerosol particle counter, which can be either battery or AC powered. The sample flow of 2.83 L/min enables the particle counter to sample air containing particle concentrations as a high as $3.5x10^6$ #/m^3. The unit reports particle counts in six different size ranges from 0.3 µm to >10 µm. Counts may be reported as total count, differential count, particles/m^3 or particles/ft^3, or distribution histograms. Up to 500 date and time stamped samples can be stored in internal memory, or the unit can be connected directly to a PC for data collection.

The particle sensor operates on the light scattering principle utilizing an elliptical mirror collection system and a 50 mW solid state laser diode. The scattered light is detected by a solid state photo detector. Other specifications for this unit include size resolution of 0.03 µm at 0.33 µm, 38 m maximum sample tube length, an operating temperature of 0 °C to 37.8 °C, and operating humidity of 10 % to 90 %.

Figure 7 Climet CI-500B

2.3 Materials tested

The materials tested in the abrasion chamber were the same tested by the NIST Polymeric Materials Group in their efforts to characterize particles released by abrasion and remaining on the material surface [13]. These materials include a commercial water-based polyurethane (PU) flooring coating and a commercial water-based latex interior paint. The PU was a typical unfilled (clear) polymer coating used for hardwood flooring, while the latex paint was a typical interior wall paint containing 30 % (based on mass of the polymer matrix) nepheline syenite tint base (aluminum silicate filler). The tests involved flooring panels with a PU coating containing Al_2O_3 nanoparticles, with diameters 20 nm according to the material supplier. The latex paints contained pigmentary particles (diameters of 200 nm to 300 nm) and TiO_2 particles (diameters of 30 nm).

Per the instructions of the material supplier, NIST applied nano-filled PU flooring coatings by brush on an oak wood substrate in four separate coats. Each layer was allowed to air dry for 8 h before the next layer was applied. The oak substrate was a solid wood material having a thickness of 6.35 mm (1/4 in.). The nano-filled latex paints were applied on a drywall substrate by roller and consisted of four layers with 4 h of air drying time between the layer applications. The drywall was a composite assembly having a thickness of 11 mm (7/16 in.), which consists of a 10 mm (0.393 in.) thick gypsum board sandwiched between two 0.5 mm (0.020 in.) thick paper boards. Some of the latex paint samples were applied to a solid wood (oak) substrate, as those samples were also used for other tests that involved submerging them in water. More information on the samples and coatings is available in Sung et al. [14].

2.4 Measurement protocol

The experiments conducted as part of this study involved installing samples into the Taber abraser and measuring the resulting airborne particle concentrations in the chamber depicted in Figure 2. These measurements employed various particle measurement instruments, as described earlier, in efforts to identify the important sizes of particles released in the chamber air volume. In addition, a number of tests were performed to evaluate the level of "cleanliness" of the chamber air without abrasion processes occurring, i.e., to demonstrate a sufficiently low background particle concentration.

Independent of the specific particle monitoring device employed, the general protocol for an abrasion test was as follows:

<u>Test Preparation</u>

- Verify that the airflow rate into the test chamber is set at 3.3L/m, which corresponds to an air change rate of 1 h^{-1}.
- Clean the abraser and test chamber interior with a wipe cloth containing a small amount of isopropyl alcohol.
- Put a test sample on the abraser in the chamber and program it to run for a defined abrasion period.

- Close the chamber door and allow the flow of clean supply air to decrease the chamber particle concentration to an essentially nondetectable level (typically about 3 h)

Abrasion Test

- Start the particle instrumentation being used in the test and verify its input parameters are as intended, e.g. size range and sample duration.
- Once the particle counter is operating as intended, perform a zero calibration test by connecting a zero-filter to the counter intake via a sampling tube and verify the measured count is zero.
- Disconnect the zero-filter and connect the counter to the chamber sampling port.
- Verify that the particle counts in the chamber air are very close to zero #/cm^3.
- Start the abraser by depressing the push rod extending though the top of the chamber. The abraser will then run for the preset test duration and the particle counter will record the data.
- Another test with the same sample can be collected after the particle counter in the chamber return to the background level.
- Before a new test is run, the chamber and the abraser are thoroughly cleaned with a vacuum and isopropyl alcohol to remove debris and deposited particles from the previous test.

2.5 Tests performed

Table 3 summarizes the key tests performed to date, including the date of the test, the substrate on which the coating was applied, the coating itself (note for tests #5 and #6 there was no coating), the location from which the air was sampled, the presence of a mixing fan in the chamber, the particle measurement instrument employed, and the size range of particles that was measured. All tests involved 1200 abrasion cycles or revolutions of the abraser over 20 minutes. The first two tests were performed on a bare wood substrate, with two different measurement devices and size ranges, to assess the particles released by the abrasion process. Any such particles would be from the wood substrate, as no coating was involved in these tests. The next two tests, #9 and #10, involved thick and thin floor coatings on wood respectively, both using the SMPS/CPS to measure particles < 100 nm in diameter in 97 individual size bins. Test #9 did not employ a mixing fan in the chamber, while Test #10 did. The fan was added in Test #10 after the results of #9 revealed very few airborne particles and it was thought that perhaps the abraser particles were not becoming airborne. Both of these tests were done with the particle sample near the abrasion site as earlier tests conducted with the sample taken at the chamber outlet as originally planned yielded particle concentrations that were essentially indistinguishable from the detection limit.

Tests #13 and #14 were performed with painted wood, with the first employing the Climet particle counter to measure particles between 0.3 μm and 0.5 μm. Test #14 used the SMPS/CPC to measure particles < 100 nm. These two tests were conducted in order to capture a broad range of particles sizes from the painted wood. In tests #15 and #16, the CPC was used without the SMPS to measure the total particle count between 2.5 nm and 3 μm. The former test involved the floor coating while the latter involved the paint. Test #17 was identical to Test #9, except that a mixing fan was used in the chamber. Finally, tests #19 and #20 were the same as #15 except that two different CPCs were used in an effort to evaluate their comparability.

Test	Date	Substrate	Coating	Sampling Location	Mixing fan	Instrument	Particle Size
5	8/2/13	Wood	none	Chamber outlet	No	Climet	0.3 µm to 0.5 µm
6	8/2/13	Wood	none	Chamber outlet	No	SMPS/CPC	<100 nm
9	8/5/13	Wood	Floor coating, thick	Next to Sample	No	SMPS/CPC	<100 nm
10	8/10/13	Wood	Floor coating, thin	Next to Sample	Yes	SMPS/CPC	<100 um
13	8/16/13	Wood	Paint	Next to sample	Yes	Climet	0.3 µm to 0.5 µm
14	8/16/13	Wood	Paint	Next to sample	Yes	SMPS/CPC	<100 nm
15	8/26/13	Wood	Floor coating, thin	Next to Sample	Yes	CPC	2.5 nm to 3 µm
16	8/26/13	Drywall	Paint	Next to Sample	Yes	CPC	2.5 nm to 3 µm
17	8/29/13	Wood	Floor coating, thick	Next to Sample	Yes	SMPS/CPC	<100 nm
19	9/6/13	Wood	Floor coating, thin	Next to Sample	Yes	CPC 1	2.5 nm to 3 µm
20	9/6/13	Wood	Floor coating, thin	Next to Sample	Yes	CPC 2	2.5 nm to 3 µm

Table 3 Summary of abrasion tests performed

3 Results

This section presents the measurement results obtained to date, focusing on the experimental objective of investigating the chamber setup, instrumentation and measurement protocol to determine their applicability to measuring airborne nanoparticle concentrations associated with material abrasion.

3.1 Background particle counts

One of the key issues in measuring the airborne nanoparticle concentrations is to distinguish the particle counts of interest from those that exist in the normal background. Previous research has shown that ambient air contains abundant nanoparticles from a range of sources, including motor vehicle exhaust and atmospheric nucleation events [15]. The air supplied to laboratory containing the nanohood by the building ventilation systems is filtered but not with sufficiently high efficiency filters to remove nanoparticles. Therefore, the background air in the space and therefore in the hood typically contains significant levels of nanoparticles. Figure 8 shows a typical particle distribution of the room air, as measured with the SMPS and averaged over a 10 min period. The particle distribution has two peaks, one around 40 nm and another around 100 nm, with the latter peak extending beyond the upper detection limit. Figure 9 shows the room air particle distribution measured with the Climet, which covers larger particles than the SMPS data in Figure 8 but over a slightly different time period. While these are fairly typical size distributions in the laboratory, the ambient and therefore the indoor particle distribution vary day-to-day if not hourly.

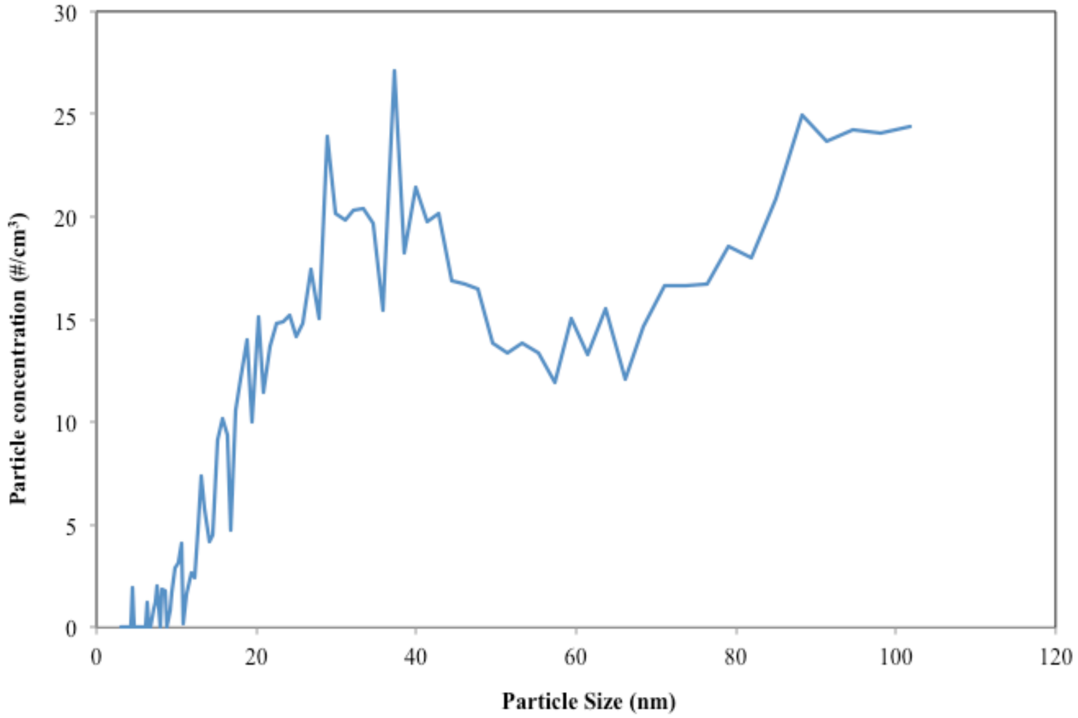

Figure 8 Room air particle size distribution averaged over 10 min

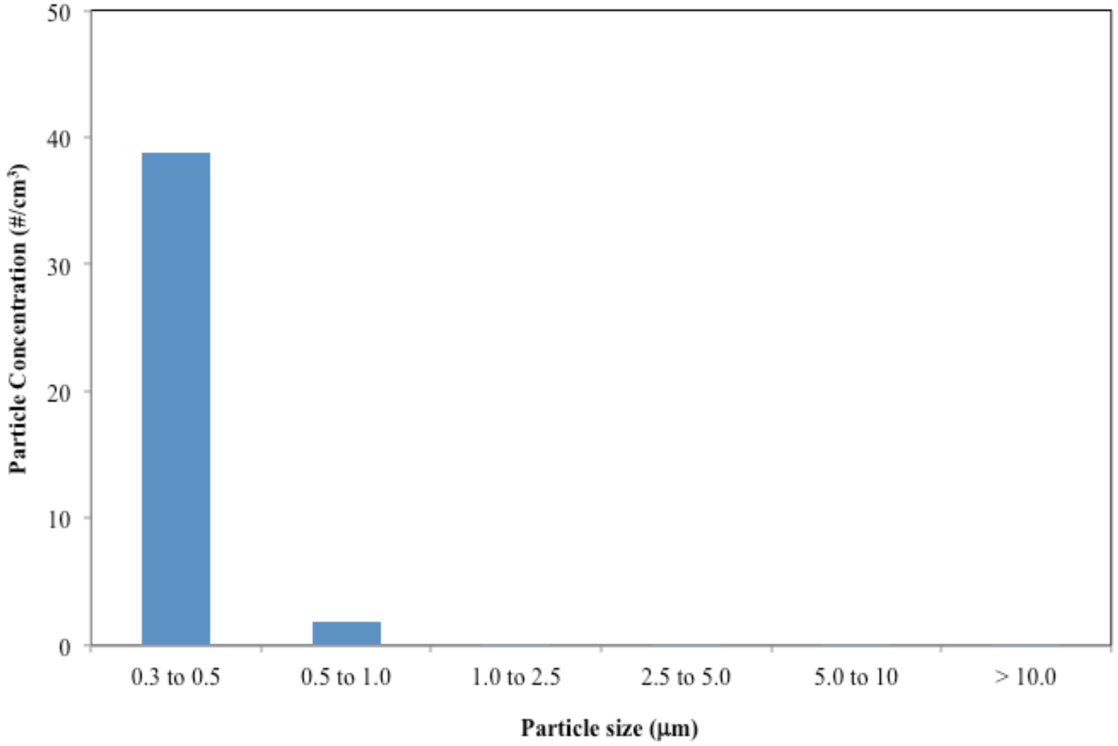

Figure 9 Room air particle size distribution between 0.3 μm and 10 μm averaged 10 min

Given the unpredictability in the indoor nanoparticle levels and the expectation that these levels are in the range of interest for the abrasion tests, it was determined that the air supply to the abrasion chamber needed to be filtered as described above. When the abrasion chamber door is opened to load a sample or to manipulate the abraser, nanoparticle-laden air from the nanohood enters the chamber. These particle levels are too high to conduct the abrasion tests, which is why the air supply to the chamber is filtered. Figure 10 shows an example of particle count decay measured using the CPC inside the test chamber starting when the chamber door is closed. As seen in this figure, a near-zero particle concentration is reached within 3 hours. For this test, the particle decay rate is about 1.4 air changes per hour (h^{-1}), which is higher than the clean air supply flow rate of 1 h^{-1}. This difference is presumably due to particle loss associated with deposition onto the surfaces inside the chamber. A deposition rate of 0.4 h^{-1}, the difference between these two values, is consistent with data in the literature for particles in 300 nm size range [16]. However, deposition rates measured in a 3-bedroom test house were lower in the 50 nm to 100 nm size range but comparable for smaller particles [15]. These results point out the need to account for deposition in the abrasion chamber by comparing the measured particle decay rate to the chamber air change rate. A key finding of these tests is that the background nanoparticle levels in the abrasion chamber are low with the supply air filtration system in place and that about 3 hours are required after the chamber door is closed to achieve a sufficiently low background level relative to the particle levels of interest.

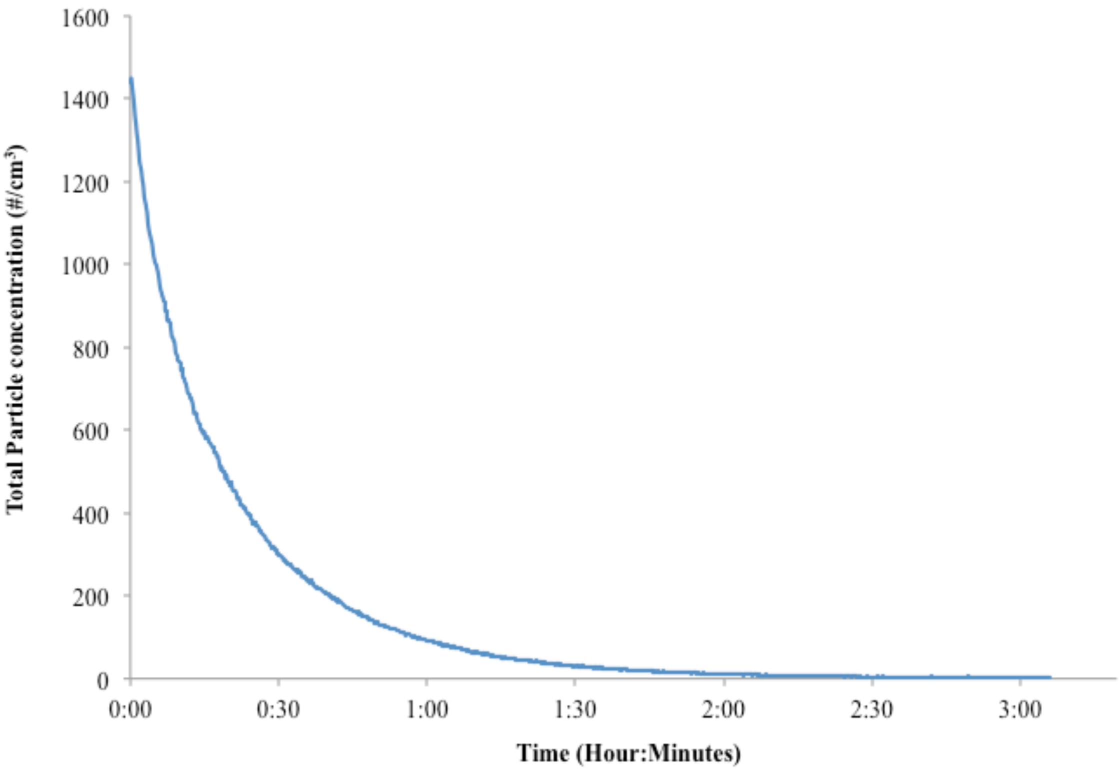

Figure 10 Decay of particle count inside the test chamber with steady clean air supply (total concentrations from 2.5 nm to 3.0 µm)

3.2 Particle instrumentation check with known source

In order to evaluate the ability of the particle counting instrumentation to detect nanoparticles in the abrasion chamber, tests were performed with a known nanoparticle source. Based on previous experiment efforts [15], a sample of known particle sizes (20 nm to 50 nm) generated from candle smoke was injected into the test chamber after it had reached the zero background particle level. The result of this test is shown in Figure 11, which are the total particle counts between 2 nm and 100 nm. These data clearly show the ability of the chamber setup and associated instrumentation to detect elevated nanoparticle concentration.

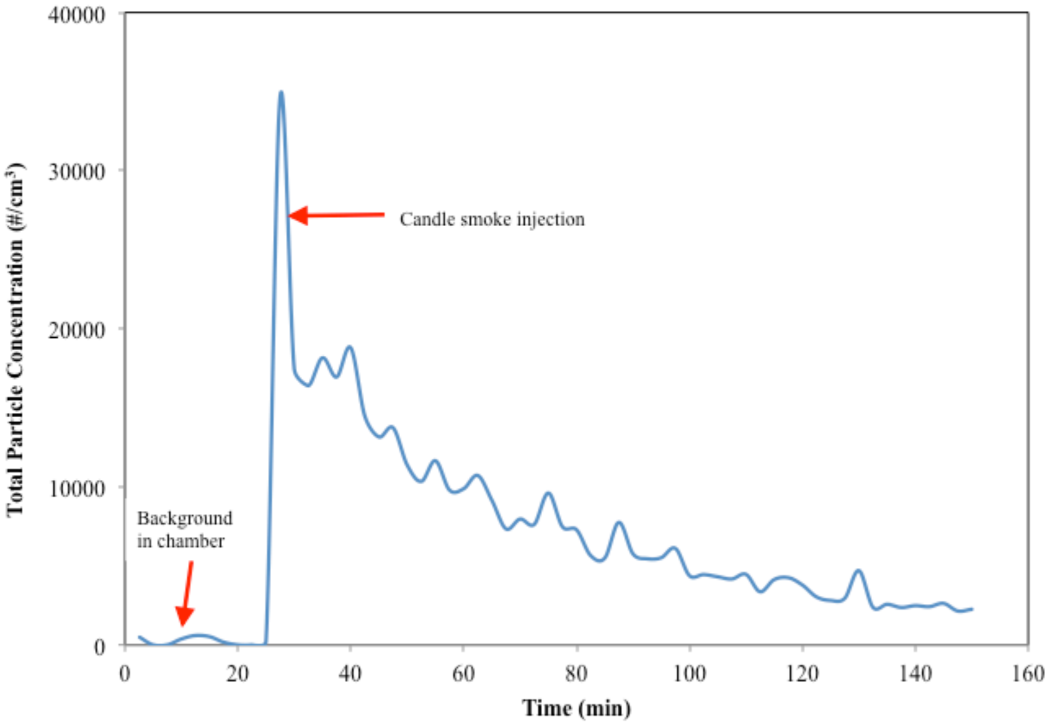

Figure 11 Total particle counts from SMPS from candle smoke injection test

3.3 Abrasion tests

Table 4 summarizes the results of the abrasion tests listed in Table 3, with each test characterized by the average and maximum particle count measured. The first two tests, #5 and #6, were performed on uncoated wood, and yielded average particle concentrations of about 20 #/cm^3 and 3000 #/cm^3 in the 0.3 µm to 0.5 µm and in the < 100 nm size ranges respectively. The concentrations did not vary much during the tests as evidenced by the maximum concentrations being so close to the average. In tests #9 and #10, the wood was treated with the floor coating, a thick layer in the former case and a thin layer in the latter. Tests of similar coated wood samples, which are not reported here due to concerns with the instrumentation, yielded extremely low particle counts in the chamber outlet. As a result, the sample location was moved from the chamber outlet to closer to the sample based on concerns that the particles might not be getting to the outlet. For these two tests, the average concentrations were only about 1 #/cm^3 to 3 #/cm^3, with maximum values about an order of magnitude higher. However, those maximum values correspond to isolated peak values that might have been measurement artifacts and not true values. Without those peak values, the averages are close to background levels.

Tests #13 and #14 involved samples with a wood substrate with a coating of paint, with the former including measured particle concentrations in the 0.3 μm to 0.5 μm size range and the latter < 100 nm. The particle counts for #13 are not significantly different from background. For the test results in the < 100 nm range (#14), the average concentration was about 4 #/cm^3, with a maximum again about an order of magnitude higher. However, this maximum is driven by isolated peak values that might have been measurement artifacts and not true values. Without those peak values, the average is indistinguishable from the background levels. Figure 12 is a plot of the results of Test #14 in the form of a particle distribution between 2 nm and 100 nm averaged over 20 min. While there are distinct peaks for particle sizes less than 25 nm, their magnitude is less than 2 #/cm^3, which is quite low and can't be ruled out as measurement noise. A closer look at the specific data points reveals these peaks are generated by a small number of data points, which is consistent with measurement noise.

Test #15 was performed with a thin layer of floor coating on the wood substrate using the CPC without the SMPS to capture the total number of particles between 2.5 nm and 3 μm. As seen in Table 4, the average concentration was less than 0.1 #/cm^3, with a maximum of about 30 #/cm^3. With the exception of a single spike in the concentration, all of the other readings are less than 1 #/cm^3. Figure 13 shows the particle counts for Test #15 over time, in which an unexplained and likely spurious peak is seen around time 00:14. Additional peaks are seen after the abrasion process is complete, for which no mechanism other than instrument noise has been identified. Test #16 also used the CPC without the SMPS, this time on the painted drywall. The average particle concentration was close to zero, with a few spurious spikes reflected in the higher maximum value. Figure 14 shows the particle counts for Test #16 over time, where no particle increase is evident during abrasion thought there are some potentially spurious peaks later in the test.

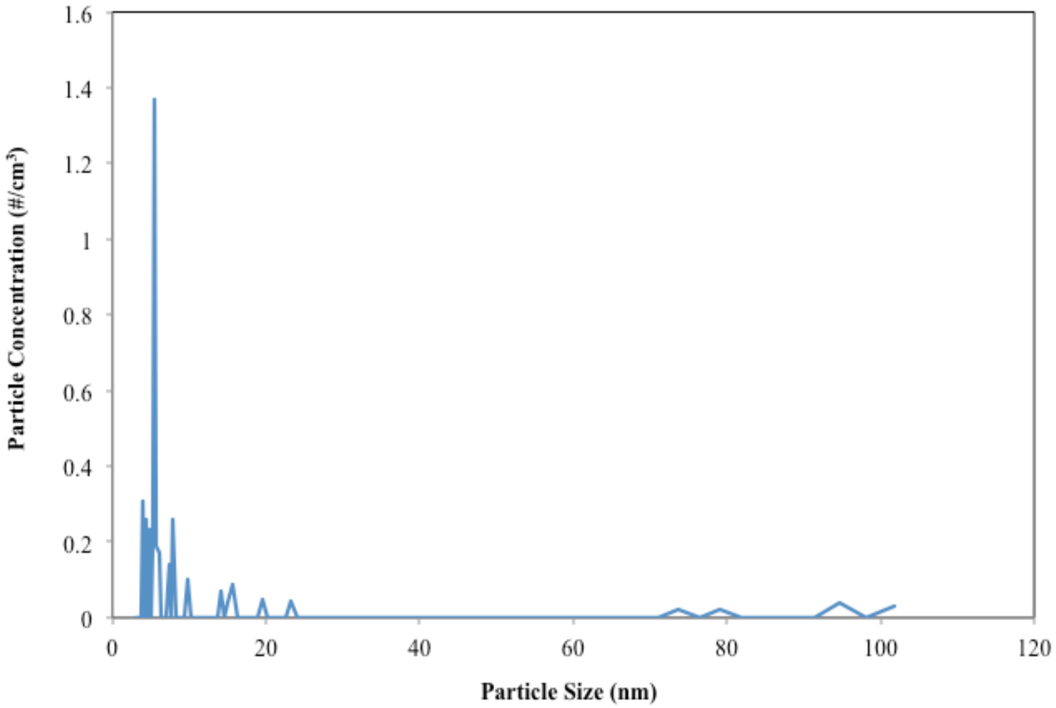

Figure 12 Particle size distribution for abrasion test #14 of painted wood

Test #17 used the SMPS on a thick layer of floor coating on the wood substrate and resulted in an average concentration of around 7 #/cm^3 and a maximum of about 40 #/cm^3. As in the other tests, these values were driven by a number of unexplained peaks. The particle size distribution for this test is shown in Figure 15, where again we see a number of isolated peaks that may be due to measurement noise. Otherwise, the airborne particle counts are essentially the same as the background levels.

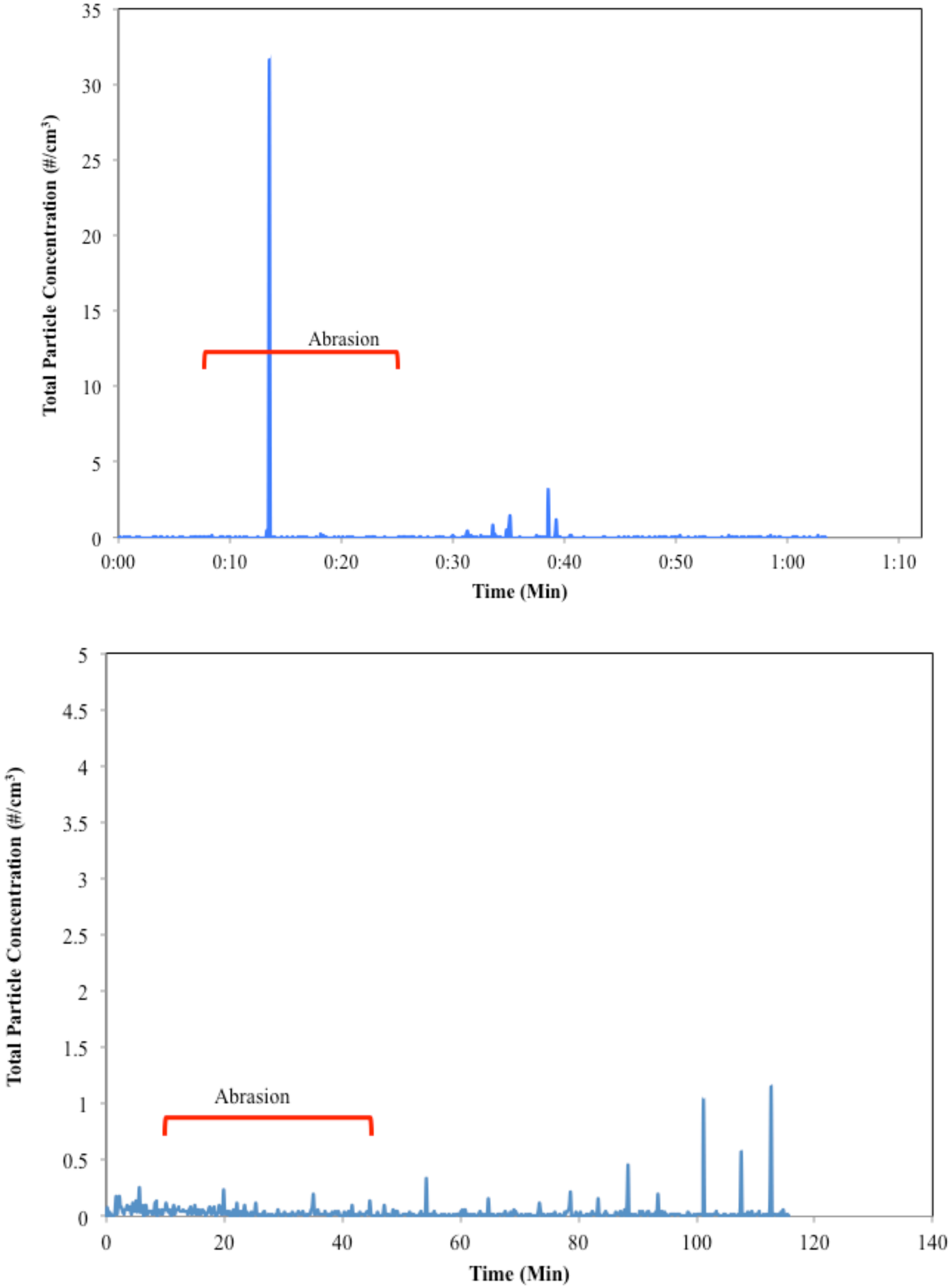

Figure 13 Total particle counts (2.5 nm to 3 μm) vs. time for floor coating (Test #15)

Figure 14 Total particle counts (2.5 nm to 3 µm) vs. time for paint (Test #16)

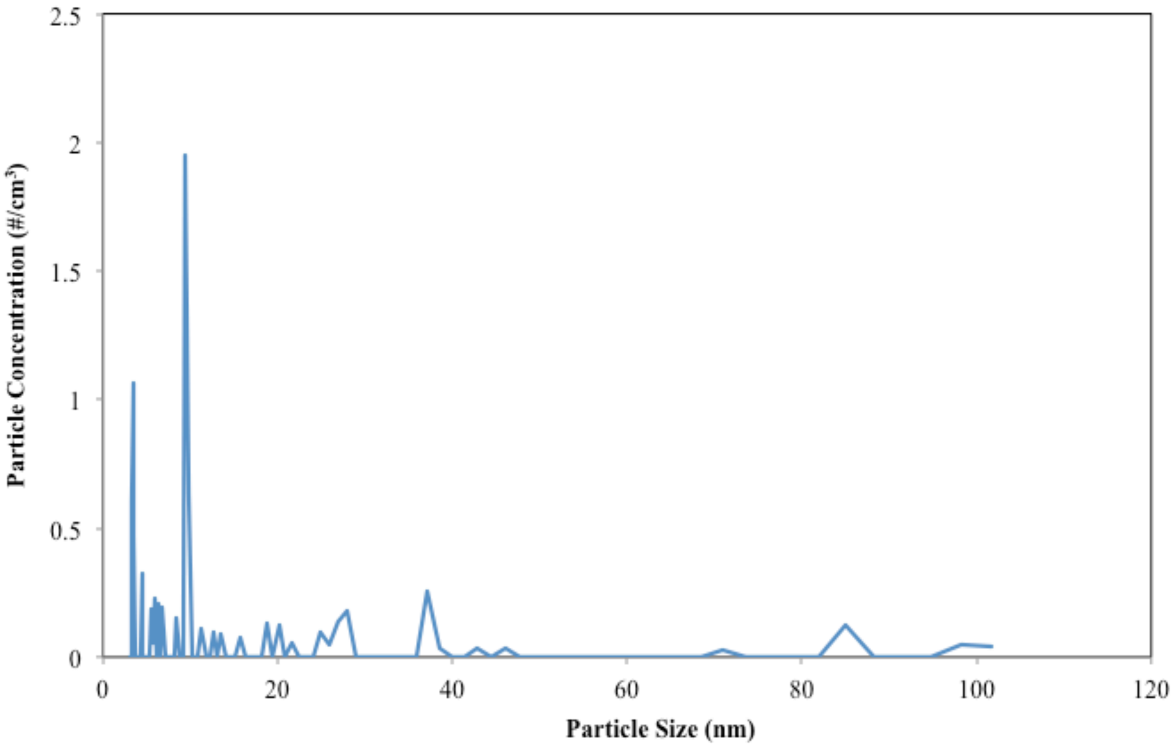

Figure 15 Particle size distribution for abrasion test #17 of floor coating

Finally, Tests #19 and #20 were both performed on the same thin floor coating but using two independent particle counters .The average values are within 1 % of one another, which demonstrates the consistency between the measurement devices used in these tests.

Test	Substrate	Coating	Sampling Location	Particle Size	Average concentration (#/cm^3)	Maximum concentration (#/cm^3)
5	Wood	none	Chamber outlet	0.3 µm to 0.5 µm	18	26
6	Wood	none	Chamber outlet	<100 nm	3096	3644
9	Wood	Floor coating, thick	Next to Sample	<100 nm	0.99	8.5
10	Wood	Floor coating, thin	Next to Sample	<100 um	2.6	31.8
13	Wood	Paint	Next to sample	0.3 µm to 0.5 µm	0.01	0.02
14	Wood	Paint	Next to sample	<100 nm	3.8	46.7
15	Wood	Floor coating, thin	Next to Sample	2.5 nm to 3 µm	0.08	31.6
16	Drywall	Paint	Next to Sample	2.5 nm to 3 µm	0.02	1.15
17	Wood	Floor coating, thick	Next to Sample	<100 nm	6.6	39
19	Wood	Floor coating, thin	Next to Sample	2.5 nm to 3 µm	0.32	2.36
20	Wood	Floor coating, thin	Next to Sample	2.5 nm to 3 µm	0.31	2.44

Table 4 Summary of abrasion test results

4 Discussion and Conclusions

A series of tests were conducted to measure the airborne particle levels associated with the abrasion of coatings containing nanoparticles. A number of abrasion tests were performed on a polymeric floor coating and an interior paint in a chamber designed for these specific tests and using a number of different measurement devices to capture different particle sizes. Particle counts on the order of background levels were measured in the tests conducted, which is consistent with the results seen in the literature for similar abrasion tests involving nanoparticle-containing coatings. Occasional peaks in the particle counts were observed, but these isolated peaks are strongly suspected to be measurement artifacts as they were neither consistent nor reproducible when performing multiple tests on similar samples. It is possible that some characteristics of the coatings, for example the manner in which they were cured and their resulting moduli of elasticity, contributed to the low levels of airborne particle generation observed.

Despite the lack of measureable particle concentrations in these tests, valuable information was learned to support additional testing of materials containing nanoparticles. Given the highly variable levels of nanoparticles in the laboratory air, even with the effects of the particulate filtration of the nanohood in which the chamber was housed, it is critical to supply clean supply air to the chamber and to keep the chamber closed and pressurized during testing. The approach used in these tests was shown to maintain very low nanoparticle concentrations in the chamber, and such filtration would likely need to be part of any standardized procedure for characterizing airborne release. In addition, the decay rate of background nanoparticles in the chamber after it was closed and supplied with clean air demonstrated the need to account for particle deposition to surfaces when analyzing nanoparticle dynamics in such a chamber.

Given the results obtained in these tests, additional tests are planned to further investigate the airborne release of nanoparticles from coatings of consumer products. These additional tests will focus on two new approaches. First, commercial products known to contain nanoparticles will be tested in order to avoid any issues related to effects of the curing process employed in this study on nanoparticle release. There is some suspicion that the curing process and the mechanical properties of the coating impacts the ability of nanoparticles or any particles at all to become airborne. In addition to the new materials, additional tests will be conducting using more aggressive abrasion methods. As noted in the literature, abrasion similar to that employed in this study did not result in measurable airborne nanoparticle levels. However, other studies showed that aggressive abrasion, using high-speed rotary sanders for sample, did generate significant levels of airborne nanoparticles, but it is important to verify this approach in the chamber setup Performing additional tests with more aggressive abrasion will not necessarily provide insight into expected airborne nanoparticle levels and exposure under typical conditions but will provide an indication of the total number of nanoparticles available for exposure, as well as their size distribution, whether that happens by inhalation, dermal or ingestion.

Despite the limited data demonstrating significant airborne nanoparticle levels, these tests have demonstrated the usefulness of this chamber set and instrumentation for characterizing airborne nanoparticles in “realistic” setting. It is expected that with some modifications, this approach will be useful for testing consumer products in the future and potentially support the development of standardized test methods.

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