Technical Data Bulletin

OH&ESD

#171

Nanotechnology and Respirator Use Issues

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Background

One of the emerging topics in industrial hygiene today is nanotechnology and the nanoparticles (those less than 100 nanometers) it may produce. There has been much discussion and speculation on the potential health effects, if any, how to measure and how to control nanoparticles. This includes questions about filtration-capturing mechanisms, especially for respirator filters, applicable in filtering nanoparticles. This technical data bulletin will discuss the terminology and what is known about how filters remove these particles.

Nanotechnology

Nanotechnology is a broad interdisciplinary area of research, development and industrial activity which has been growing rapidly world wide for the past decade. The use of the term "nanotechnology" is not limited to a single technology or scientific discipline but rather encompasses a multidisciplinary grouping of physical, chemical, biological, engineering, and electronic processes, materials, applications and concepts in which the defining characteristic is one of size. The U.S. National Nanotechnology Initiative (NNI) defines a technology as nanotechnology only if it involves **all** of the following:

- Research and technology development involving structures at least in one dimension in approximately the 1–100 nanometer (nm) range, frequently with atomic/molecular precision:
  - Creating and using structures, devices and systems that have novel properties and functions because of their nanometer scale dimensions; and
  - Ability to control or manipulate on the atomic scale.[1]
- Nanoparticles are the end products of this technology and include nanotubes, nanowires, and quantum dots.

Uses

Engineered nanoparticles are being used in a number of industries that include: electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy and catalytic applications. Examples of products benefiting from the unique properties of nanoscale materials are:

- Step assists on vans
- Bumpers on cars
- Paints and coatings to protect against corrosion, scratches and radiation
- Protective and glare-reducing coatings for eyeglasses and cars
- Metal-cutting tools
- Sunscreens and cosmetics
- Longer-lasting tennis balls
- Light-weight, stronger tennis racquets
- Stain-free clothing and mattresses
- Dental-bonding agent
- Burn and wound dressings
- Ink
- Automobile catalytic converters

Terminology

Nanoparticles are often defined as particles in the size range of 1–100 nanometers (nm). A nanometer is 1×10^{-9} m or one millionth of a millimeter. Figure 1 provides examples of items in this size range. In this bulletin, the term nanoparticles (unless it is from a reference that used it differently) will refer to those particles engineered by using nanotechnology that are less than 100 nm.

Many industrial processes produce particles that have dimensions in the nanometer size range. These unintentionally produced nanosize particles are often referred to as ultra fines, ultra fine particles, or ultra fine aerosols. Ultra fine particles have been defined as particles with aerodynamic diameters less than 100 nm.[2] Ultra fines tend to be formed through nucleation, gas to particle reactions, or evaporation.[2] One example is the synthesis of carbon black by flame pyrolysis producing a powdered form of carbon with a very high surface to

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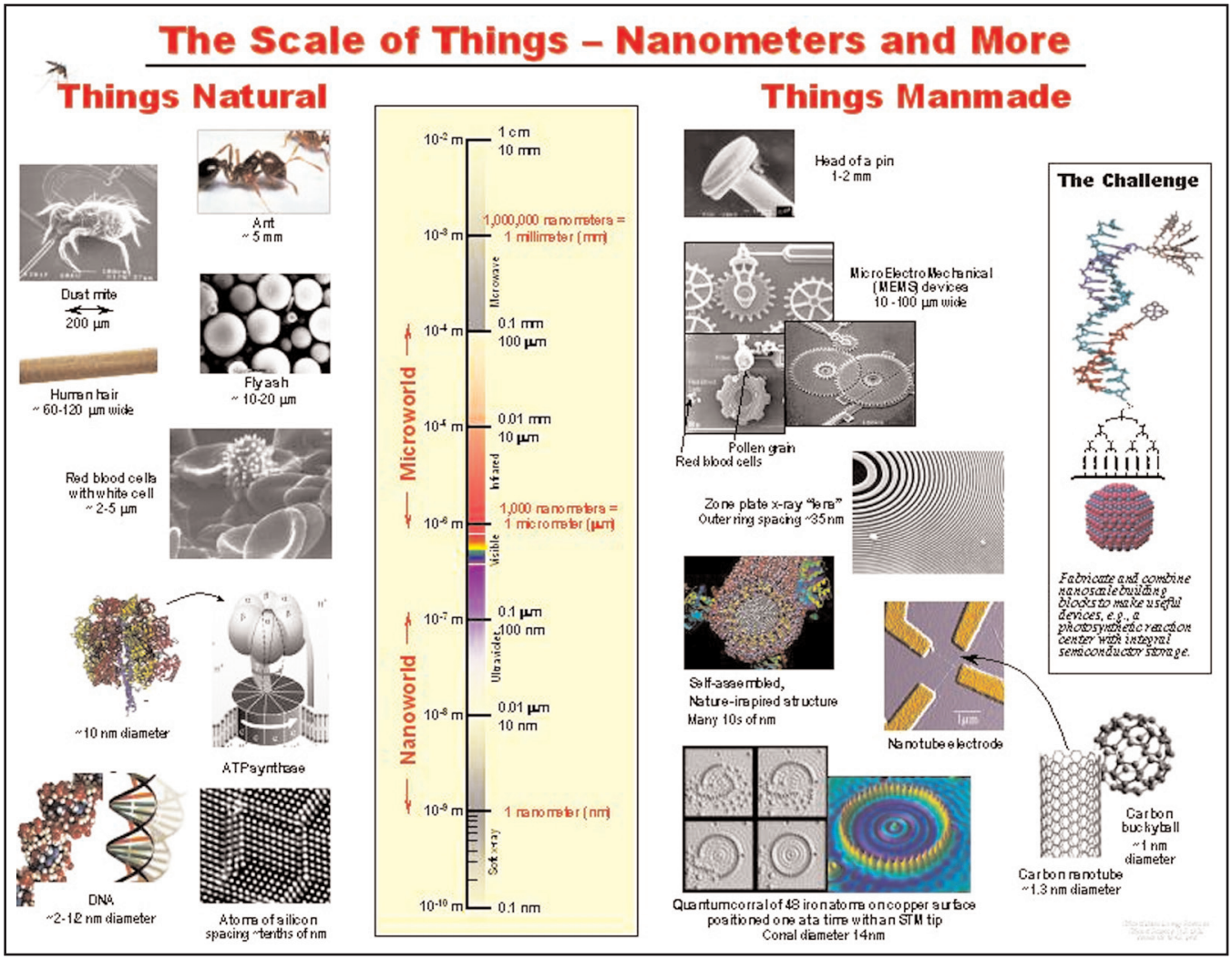
mass ratio. This is usually highly agglomerated but has a primary particle size in the order of 100 nm. Other common materials produced by flame pyrolysis or similar thermal processes include fumed silica (silicon dioxide), ultrafine titanium dioxide (TiO_2) and ultrafine metals such as nickel.

Other industrial processes, such as thermal spraying and coating, create and use nanosize particles as part of the process. Welding can generate ultrafine particles in a plume of aggregated nanosize particles. Ultrafine particles are also produced in large quantities from diesel engines and from domestic activities such as gas cooking.

Ultrafine particles are also found in the atmosphere where they originate from combustion sources (traffic, forest fires), volcanic activity, and from atmospheric gas to particle conversion processes such as photochemically driven nucleation. Nanoparticles and ultra fines are both nanosize particles.

It is important to note that the definition of nanoparticles or ultrafines has not been officially agreed upon. While there is widespread agreement that nanoparticles are those with a diameter "less than" 100 nm, HSE Research Report 274 finds that it is not clear what type of diameter this number describes. This report states, "Generally this was taken to imply the physical diameter of the particles although it could imply a diffusion diameter as instruments to measure

Figure 1 — Particles of various size ranges from www.nano.gov.



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particles in this size range often use diffusion as a classifying mechanism. Particles are seldom present as a single size (monodisperse) but rather can be represented by a distribution of sizes that is commonly characterized by a median (in terms of mass or number) and a geometric standard deviation. This simplistic definition (less than 100 nm) fails to take account of size distribution. It is not clear for example, whether the definition implies all particles less than 100 nm, 95% of particles less than 100 nm, a mean (or median) of less than 100 nm or any particles less than 100 nm. Sometimes, the term "nominal diameter" has been used to provide an effective dimension, where information about particle shape was not available or the particles were known not to be spherical. Similarly, an ultra fine aerosol is an aerosol consisting of primarily ultra fine particles."[3] As used in this bulletin, nanoparticles are those engineered particles physically less than 100 nm in at least one dimension.

Health Effects

Nanoparticles may differ from larger, but still respirable, particles with respect to deposition and alveolar clearance.[2] This is true for all particles of differing size. Size selective TLVs that identify an acceptable concentration in mass terms for specific size fractions; inhalable, thoracic, and respirable, exist today.[4] The nanosize particle fraction may be an additional fraction to separate from the inhalable dust exposure if it is shown that the specific health effects are related to this size fraction. The health effects of nanoparticles have not been definitively resolved and many industry groups and governmental agencies, such as the National Institute for Occupational Safety and Health (NIOSH) and the Environmental Protection Agency (EPA), are researching this issue.

Exposure Metrics

Another area of debate in this field regards the exposure metric that is most appropriate: aerosol mass, surface area or number (count). Most of the current occupational exposure limits for particles are based on mass. The nanoparticle debate involves the position that while the concentration might be small in terms of mass, it might be quite large based on surface area, and even greater in terms of particle numbers. Typically for industrial hygienists a personal sample that collects the most appropriate, biologically relevant fraction is desired. As a result, monitoring results would need to be expressed in either mass, surface area, or particle count. In addition, one of the knowledge gaps identified in the HSE report is that convenient methods do not currently exist by which exposures to nanoparticles in the workplace can be accurately measured and assessed.[3] Until these issues are resolved, the establishment and justification for appropriate regulatory occupational exposure limits may be delayed.

Respirator Use

Even though the need for respiratory protection for all nanoparticles has not been established, respirators may be used to help reduce exposures to nanoparticles. Selecting the appropriate respirator includes knowing the assigned protection factor (APF) needed. Although traditional permissible exposure limits (PEL) exist for many of the substances that nanoparticles are made from, the PEL for a nanoparticle of these substances is not yet clear. Nonetheless, respirators can be used to help reduce risk by lowering exposure in accordance with the respirator APF. Two key respirator performance criteria are filtration efficiency and face seal leakage. These attributes will now be discussed as they relate to filtration and face seal leakage of nanosize particles.

Filtration theory of particulate removing respirators is well understood and has been extensively described by several authors.[5,6] Basically, as an aerosol navigates through a filter, the trajectories of the particles deviate from the air streamline around the filter fibers due to various well-understood mechanisms. As a result, particles may collide with the filter fibers and become deposited on them. The removal mechanisms include diffusion, interception, inertial impaction and gravitational settling. Electrostatic forces can also play a role in some filter types.

For particles less than 100 nm, single fiber filtration theory indicates that

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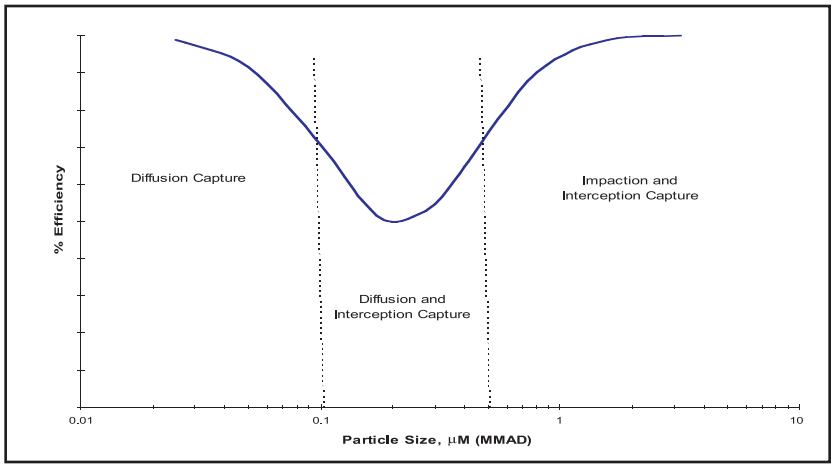
Brownian diffusion is the dominant removal mechanism. This theory predicts that filtration efficiency due to Brownian diffusion increases as particle size decreases (Figure 2). Brownian diffusion is caused by collisions between particles and the air molecules to create random paths that the particles follow. The random motion increases the probability of a particle contacting one of the filter fibers. Once the particle is collected onto a fiber, it will adhere to the filter fiber due to Van der Waals forces. Therefore, filters are likely to be good collectors of nanoparticles.

When the results of all the filtration mechanisms are summed, the result is a graph similar to that shown in figure 2. The point where the lines for the removal mechanisms for large particles intersects with the line for the removal mechanism for small particles indicates the most penetrating particle size for that filter. This graph predicts that for uncharged filter media, the most penetrating particle size has a mass median aerodynamic diameter in the range of 200–400 nm size. Particles in this size range are considered to be a much more penetrating aerosol for these filters than nanoparticles due to the decreased influence of Brownian diffusion at this particle size. NIOSH standards for particulate removing respirators require that these devices be tested against sodium chloride aerosols with a count median diameter of 75 nm or dioctyl phthalate (DOP) aerosol with a count median diameter of 185 nm.[7] Again the choice of the test aerosols' size is based on an expectation that this would be the most penetrating particle size.

Some authors have suggested that penetration of nanometer particles through wire screens (filters) can deviate from the classical penetration models if the effect of thermal rebounds is significant.[3] Both experiment and theory suggest significant thermal rebounds and increased penetration for particles smaller than 2 nm for these filter types and circular diffusion tubes.[3] At this point in time, the effect of thermal rebound in respirator filters is no more than speculation.

Figure 2 — Schematic of Filter Efficiency vs. Particle Size



Another study that is often cited by individuals who believe that thermal rebound is significant was conducted on filters typical of furnace filters.[8] The authors of this paper reported increased penetration in particles less than 20 nm. However, several questions exist regarding the experimental design and how the results apply to respirator filters. In addition, 3M researchers have not been able to reproduce the results. Recently, the authors of this study have indicated that, "Unfortunately, those results were erroneous due to the aerosol spectrometer malfunction (WPS, made by MSP Corp.). Now, the instrument is upgraded by the manufacturer and we have also worked out a new experimental procedure; as a consequence, such a decrease of the filtration efficiency is no longer observed. We are going to submit a paper on this subject to *Aerosol Sci & Technol* soon."[9]

At a conference by CFR (Center for Filter Research) in April 2005, researchers from the University of Minnesota presented filtration information on fiberglass filter paper against nanosize particles. Figure 3 is a summary graph combining the data from these researchers. One researcher used nanosize sodium chloride (NaCl) particles and the other used nanosize silver particles. The filter papers tested (4) represented a fairly high range of dioctyl phthalate (DOP) test penetration of 12-80% at 32 lpm. Figure 3 shows filter efficiency increased with decreasing particle size from the traditional most penetrating particle size. The graph

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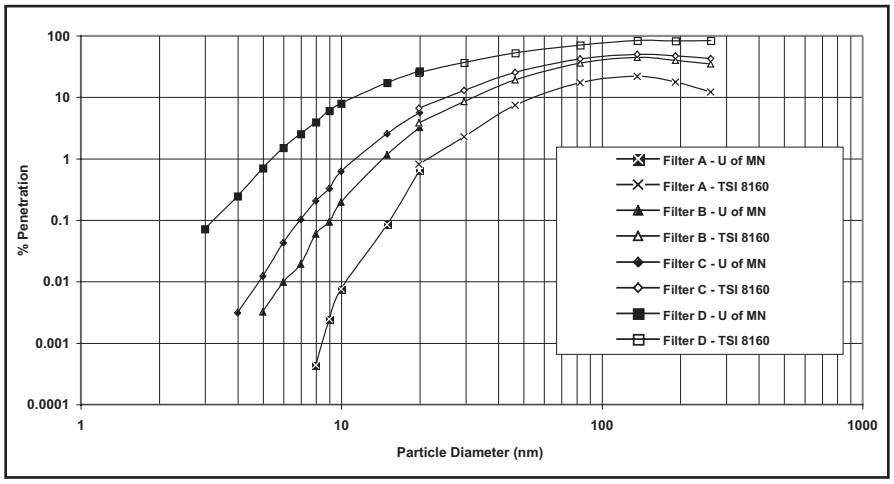
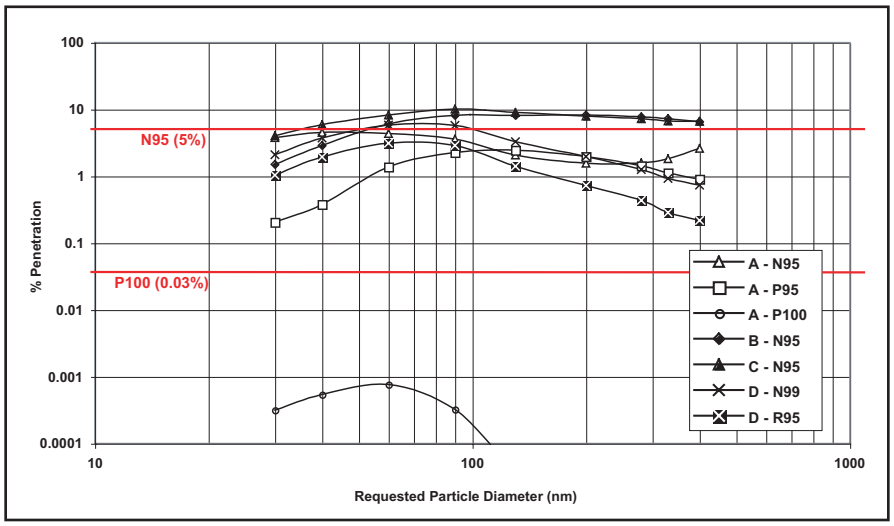
Figure 3 — Nano-sized Particle Percent Penetration Comparison for Four Fiberglass Filter Papers: U of MN Test (Silver Particles) and 3M Company TSI 8160 (NaCl Particles)* at 10 cm/s



* Research conducted by Center for Filtration Research, University of MN, presented by S-C. Kim and L. Franklin at 27th CFR Review Meeting, April 2005. Fiberglass filter paper donated by Hollingsworth and Vose.

Figure 4 — NIOSH Testing at 85 lpm (equiv.) on the TSI 8160 for Respirators and Cartridges from Various Manufacturers (Average of two tests—Martin and Moyer (2000) and Moyer (2002)



also indicates no particle bounce evidence, as there was no increase in penetration of particle sizes smaller than 5 nm.

A recently published abstract in Aerosol Science and Technology reported that, "even for particle sizes as small as 2.5 nm there was no measurable deviation from the classical single-fiber-efficiency theory. This conflicts with recently published work (Balazy et al. 2004) which claimed that the thermal bounce of nanometer sized aerosol particles begins to occur at a much larger particle size than previously thought."[10]

Little work has been done to quantify the performance of respirator filters against particles in the nanoparticle size range. It is still widely accepted that with diffusion as the dominant mechanism, the efficiency of filters will be high. In addition, all of the particulate filters approved by NIOSH (95–99.97%) exhibit filter efficiencies greater than that of the fiberglass filter papers shown in Figure 3. In an AIHCE (American Industrial Hygiene Conference and Exposition) presentation on respirator filter testing by Moyer in 2002, data were presented for various particle sizes.[11] This study tested various types of filters from NIOSH approved particulate respirators. While the objective of the study was not to evaluate nanosize particles, some of the data include particles in this range. This work shows that for respirator filters, filter efficiency increased for particles in the 30–60 nm range (Figure 4).

Face Fit

Another factor affecting respirator performance is face seal leakage. Face seal leakage is dependent on many factors including the fit of the respirator to the face, duration of wearing, and work activity.

Some individuals have speculated that face fit is even more critical for nanoparticles because of their small size, implying that face fit is more critical for nanosize particles than for other contaminants. It is often stated, however, that nanoparticles may behave like gases and vapors and respirators have been fit tested and successfully used for protection

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against gas and vapor contaminants for years. In particular, the fit test methods in use today have been widely used to fit respirators for use against gases and vapors. One workplace protection factor study in a styrene vapor environment has shown that half face piece respirators fit tested using the saccharin protocol provide protection levels in excess of the APF for a half facepiece respirator.[12] There is no evidence to indicate that the OSHA fit test protocols are not sufficient for fit testing respirators that will be used to reduce exposures to nanoparticles.

Conclusion

There has been much speculation whether the performance of respirator filters are sufficient for removal of nanoparticles. Preliminary research on filter paper tested against nanosize particles at the University of Minnesota and the study published in Aerosol Science & Technology contradict this speculation. At this time there is no evidence to suggest that the filter will be the limiting factor in the use of air purifying respirators against nanoparticles. Rather, proper fit testing and wearing the respirator during all times of exposure will continue to be the more significant considerations for reducing exposure when using a respirator.

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