3M Technical Data Bulletin

PSD

<u>#171: Nanotechnology and Respirator Use</u> Revised June, 2015

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 how to measure and control nanoparticles, including questions about filtration mechanisms for particulate respirators. This technical data bulletin will discuss the terminology and give an overview of what is known about how filters remove these particles.

Nanoparticles

A nanometer is 1 one billionth of a meter. The U.S. National Nanotechnology Initiative (NNI) defines nanotechnology as "the understanding and control of matter at dimensions between approximately 1 and 100 nanometers (nm), where unique phenomena enable novel applications not feasible when working with bulk materials or even with single atoms or molecules."¹ Similarly, the EU Commission defined 'nanomaterials' as "a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range between 1 nm and 100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1% and 50%."² Engineered nanoparticles are the end products of this technology and include nanotubes, nanowires, and quantum dots.

Besides engineered nanoparticles, many industrial processes produce particles that have dimensions in the nanometer size range, often referred to as "ultra fines." Ultrafine particles tend to be formed through nucleation, gas to particle reactions, or evaporation.³ The synthesis of carbon black by flame pyrolysis produces a powdered form of carbon which is usually highly agglomerated but has a primary particle size in the order of 100 nm. Flame pyrolysis or similar thermal processes are used to produce fumed silica (silicon dioxide), titanium dioxide (TiO₂) and forms of metals such as nickel. Thermal spraying and coating, welding, and diesel engines can generate ultrafine particles.

Ultrafine particles are also found in the atmosphere where they originate from combustion sources (traffic, forest fires), domestic activities such as gas cooking, volcanic activity, and from atmospheric gas to particle conversion processes.

Exposure Metrics

Most of the current occupational exposure limits for particles are based on mass. While the concentration of nanoparticles might be small in terms of mass, it might be quite large based on surface area, and even greater in terms of particle numbers. Since there is still much debate as to which is the most important measurement, there is no single method to assess exposure to nanoparticles. Rather, a combination of methods might be used to measure exposure in terms of mass, surface area, or particle count within different size ranges. Until these issues are resolved, the establishment and justification for appropriate regulatory occupational exposure limits may be delayed.

Respirator Use

In order for particulate respirators to help reduce exposures to nanoparticles, they must be able to filter nanoparticles, and tight fitting respirators must be able to seal adequately to the user's face.

Filtration theory of particulate removing respirators is well understood and has been extensively described.^{4,5} For particles smaller than 100 nm, diffusion is the dominant removal mechanism. Brownian diffusion is caused by collisions between particles and air molecules. The resulting random motion increases the probability of a particle contacting one of the filter fibers. Filtration efficiency due to Brownian diffusion *increases* as particle size decreases. Once the particle is collected onto a fiber, it will adhere to the filter fiber due to Van der Waals forces.

Because of the complex methods by which particulate filtration occurs, most particulate filters have a region of lesser filtration efficiency somewhere between 50-500 nm.⁵ Particles in this range are large enough to be less effectively pushed around by diffusion, but small enough to be less effectively captured by interception or impaction onto a filter fiber. The most penetrating particle size (MPPS) will depend on the filter media, air flow, and electrostatic charge on the particle. Filters that use electrostatic attraction may have a MPPS shifted to a slightly smaller size range.

Numerous studies have shown that particulate respirators tested and certified under the current NIOSH test methods are able to filter nanoparticles.^{6,7,8,9} Filtration efficiencies of six different NIOSH approved N95 filtering facepiece respirators from various manufacturers are shown in Figure 1. Averaged filtration efficiencies (n=10) are shown as a function of different sized sodium chloride particles at a flow rate of 85 liters per minute. While there was variability between different samples of the same model respirator, and between different models, the MPPS included particles with a diameter between 40 and 100 nm. As seen in Figure 1, particles that are smaller or larger than the MPPS are captured with higher filtration efficiency.



Figure 1. Averaged filtration efficiencies for 6 different models of N95 filtering facepieces when challenged with NaCl aerosol at flow rate of 85 liters/minute.

European FFP2 and FFP3 particulate respirators have also been shown to filter nanoparticles.¹⁰ Figure 2 shows filtration efficiencies of 3 different European filtering facpiece respirators from one manufacturer. Averaged filtration efficiencies (n=10) are shown as a function of different sized sodium chloride particles at a flow rate of 85 liters per minute. The minimum filter efficiencies for the tested FFP2 (94%) and FFP3 (99%) were achieved. Note that the test conditions used in this study differ from those used in the European standard under which filtering facepieces are approved, EN 149:2001+A1:2009. Other research has confirmed that filter efficiency increases with decreasing particle size, even for particles as small as 3 nm.¹¹



Figure 2. Averaged filtration efficiencies for 3 different models of European filtering facepieces when challenged with NaCl aerosol at flow rate of 85 liters/minute (2012).

Face Fit

Another factor affecting respirator performance is face seal leakage. Some individuals have speculated that face fit is even more critical for nanoparticles because of their small size. Face seal leakage is dependent on many factors including the fit of the respirator to the face, duration of wearing, and work activity. Several studies investigated respirators mounted on manikin head forms with artificial leaks to see how these would affect nanoparticle faceseal leakage.^{12,13,14,15} However, correlation between this and human users is unknown. A study on human subjects wearing N95 filtering facepiece respirators showed that faceseal leakage for nanoparticles was not larger than face seal leakage for "all size" particles.¹⁶

It is often stated that nanoparticles may behave like gases and vapors. For years, respirators have been fit tested and successfully used for protection against gas and vapor contaminants. One workplace protection factor study in a styrene vapor environment has shown that respirators fit tested using the saccharin qualitative fit test protocol provided protection levels in excess of the assigned protection factor of 10 for a half mask respirator.¹⁷ There is no evidence to indicate that approved fit test protocols are not sufficient for fit testing respirators which will be used to reduce exposures to nanoparticles.

US and UK Recommendations

NIOSH has published several documents on nanotechnology including:

- Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials ¹⁸
- Current Intelligence Bulletin 63: Occupational Exposure to Titanium Dioxide ¹⁹
- General Safe Practices for Working with Engineered Nanomaterials in Research Laboratories ²⁰
- Current Intelligence Bulletin 65: Occupational Exposure to Carbon Nanotubes and Nanofibers ²¹

NIOSH cites recent studies and concludes that particulate respirators (e.g. N95, P100) may be used to help reduce exposure to nanoparticles if used as part of a complete respiratory protection program, including fit testing.

The UK Health and Safety Executive (HSE) has also published several research reports and guides on nanomaterials. Furthermore, the HSE has made similar recommendations to NIOSH, namely that "RPE must be suitable for the task and in accordance with COSHH must be face-fitted for the individual. Disposable masks (no less than FFP3 AFP 20 standard) are suitable as a precautionary measure against accidental spillage. Full-face P3 AFP 40 particulate respirators (preferably powered if used for over one hour) would be required for work in an atmosphere containing free airborne nanomaterials."²²

Conclusion

When engineering controls are not adequate, or while they are being implemented, particulate respirators may be used to help reduce exposure to nanoparticles according to the respirator's protection factor when used correctly as part of a complete respirator program.

In the U.S., a written respiratory protection program must be implemented meeting all the requirements of OSHA 1910.134, including training, fit testing and medical evaluation. In Canada, CSA standard Z94.4 requirements must be met and/or requirements of the applicable jurisdiction, as appropriate. In Europe, the requirements of EN 529:2005 should be followed, in addition to national and European regulations and directives pertaining to the control of chemical substances and health and safety at work.

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