CHAPTER 7

# Controlling Nanoparticle Exposures

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**Chapter Outline**



## 7.1 Introduction

In many cases, assessing nanoparticle exposures establishes a need to control the exposures should they present unacceptable risks to human health. The Merriam-Webster Online Dictionary (2010) defines the verb form of "control" as "to reduce the incidence or severity of especially to innocuous levels." When exposures exceed innocuous levels (e.g., greater than occupational exposure limits), control measures must be instituted to reduce the concentrations. The success of these measures to control exposures must be

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determined by reassessing exposure concentrations. If concentrations still pose unacceptable risks, then additional control measures may be warranted.

This chapter focuses on control measures for airborne nanoparticles in work environments. First, the hierarchy of control measures is presented and ways to prioritize control options within that hierarchy are discussed. Then, the suitability of different types of control measures to reduce nanoparticle exposures is considered, with particular emphasis on the ability of filters to capture airborne nanoparticles.

In practice, airborne nanoparticles may occur individually or as aggregates—chains of multiple nanoparticles. Nanoparticle aggregates are large particles, for which many control options are available. In contrast, individual nanoparticles may be closer in size to gas or vapor molecules than they are to super-micrometer particles. Therefore, measures that are used to control exposures to gases and vapors may be appropriate for controlling exposures to individual nanoparticles. A recurring theme in this chapter is that many of the control measures that are presently used to control exposures to gaseous and particulate pollutants can be implemented successfully for nanoparticles. Novel control methods are generally not necessary to reduce exposures to below innocuous levels.

## 7.2 The Hierarchy of Control

Figure 7.1 illustrates the hierarchy of control. The hierarchy provides a preference ranking for broad categories of control measures in the absence of mitigating factors such as cost or availability. Elimination—the complete removal of a hazardous agent from the workplace—is on the top tier of the hierarchy because the exposure potential is eliminated completely. Prohibition of smoking in a restaurant or bar illustrates this concept in that

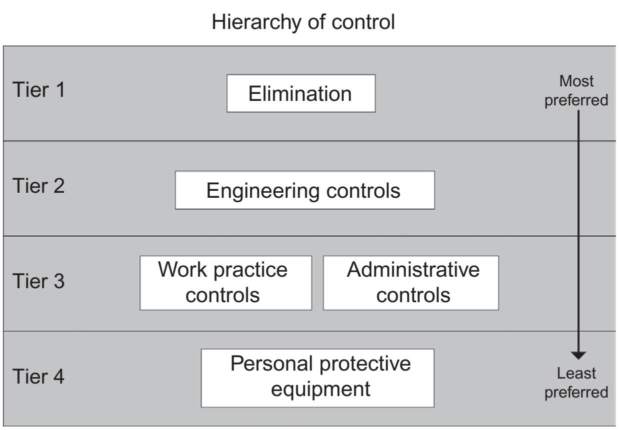


**Figure 7.1**
A conceptual diagram of the hierarchy of control.

workers have no opportunity for exposure to environmental tobacco smoke. Nanoparticles, however, are often produced or incorporated into a process or product because of their unique, beneficial properties imparted by their size. Therefore, elimination is often impractical for nanoparticles without decreasing the value or functionality of the process or product.

Engineering controls are physical, chemical, or biological changes made to a process or a product that reduce human exposure to a hazardous agent. These measures are second in the hierarchy because, although not eliminating the agent from the workplace, they offer reduced exposures particularly for those workers at risk without placing the responsibility of implementation on the exposed workers. Engineering controls include substitution of a less hazardous material or process step for one that is more hazardous, automation of a process, isolation of a hazardous process or product from workers or the workers from the process or product, and ventilation with or without the use of air pollution control equipment. Engineering controls are among the most frequent measures used to reduce exposures to airborne nanoparticles.

Work-practice controls are changes in how work is performed to reduce exposures. For example, a wet mop instead of a broom can be used to clean dusty floors, while dramatically reducing the resuspension of potentially hazardous powders. These kinds of measures are lower in the hierarchy than engineering controls because they rely on management to institute these changes and on workers to implement them. However, work-practice controls can be broadly effective when implemented properly.

Administrative controls are changes in when or by whom work tasks are performed. For example, a change to conduct tasks with high exposure potential from day to night may place substantially fewer workers at risk. Similarly, workers can rotate through tasks with varying exposures to distribute health risk among several workers so that no one worker will receive a dose of a potentially harmful agent that presents an unacceptable risk. Administrative controls are lower in the hierarchy than engineering controls because they do not reduce the dose each time a worker performs the tasks. These measures may spread the dose around among several workers, or they may reduce the number of workers nearby at the time the tasks are performed. One advantage of administrative controls is that the responsibility for change is not placed on each worker individually. However, the role of a supervisor is critical to ensure that changes are carried out according to plan.

Personal protective equipment (PPE) is a device or clothing worn by workers to reduce their exposure to potentially hazardous agents. This control measure is lowest on the hierarchy of control because PPE does nothing to eliminate the hazard from the workplace and places responsibility on the workers to don and use the PPE properly every time they wear it. Examples of PPE include respiratory protection, chemical protective clothing, gloves, and protective eyewear.

## 7.3 Criteria for Prioritizing Control Options

With all else being equal, control measures on higher tiers of the hierarchy are preferable to those on lower tiers. However, other factors—especially cost—may make options higher in the hierarchy unacceptable, and options lower on the hierarchy might need to be considered. Measures from multiple tiers may be instituted together to provide larger reductions in exposures than possible with individual measures. Even within each tier, selections among several control options may need to be made. Therefore, additional criteria for choosing from among control options may need to be considered.

The effectiveness of the control measure may be the most relevant factor to consider. A control measure that reduces nanoparticle exposures by 90% will be more effective than one that reduces concentrations by 50%. Effectiveness may be especially important if exposures must be reduced to reach an occupational exposure limit (OEL). Typical examples of engineering controls that have different effectiveness are local exhaust ventilation (LEV) systems that include full enclosures around a process versus LEV systems that include an exhaust opening adjacent to, but not surrounding, a nanoparticle generation source. A well-designed enclosure provides better capture of nanoparticles than an adjacent duct opening.

Cost is also one of the most important criteria when selecting among several control measures. Two primary components must be considered: (i) the capital costs required to install a measure and (ii) operating costs after the measure is implemented. Capital expenditures include capital costs and installation costs for pieces of equipment. Operating costs may include energy-related expenditures, parts, labor costs for maintenance, and labor costs for tasks that may take longer in PPE or if different work practices are used. Engineering control measures may be deemed unfeasible due to costs, or a low-cost LEV system with a duct opening adjacent to the nanoparticle generation source may be considered effective enough if it costs much less than an LEV system with a full enclosure around the source.

Several other factors should be considered when prioritizing control options. These factors include:

- *Reliability:* Is the potentially hazardous agent so toxic that you need a control measure that has little risk of failure? Should you implement redundant control measures in case one fails?
- *Exposed populations:* Do you need to consider protecting the public in addition to workers? Do some control measures protect a larger proportion of the workforce than others?
- *Exposure setting:* Are you concerned about exposures in just certain parts of the facility, such as the packaging area? Do you need to worry about exposures of your customers?

- *Frequency of exposure:* Are you producing product continuously or is the equipment adjusted between batches? Are you instituting control measures for tasks that are undertaken only a few times a year for which costly measures may not be feasible?
- *Acceptability of intervention:* Does an intervention make it difficult to control a process? Does a control measure make it difficult for a worker to perform certain tasks?

Integrating these factors together with the hierarchy of control and information on effectiveness and costs helps occupational health specialists select a control measure or a combination of several measures that best suits a particular situation.

## 7.4 Form of Nanomaterials

Airborne nanoparticle exposures can be reduced substantially if nanomaterials (NMs) are placed in a form that makes aerosolization difficult. For example, exposures can often be reduced by handling a liquid suspension of nanoparticles compared with a dry powder. Similarly, nanoparticles incorporated into a polymer matrix are difficult to remove from that matrix. Bello et al. (2009) investigated the cutting of composites of carbon and alumina fibers in an epoxy resin. Carbon nanotubes were included in some of the composites but not in others. Although particle number concentrations increased dramatically as cutting occurred, concentrations were similar or lower when the nanotubes were part of the composite than when they were excluded. There was no evidence that individual nanotubes were aerosolized when they were present.

## 7.5 Local Exhaust Ventilation

Local exhaust ventilation involves the capture of air contaminants at a source. A local exhaust ventilation system consists of a hood or enclosure to capture a contaminant, an air pollution control device to clean the air, and an air mover to provide air flow through the system. These systems range from small portable units, such as a high-efficiency particulate arrestance (HEPA)-vacuum system (Figure 7.2a), to extensive, permanent installations typical of large industrial facilities (Figure 7.2b).

As illustrated in Figure 7.3, two forms of capture are most relevant to the control of nanoparticles: exterior hoods and ventilated enclosures. Exterior hoods require exhaust sufficient to draw particles into the hood opening. In contrast, enclosures surround the source of airborne nanoparticles and typically require low air flow to prevent particles from escaping through the openings in the enclosure.

### 7.5.1 Exterior Hoods

Airborne nanoparticles tend to follow air streamlines in the absence of large temperature gradients, electrostatic fields, or magnetic fields. Consequently, nanoparticles are likely to

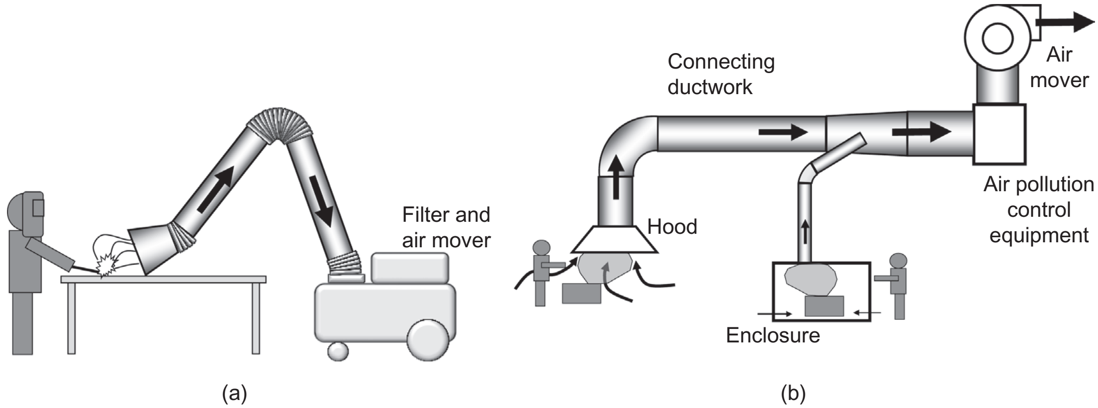


**Figure 7.2**
Local exhaust ventilation systems range in size from small, portable units such as those used for control of welding fume (a) to large, permanent installations (b).

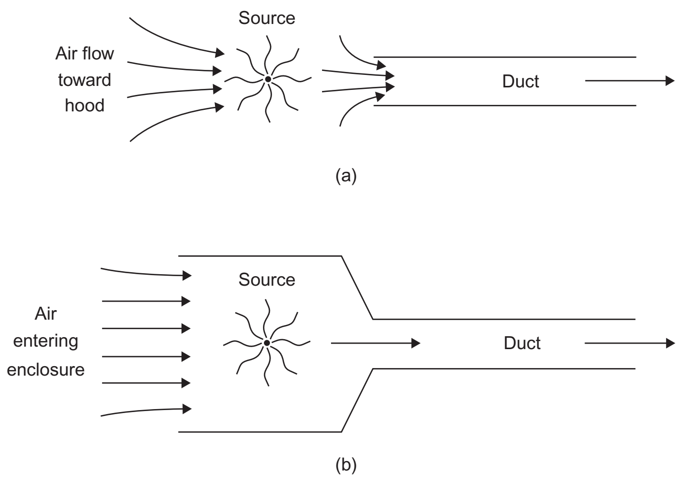


**Figure 7.3**
Conceptual diagrams of two types of local exhaust ventilation: (a) an exterior hood and (b) a ventilated enclosure.

be captured by an exterior hood to the extent that air is drawn into the hood (Schulte et al., 2008). Therefore, the goal of exterior hood design for effective nanoparticle capture is to draw in as much of the contaminated air as possible.

Design procedures for exterior hoods are largely empirical based on past experience in most cases, as described by the American Conference of Governmental Industrial Hygienists (ACGIH, 2013) and Burgess et al. (2004). Key factors that affect the design of an exterior hood are the size of the region across which nanoparticles are released into the air, the distance from the hood opening to the release points, and the magnitude of air currents in the room that can interfere with the air flowing into the hood. The designer must first decide how large a "capture velocity" is required for the hood to overcome any air currents in the room and to ensure that the contaminated air is drawn into the hood. Then, the designer must determine the air flow that is necessary to achieve that capture velocity given the opening size of the hood.

Exterior hoods can be used effectively for the control of nanoparticle exposures. Old and Methner (2008) measured the airborne particle concentrations during cleanout of a reactor for producing metal catalytic NMs with and without an exterior hood. As shown in Figure 7.4, the exterior hood consisted of a portable fume extractor with a round, flanged opening positioned adjacent to the cleaning process. Airborne concentrations were reduced from 75% to 96% by mass and from 85% to 100% by number.

Several issues may compromise the effectiveness of an exterior hood. A selected capture velocity that is too low or one that requires the hood to be positioned closer to the source than is practical can lead to incomplete capture of nanoparticles. Frequently, nearby workers may disrupt air flow into an exterior hood. For example, real-time measurements were made of the ability of an exterior hood to capture engineered nanoparticles dried as a thin nanopowder on a support belt in a machine as the nanopowder separated from the belt and dropped into a hopper. During most periods, nanoparticle concentrations were indistinguishable from background particle concentrations. However, nanoparticle concentrations rose markedly each time the machine operator checked on the process, indicating that the operator drew contaminated air away with her as she left the machine.

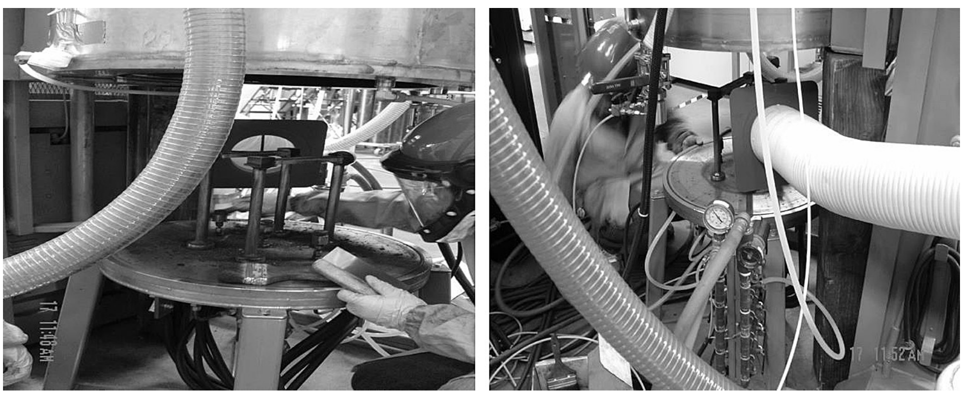

**Figure 7.4**
Photographs of an exterior hood from a portable fume extractor used to collect particles produced during the cleaning of a reactor that produced nanoscale metal catalytic materials.
*From Old and Methner (2008).*

### 7.5.2 Ventilated Enclosures

Examples of ventilated enclosures include booths and tunnels in production processes and laboratory hoods in research facilities. Enclosures are superior to exterior hoods for two reasons. First, enclosures contain emitted particles at the point of their release rather than drawing them from within the workplace into the LEV system. Second, compared with exterior hoods, enclosures require substantially lower air flows because they must ensure only that particles do not escape from openings in the enclosure. Openings include those present at all times and additional ones that may be created as workers interact with the process, such as a door or access port. Examples of these interactions could include a researcher opening a sash on a laboratory hood or a production operator entering a panel to make an adjustment to a piece of equipment.

In most cases, enclosures are designed so that the velocity at the face of any openings is in the range of 0.5–1.0 m/s (100–200 ft/min) (Burgess et al., 2004). For laboratory hoods, face velocities of about 0.5 m/s (100 ft/min) are typical because higher velocities tend to create eddies in front of workers standing at the openings to hoods. These eddies can draw contaminated air out of the hood into the worker's breathing zone (Kim and Flynn, 1991). Other design considerations include making the enclosure as complete as possible and ensuring that airflow is distributed as evenly as possible across openings (Burgess et al., 2004).

Fume hoods are an essential engineering control to protect those working with NMs in laboratories (NIOSH, 2012). However, the hoods must be operated properly to ensure maximum protection of the workers. Tsai et al. (2009a) evaluated the ability of a conventional constant-flow laboratory hood with its sash set to different heights to contain airborne nanoalumina particles generated by a pouring operation. Nanoalumina particles escaped the hood when a low sash produced a high face velocity of 1.0 m/s (200 ft/min), but not at higher sash heights when face velocities were only 0.6 m/s (120 ft/min) and 0.4 m/s (80 ft/min). Thus, having too high a face velocity is disadvantageous for controlling nanoparticles generated in a hood.

Some types of laboratory hoods contain nanoparticles more effectively than others. In constant-velocity hoods, also called *variable air volume* hoods, fan speed is varied as sash height is changed to maintain constant velocity at the hood face. Tsai et al. (2009b) demonstrated that at least 99.4% of nanoscale particles generated by a reactor producing single-walled carbon nanotubes (SWCNTs) or multiwalled carbon nanotubes (MWCNTs) were contained by a constant velocity laboratory fume hood. In air-curtain hoods, a sheath of clean air flow is passed downward across the face of the hood to more effectively separate the worker from the contaminant in the hood. Tsai et al. (2010) observed effective containment of nanoparticles during transfer and pouring of nanoalumina using a constant-velocity hood operating with a face velocity of 0.5 m/s (100 fpm) and an air-curtain hood, but not with a conventional constant-flow hood. When the sash of the constant-velocity hood was opened to its high level, the 0.5 m/s face velocity could not be maintained, allowing nanoalumina particles to escape when poured. Cena and Peters (2011) observed that a biosafety cabinet with an air curtain reduced respirable dust concentrations for workers sanding a nanocomposite containing MWCNTs much more effectively than a constant-flow, custom-built fume hood.

Schulte et al. (2008) discussed ventilation of nanoparticles according to different types of workplaces: research settings, development facilities, and production/manufacturing. Laboratory hoods are typically available and readily used in research settings, whereas full enclosures are often appropriate for production/manufacturing-scale operations. For development activities such as laboratory scale-up, process development, and product development, frequent modification to operations may preclude the use of full enclosures, and reliance on exterior hoods is more common. However, as stated earlier, the effectiveness of exterior hoods is dependent on proper placement in relationship to the nanoparticle generation source. Consequently, the effectiveness of exterior hoods should be assessed more frequently than other hood types.

## 7.6 Air Pollution Control Devices

A variety of control measures are available for removing particles from contaminated air streams. The most common technologies include gravitational settling, centrifugal collection, wet scrubbing, electrostatic precipitation, and filtration. Of these devices, electrostatic precipitation and filtration are typically used for nanoparticles and will be discussed further. Gravitational settling units and centrifugal collectors, such as cyclones, are only effective for removal of large particles (nominally $>10\,\mu m$). Wet scrubbers are typically not selected for nanoparticles because they require treatment of water before discharge and are generally considered ineffective for particles smaller than 500 nm in diameter (ACGIH, 2013).

### 7.6.1 Electrostatic Precipitators

Electrostatic precipitators (ESPs) operate by charging incoming particles in high-voltage environments. As shown in Figure 7.5, two primary configurations are available in electrostatic precipitation: single-stage and two-stage collectors. In a typical single-stage collector, particle-laden air moves through a series of highly charged wires strung between grounded plates. The particles are charged by the electrical fields and the ions generated by the charged wires and then migrate toward and collect on the grounded plates. In a typical two-stage collector, particles are charged in a short, first-stage charging section with a geometry similar to the single-stage collector. Particles are then collected in a second stage that has alternating charged and grounded plates. The collection efficiency of two-stage ESPs is often higher than single-stage ESPs because the collection plates can be operated much closer together.

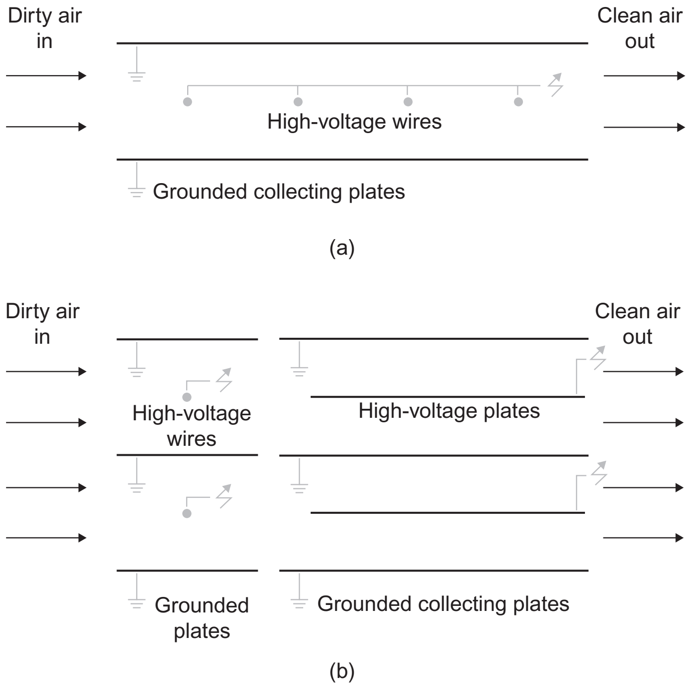


**Figure 7.5**
Conceptual drawings of (a) a single-stage electrostatic precipitator (ESP) and (b) a two-stage ESP.

In ESPs, field charging is the predominant mechanism for charging particles with diameters larger than 1 μm, whereas diffusion charging is predominant for particles smaller than 100 nm (Hinds, 1999). However, particles a few hundred nanometers in diameter are more difficult to collect by electrostatic precipitation because the combined mechanisms are not as effective as at larger or smaller sizes. In addition, applying charge to particles smaller than about 75 nm in diameter is challenging, leading to decreases in efficiency for the smallest nanoparticles when ESP voltages are not sufficiently high (Zhuang et al., 2000).

Huang and Chen (2002) studied the ability of both single-stage and two-stage ESPs to capture nanoparticles under a variety of operating conditions. As shown in Figure 7.6, they were able to collect nanoparticles with close to 0% penetration (100% collection efficiency) in both configurations at high voltages. These researchers concluded that a two-stage ESP was more economical to collect particles larger than 16 nm in diameter, whereas a single-stage ESP was more efficient for smaller particles.

Cost considerations generally limit single-stage systems to large applications such as power plants (Burgess et al., 2004). Two-stage precipitators can be found in heating, ventilating, and air conditioning (HVAC) systems, as stand-alone units designed to collect pollutants such as smoke or welding fumes, and as part of some LEV systems. However, they are less

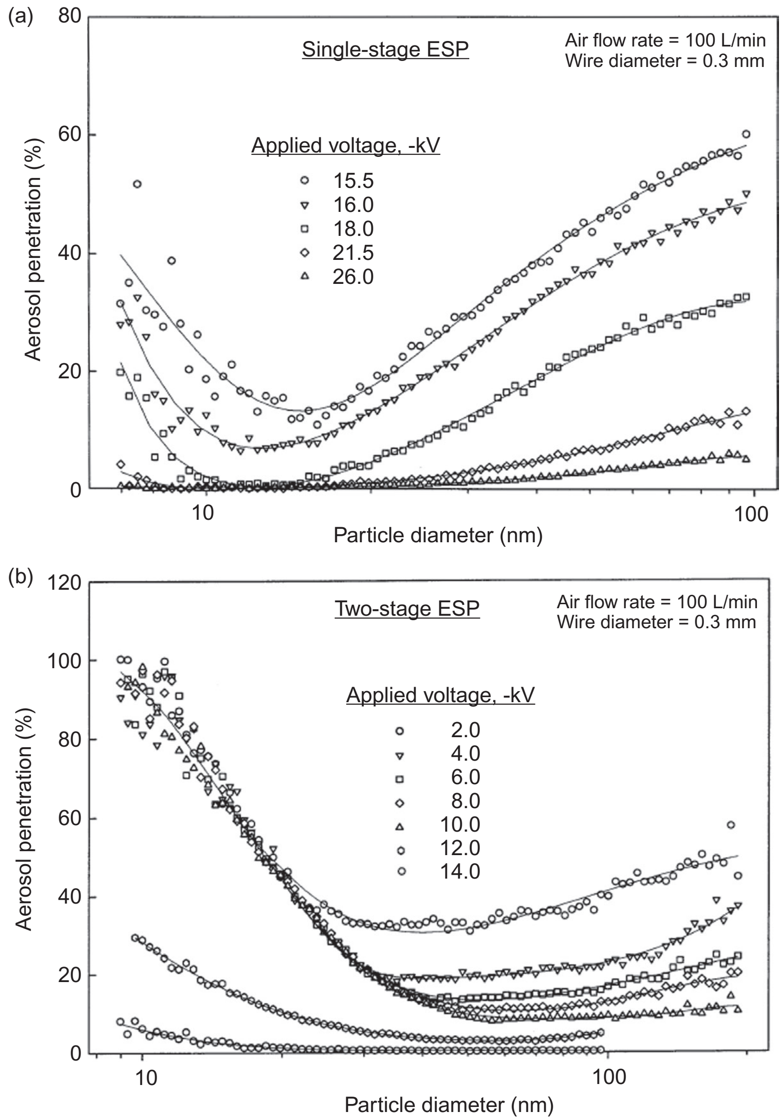


**Figure 7.6**
Particle penetration versus diameter for (a) single-stage and (b) two-stage electrostatic precipitators (ESPs) over a range of applied voltages. *From Huang and Chen (2002)*.

prevalent than filtration systems for several reasons. First, relatively few manufacturers sell precipitators that are suitable for workplaces. Second, they are typically more expensive to purchase than equivalent filtration systems, although their operating costs are usually lower because of a lower resistance to air flow. Third, the collection plates must be cleaned regularly or the precipitator will lose efficiency. This may be a special difficulty with nanoparticles that tend to stick well to surfaces. Systems are available for washing the plates, but then the wash water requires treatment before discharge.

### 7.6.2 Air Filters

Air filtration is relatively easy and flexible to implement, making it widely used throughout nanotechnology. Fabric and fibrous filters are used for airborne particle control. Fabric filters are composed of woven and felted fabrics that collect particles primarily on a dust cake that develops over time on their surface. They are frequently used in large industrial applications in the form of bags that are hung within a large housing. Fibrous filters, used more frequently in workplace applications, consist of a nonwoven mat of individual fibers oriented randomly and perpendicular to air flow. Particles are frequently collected throughout the depth of a fibrous filter rather than just on its surface. The range of fiber diameters for a given filter is usually broad, and these diameters can range from smaller than 1 μm to several hundred micrometers. Fibers are made from a variety of materials, including fiberglass and various polymers. Investigators have studied the mechanisms by which fibrous filters collect particles theoretically, experimentally, and using numerical modeling.

The most predominant mechanisms contributing to particle collection are interception, inertial impaction, and diffusion. Interception occurs when a particle moving with air flow around a fiber passes within one particle radius of the fiber. Larger particles are collected with higher efficiency by interception than smaller particles because of their larger radius. In inertial impaction, the inertia of a particle causes it to persist in moving toward and hitting a fiber rather than following the curved streamlines around the fiber. Collection efficiency by impaction increases with particle diameter squared. Collection of particles by diffusion is caused by Brownian motion, the irregular jittering of an airborne particle caused by constant bombardment by air molecules. This jittering sometimes causes a particle to hit a fiber as it moves with air flowing around the fiber. Because Brownian motion increases as particle diameter decreases, the capture of particles by diffusion increases as particle size decreases.

The net effect of these forces is presented in Figure 7.7, which shows a typical curve for collection efficiency as a function of particle size. Particle collection efficiency is high for large particles because of interception and inertial impaction and for small particles because of diffusion. However, these collection mechanisms are minimally effective together for particles around 200–300 nm in diameter, resulting in a minimum efficiency. The particle diameter at which the minimum efficiency occurs is termed the most penetrating particle size (MPPS).

In certain situations, electrostatic attraction and gravitational settling may also contribute to particle capture. Although gravitational setting is negligible for nanoparticles, electrostatic attraction can be important for particles of all sizes. Electrostatic attraction can be used to enhance collection efficiency of filters by attaching permanent electrostatic charges to

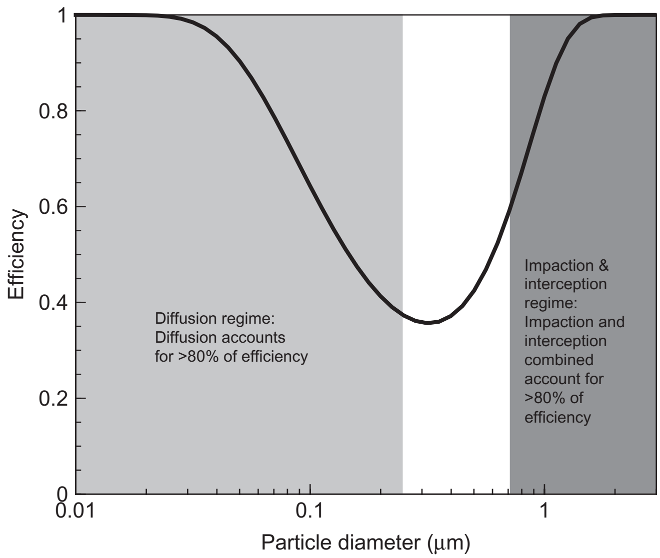


**Figure 7.7**
Filter efficiency as a function of particle diameter predicted from theory for a conventional fibrous filter having a uniform fiber diameter of 5 μm, a packing density of 0.05, a thickness of 2 mm, and operating at an air flow velocity of 10 cm/s. Particle density is 1 g/cm$^3$. The diffusion and impaction/interception filtration regimes are indicated on the figure.

synthetic polymer fibers. The charged fibers attract oppositely charged particles and induce a temporary dipole in similarly charged particles. Both phenomena move the particle closer to the fiber as the air passes through the filter, thereby increasing collection efficiency. Properly designed electrostatically enhanced filters have higher efficiency than conventional filters for the same resistance to air flow, or less resistance to air flow for the same efficiency. Capture by electrostatic attraction increases with particle diameter, leading to a smaller MPPS for filters made with charged fibers (typically 40–100 nm) compared with those made with noncharged fibers (Brown, 1993; Rengasamy et al., 2009).

Wang and Kasper (1991) suggested that nanoparticles smaller than 10 nm may be sufficiently small and have enough Brownian motion to act like air molecules rebounding from a fiber rather than sticking to it. Balazy et al. (2004) presented experimental results which suggested that rebound occurred for particles smaller than 20 nm in diameter. However, Heim et al. (2005) showed that the condensation particle counter used by Balazy et al. had low and potentially inconsistent counting efficiency for particles smaller than 12 nm in diameter. These authors used other instruments that indicated that the measured efficiency matched the theoretical efficiency and exhibited no sign of rebound for particles as small as 2.5 nm in diameter. Measurements by Kim et al. (2007) showed no rebound for particles larger than 2 nm in diameter. As shown in Figure 7.8, Kim et al. (2006) observed an increase in

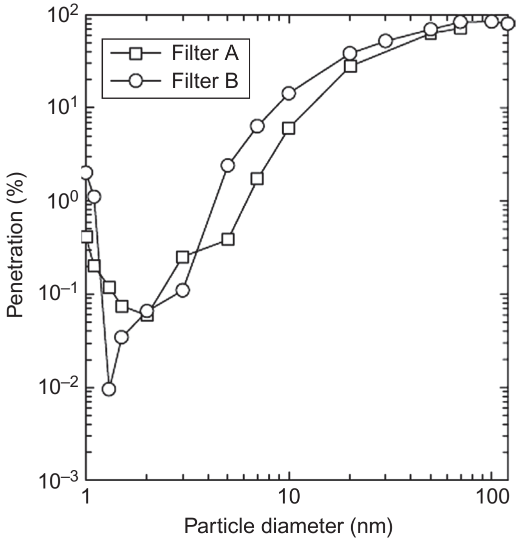


**Figure 7.8**
Filter penetration as a function of particle diameter for two test filters. *From Kim et al. (2006)*.

penetration, which is a decrease in efficiency, for two filters, but only for particles smaller than 2 nm in diameter.

The evidence is clear that particle rebound occurs only for particles smaller than about 2 nm in diameter. In most real-world situations, particles with diameters 2 nm or smaller will not be present in an atmosphere for long because they tend to agglomerate quickly, effectively becoming larger particles that can be readily filtered. HEPA filters are available that have efficiency ≥99.97% even at the MPPS. For particles with diameters between 2 nm and the MPPS, HEPA filter users should be confident that the efficiency will be at least 99.97% when the filter is new and installed correctly.

Filtration measurements indicate that nonspherical nanoparticles are collected effectively by filters. Seto et al. (2010) found that MWCNTs with mobility diameters of 200–300 nm were collected with higher efficiency compared with spherical particles having the same mobility diameter. Similarly, Kim et al. (2009) observed that agglomerated particles having mobility diameters from 100–300 nm were collected at higher efficiency than nonagglomerated spherical particles with the same mobility diameter.

Most nanoparticles remain trapped on filter fibers when filters are changed. However, some may become airborne, especially for filters that are heavily loaded with particles, presenting an important exposure risk to maintenance personnel. The National Institute for Occupational Safety and Health (NIOSH, 2013) recommends removing air filters that have collected NMs directly into plastic bags to reduce exposures during filter change-outs. Some manufacturers

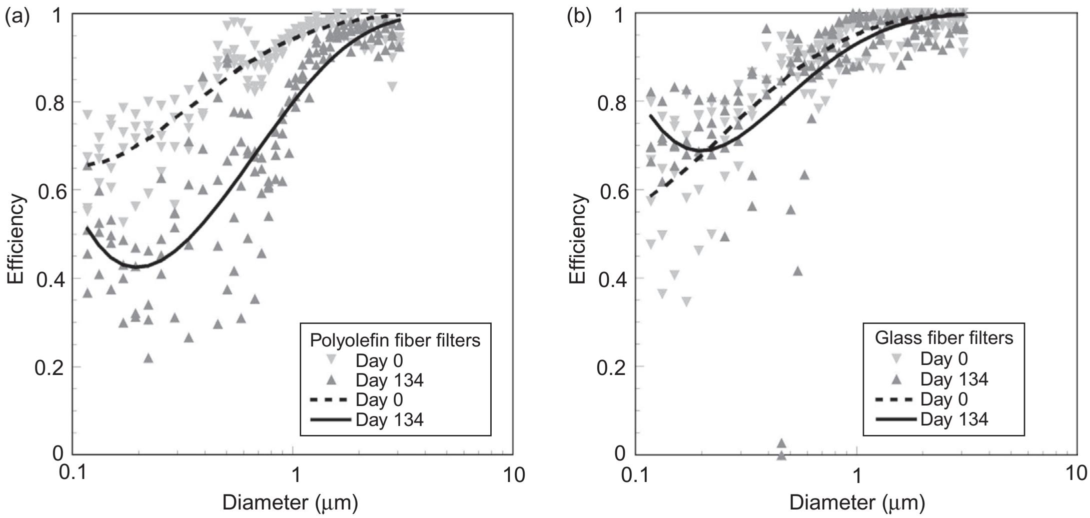


**Figure 7.9**
Filter efficiency as a function of particle diameter for filters made from (a) synthetic polymer fibers carrying electrostatic charge and (b) conventional glass fibers when the filters are new and clean (Day 0) and after 134 days of use. *From Raynor and Chae (2004).*

sell bag-in/bag-out housings to facilitate this procedure. Maintenance workers should wear appropriate PPE during this task.

### *7.6.3 Filter Performance Over Time*

As filters collect particles, their performance has the potential to change. Raynor and Chae (2004) and Raynor et al. (2008) found that the efficiency for filters made from synthetic fibers that carried electrostatic charge declined dramatically for particles with diameters between 100 nm and 3 μm as the filters collected atmospheric particles. Fiberglass filters collecting the same atmospheric particles exhibited essentially no change in efficiency. The results from Raynor and Chae (2004) are presented in Figure 7.9. The likely explanation for the efficiency decrease for the synthetic filters is that the charges on the fibers were blocked and made ineffective by the collected particles.

Raynor and Chae (2003) showed that the efficiency decline for synthetic filters occurred as the filters collected atmospheric particles comprised primarily of nanoscale particles, but not when filters were loaded with particles primarily larger than 1 μm in diameter. This suggests that synthetic filters collecting nanoparticles in workplaces may experience efficiency reductions as they are used. Until measurements are performed to determine how important these efficiency reductions are for nanoparticles in workplace environments, a conservative approach should be taken by assuming that efficiency reduction will occur to some extent for filters made from synthetic fibers carrying electrostatic charges. For the purposes of control, fiberglass filters are a safer approach for capturing nanoparticles with a consistent efficiency over time, even though they have greater resistance to air flow than electrostatically enhanced filters with the same initial efficiency.

For most workplace applications, filters are the best collection method for capturing nanoparticles from air streams. Theory and measurements both indicate that HEPA filters made from fibers that do not carry electrostatic charges will collect nanoparticles with high efficiency both when the filters are new and after they have been used for a long period. The lifetime of these filters is likely to be limited primarily by increases in pressure drop across the filters as particles continue to load onto them. As in other applications, filters must be seated properly in their housings to prevent leakage of contaminated air around the filters.

## 7.7 Work Practices

The way that nanopowders are handled can influence the generation of nanoparticles in dry operations. In general, more airborne particles are generated when greater energy is part of a powder handling process. The height from which a powder is dropped during handling is typically the most important factor dictating particle aerosolization during handling because it is strongly correlated to the energy imparted to the powder (Plinke et al., 1995). Tsai et al. (2009a, 2010) found that transferring nanoalumina powders with a spatula generated fewer airborne nanoparticles than pouring the same quantity of powder. Not surprisingly, these authors also observed that handling smaller quantities of powder reduced the concentrations of airborne nanoparticles. Process design is a critical determinant of exposure. At one site, Heitbrink et al. (2015) reported that worker exposures to airborne nanoparticles were virtually eliminated by simply waiting 30 min before harvesting nanographene product at the end of a batch process.

NIOSH (2009) offers an excellent summary of work practices to consider when cleaning areas where tasks with NMs have occurred. Work surfaces should be cleaned at least once per shift to prevent buildup of particles that could be transferred to the worker. Whenever possible, damp cleaning methods should be utilized to keep deposited nanoparticles from being resuspended. In particular, activities such as dry sweeping and using compressed air to blow off a surface should be avoided. A wet mop or sponge is better for cleaning floors and surfaces. If surfaces must be vacuumed, only vacuum cleaners with certified HEPA filtration should be used. In addition, the vacuuming should occur without vigorous rubbing of the surface being cleaned.

Suitable hygiene practices can also contribute to reduction in worker exposures to nanoparticles (NIOSH, 2009). Before eating, drinking, smoking, or leaving the workplace, workers should wash their hands thoroughly. Showering and changing clothes before leaving work can prevent transfer of NMs from the workplace to the home environment. Food and drink should not be consumed or stored in locations where NMs are handled. Storage containers for NMs should be sealed tightly, whenever possible.

## *7.8 Personal Protective Equipment*

NIOSH (2009) recommends the use of protective clothing and gloves to prevent dermal exposures to nanoparticles, especially to cover skin that is injured. Respiratory protection may be required if airborne nanoparticle concentrations are above exposure guidelines. Eye protection should generally be worn in laboratory and industrial settings; splash protection may be needed for the eyes if NMs are contained in liquid suspensions. Table 7.1 presents a list of the types of PPE that might be utilized to reduce worker exposure to nanoparticles along with a description of different options available and situations in which each might be used.

**Table 7.1 Types of personal protective equipment (PPE) frequently used when working with nanoparticles**

| Category of PPE | Specific Types Available | Common Uses |
|---|---|---|
| Gloves | Work gloves | • Partial barrier to nanopowders<br>• Limited protection against nanoparticle suspensions<br>• Nanoparticles may penetrate or migrate through glove fabrics |
| | Thick, reusable, chemical-resistant gloves; many materials available | • Good protection against splash and immersion exposures to nanoparticle suspensions<br>• Useful in production operations |
| | Thin, disposable nitrile or latex gloves | • High level of finger dexterity<br>• Suitable for most laboratory work<br>• Can be used under work gloves or thicker chemical-resistant gloves |
| Protective clothing | Laboratory coat | • Protects garments and skin from direct deposition of airborne nanoparticles or contact with nanopowders<br>• Nanoparticles may penetrate or migrate through fabrics |
| | Liquid-resistant apron | • Protects clothing from splashes and sprays from nanoparticle suspensions<br>• Coverage usually strongest for front of body and weaker for sides and back |
| | Disposable suits | • Protects skin and clothing from airborne nanoparticles and nanopowders<br>• Provides protection against small amounts of splashing from nanoparticle suspensions<br>• Can include integral hoods and foot coverings |

*(Continued)*

**Table 7.1 Types of personal protective equipment (PPE) frequently used when working with nanoparticles (Continued)**

| Category of PPE | Specific Types Available | Common Uses |
|---|---|---|
| Eye protection | Safety glasses | • Protects eyes against small direct splashes from nanoparticle suspensions<br>• Unsuitable for protection against sprays or large splashes because glasses do not fit tightly to face<br>• Provides impact protection |
| | Tight-fitting goggles | • Protects eyes against splashes and sprays from nanoparticle suspensions and against secondary exposures from liquids on face<br>• Unvented goggles prevent any penetration of liquids into interior of goggles |
| | Face shields | • Provides protection to entire face against direct splashes from nanoparticle suspensions<br>• Limited protection against sprays because shield does not fit tightly to face |
| Respiratory protection | Disposable filtering facepiece respirator | • Ideal for short duration tasks<br>• N95 is the most common designation<br>• Typically, the respiratory protection most readily accepted by wearers |
| | Half-mask or full facepiece elastomeric air-purifying respirators | • Fit of respirator to face can be checked easily each time the wearer puts the respirator on<br>• Full facepiece respirators provide eye protection in addition to respiratory protection<br>• Filter cartridges less susceptible to damage than filtering facepiece respirator |
| | Powered air-purifying respirator (PAPR) | • Provides high level of protection with a tight-fitting full facepiece<br>• Loose fitting hoods, helmets, and facepieces can be used for workers with facial hair or scars<br>• Filter cartridges less susceptible to damage than filtering facepiece respirator |

### *7.8.1 Protective Clothing and Gloves*

The ability of protective clothing materials to prevent penetration of nanoparticles is difficult to assess because no standard methods have been developed to test this property. Researchers have used filter test methods to evaluate particle penetration under the assumption that some air will flow through protective clothing as it flexes when the wearer moves. Golanski et al. (2009) measured particle penetration through three fabrics for particles ranging between 10 and 100 nm in diameter at a velocity of 0.6 cm/s through the fabrics. The results of their measurements are presented in Figure 7.10. Penetration across all fabrics and particle diameters ranged from 0.6% to 27%, indicating that a significant fraction of particles can penetrate a fabric with air flow. Penetration through a nonwoven high-density polyethylene

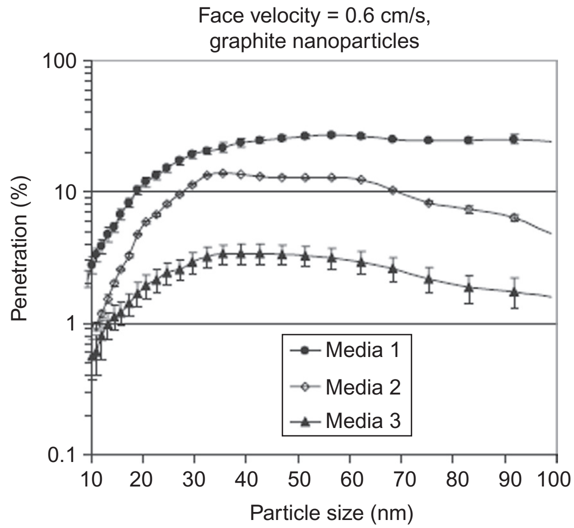


**Figure 7.10**
Penetration of woven cotton (Media 1), nonwoven polypropylene (Media 2), and nonwoven high-density polyethylene textile (Media 3) fabrics by graphite nanoparticles at a face velocity of 0.6 cm/s. *From Golanski et al. (2009).*

textile fabric was approximately an order of magnitude lower than penetration through a woven cotton fabric. Penetration through a nonwoven polypropylene fabric was in between.

Golanski et al. (2009) also measured the ability of various kinds and sizes of nanoparticles to pass through fabrics by diffusion in the absence of bulk air flow through the fabrics. These authors found that two distributions of graphite nanoparticles peaking at roughly 40- and 80-nm particles were able to penetrate through a woven cotton fabric at a rate 2500 times greater than through a nonwoven high-density polyethylene textile fabric. Similarly, penetration of 10 nm-diameter titanium dioxide ($TiO_2$) and platinum nanoparticles through a woven cotton fabric by diffusion alone was three orders of magnitude greater than penetration through a nonwoven high-density polyethylene textile fabric (Golanski et al., 2010).

Chemical-protective gloves should be worn when handling materials containing nanoparticles to protect the hands from exposure to dry particles or from splashing or immersion in suspensions containing nanoparticles. Golanski et al. (2010) measured the penetration of airborne $TiO_2$ and platinum nanoparticles 10 nm in diameter through 100-μm thick nitrile, 150-μm thick latex, and 700-μm thick neoprene gloves by diffusion. The researchers did not observe any particles penetrating the gloves. On the other hand, Vinches et al. (2013) found that nano-$TiO_2$ particles in a liquid suspension could pass through thin nitrile gloves after the gloves were repeatedly deformed to simulate use. Additional tests are needed to evaluate penetration of airborne particles and liquid particle suspensions through different types of gloves over long periods and with the gloves stretched to identify conditions for which gloves may not be sufficiently protective.

### 7.8.2 Respiratory Protection

If respiratory protection is required, the choice of respirator is made by comparing measured personal exposures to an occupational exposure limit. Until definitive and/or regulatory occupational exposure limits are widely available for airborne nanoparticles, ad hoc limits or benchmark exposure levels may be used for choosing a class of respirator. NIOSH has developed a “selection logic” to help users choose appropriate respiratory protection (Bollinger, 2004). The selection logic must be used in conjunction with the assigned protection factors in Table 7.2 to determine which levels of respiratory protection are acceptable for each nanoparticle application. Assigned protection factors (APFs) are specified in the United States by Occupational Safety and Health Administration rules to define the ability of a class of respirator to provide a particular level of protection taking into consideration both respirator fit to the wearer’s face and penetration of particles through a filter or gases and vapors through a sorbent cartridge (OSHA, 2009). An APF is the factor by which a class of respirators can be expected to reduce exposure concentrations.

In most cases, the respirators used for personal protection against nanoparticles are air purifying respirators, respirators that pass air contaminated with nanoparticles through a filter material before it is breathed in by the wearer. Disposable filtering facepiece respirators use a filter material as the entire facepiece or as a primary part of the facepiece. Half-mask respirators have nondisposable elastomeric facepieces that cover the nose and mouth of the wearer and must be used with disposable filter cartridges that attach to the facepiece. Full-facepiece respirators cover the entire face, providing eye protection and better fit, while using the same kinds of filter cartridges as half-mask respirators. Powered air purifying respirators (PAPRs) use a battery-powered blower with intakes filtered by cartridges to provide a flow of air to a facepiece, which ensures outward flow around the facepiece should

**Table 7.2 Assigned protection factors (APFs) for types of respiratory protection that are likely to be used to reduce exposures to airborne nanoparticles (OSHA, 2009)**

| Type of Respirator | APF |
|---|---|
| Disposable filtering facepiece respirator | 10[a] |
| Half mask elastomeric air-purifying respirator | 10[a] |
| Full facepiece elastomeric air-purifying respirator | 50[a] |
| Half-mask powered air-purifying respirator (PAPR) | 50[a] |
| Full facepiece PAPR | 1000[a] |
| PAPR with helmet or hood | 25/1000[b] |
| PAPR with loose-fitting facepiece | 25 |

[a]Wearers must pass a fit test with this type of respirator to qualify for the APF.
[b]To qualify for an APF of 1000 for a specific model of PAPR with a helmet or hood, the employer must possess evidence provided by the manufacturer that testing of that model demonstrates that it can provide a level of protection of 1000 or greater.

it not fit tightly to the wearer's face. PAPRs can be used with tight-fitting or loose-fitting respirators, providing an option for those who cannot wear other air-purifying respirators because they cannot achieve a tight fit to the face due to facial hair.

In the United States, filters used in air-purifying respirators are designated by NIOSH using a letter and a number. The letter designations are as follows:

N = Not resistant to oil aerosols
R = Resistant to oil aerosols for 8 h
P = Oil-proof

The number designations are as follows:

95 = Achieves at least 95% filtration efficiency in NIOSH standard test
99 = Achieves at least 99% filtration efficiency in NIOSH standard test
100 = Achieves at least 99.97% filtration efficiency in NIOSH standard test

Respirator and filter combinations must be certified by NIOSH before they can be sold and utilized legally as respiratory protection. The designations of filters used most commonly are N95 and P100. The European Union has a similar series of designations in its regulations for respirators.

Respirators can only be used in the United States as part of a written respiratory protection program as indicated in 29 CFR 1910.134. The written program must be specific to the work site and have a named individual identified as its administrator. Important elements of a respiratory protection program include provisions for respirator selection and issuance, medical evaluations for wearers, initial and annual fit testing for wearers, proper respirator use, and inspection, cleaning, maintenance, and storage of respirators. Training must be provided to wearers on the hazard for which the respirator is being used and on the proper utilization of the respirator.

Most respirator filters utilize the three primary mechanical filtration mechanisms discussed earlier—impaction, interception, and diffusion—in addition to permanent electrostatic charges to provide capture of incoming particles at a relatively low resistance to air flow that makes breathing easier. Rengasamy et al. (2009) measured the penetration of eight models of filtering facepiece respirators, four sold in the United States and four sold in Europe, as a function of particle diameter. As shown in Figure 7.11, these authors found that the MPPS for these filters ranged from 30 to 60 nm. All filters performed to their rated designations. When the same filter models were exposed to isopropanol to dissipate the electrostatic charges, the MPPS shifted to the 200–300 nm range and particle penetration far exceeded the ratings for the filters.

The findings of Rengasamy et al. (2009) suggest that any process that could block or render ineffective the electrostatic charges on the filters could lead to unacceptable penetration of

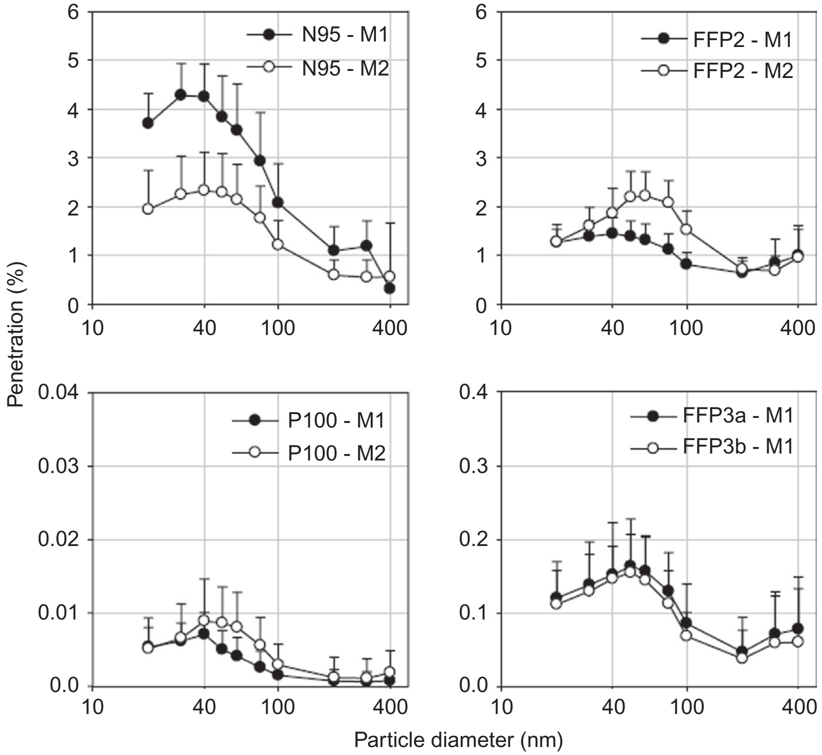


**Figure 7.11**
Penetration as a function of particle diameter for eight different models of filtering facepiece respirators. *From* Rengasamy et al. (2009).

particles through the respirator filter media. As shown previously, the deposition of significant levels of atmospheric particles can cause substantial increases in particle penetration for synthetic filters that rely on electrostatic charge (Raynor and Chae, 2004; Raynor et al., 2008). Moyer and Bergman (2000) conducted tests on filtering facepiece respirators that showed similar results for intermittent loadings with sodium chloride aerosol particles. Clearly, the potential exists for some level of deposition of nanoparticles on respirator media that carry electrostatic charges to cause a similar large increase in penetration. The duration of use that would cause a significant degradation of performance is expected to be many days, but this is uncertain. Therefore, a conservative recommendation for workers wearing air purifying respirators for protection against nanoparticle exposures is to replace filtering facepieces or filter cartridges at least daily if the filters are regularly collecting airborne nanoparticles. If the respirators are being worn primarily as a precaution in the event of an unanticipated release, the change period could be longer.

As with all situations in which air purifying respirators are used, the most important factor for matching the expected performance of the respirator is to ensure that the fit of the device to the wearer's face is adequate. A good fit can be achieved by suitable fit testing on an annual basis and by fit checks each time workers don their respirators.

## 7.9 Summary and Recommendations

Options highest on the hierarchy of controls (e.g., elimination and substitution) should be considered first in the control of nanoparticles, although they are often impractical. Local exhaust ventilation, in contrast, is widely applied to effectively control worker exposures to airborne nanoparticles. Ventilated enclosures that surround nanoparticle sources are better at controlling exposures than exterior hoods that must draw the nanoparticles in after they are released. Laboratory hoods in research facilities are capable of containing nanoparticles, but some designs such as air-curtain hoods work better than others such as constant-flow hoods. Any laboratory hood can be defeated if the user is careless in hood settings and in their own work practices. LEV used in product development operations may perform less than optimally because development work typically involves frequently altered batch operations that are not amenable to enclosure and that are larger than laboratory hoods can contain. These operations require careful consideration in exposure control.

Filters are the most widely used and effective air pollution control devices to capture nanoparticles from moving air streams. Several reputable studies show that high-efficiency filters can effectively capture almost all airborne nanoparticles larger than about 2 nm in diameter. For filters made from synthetic fibers that rely on electrostatic forces to capture particles, the loading of the filters with nanoparticles over time may lead to substantial decreases in collection efficiency. Using filters made from glass fibers is the safest approach for providing consistent filtration performance, with a penalty of higher energy costs due to greater resistance to air flow. Electrostatic precipitators can be designed with high efficiency for nanoparticles. However, fewer options are available than for filtration systems, capital costs are high, and high voltages are required for high capture efficiency.

Work practices can minimize worker exposures to nanoparticles. Energy input should be minimized when transferring NMs. In particular, the height that nanopowders are dropped should be minimized, wherever feasible. The cleaning of areas in which deposited nanoparticles could be present should be accomplished primarily through wet cleaning rather than by vacuuming, sweeping, or wiping with dry cloths. Workers should wash hands before eating, drinking, smoking, or leaving the workplace.

Although the effectiveness of clothing and gloves at preventing dermal exposure to NMs is still uncertain, published research to date suggests that protection can be adequate. Thin, disposable latex and nitrile gloves appear to have little potential for being penetrated by dry nanoparticles. In addition, nonwoven high-density polyethylene textile fabrics (e.g., Tyvek) appear to have low penetration for NMs.

Filtering facepiece respirators and filter cartridges used in other air-purifying respirators can capture nanoparticles with high efficiency. A P100 filter designation will provide the highest level of protection for workers wearing these kinds of respiratory protection. With use, the performance of respirator filters may degrade if the filters rely on electrostatic charging to capture particles. Therefore, changing filtering facepieces and filter cartridges on a daily basis is a sensible approach for workers potentially exposed to nanoparticles. Maintaining a good fit of the facepiece to the wearer's skin is essential for effective respirator performance.

As stated at the beginning of the chapter, many of the control measures that are presently used to control exposures to gaseous and particulate pollutants can be implemented successfully for nanoparticles. However, the occupational health and safety specialist must keep in mind the special properties of nanoparticles to ensure that these "tried and true" control measures work as well for nanoparticles as they do for other workplace pollutants.

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