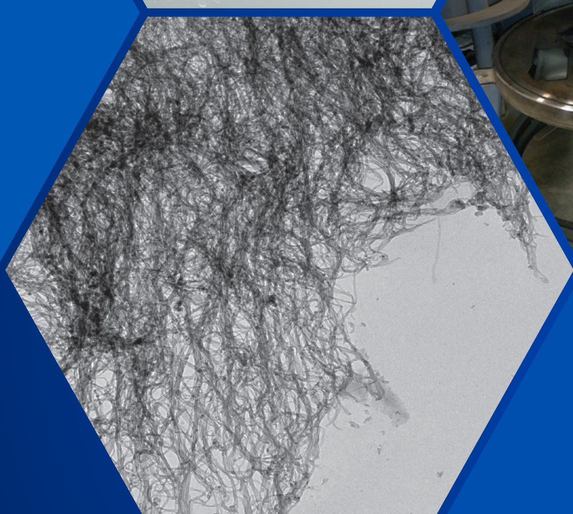
CURRENT STRATEGIES FOR ENGINEERING CONTROLS IN

Nanomaterial Production and Downstream Handling Processes



DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health

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Suggested Citation

NIOSH [2013]. Current strategies for engineering controls in nanomaterial production and downstream handling processes. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2014–102.

DHHS (NIOSH) Publication No. 2014–102

November 2013

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Foreword

The National Institute for Occupational Safety and Health (NIOSH) is charged with protecting the safety and health of workers through research and training. An area of current concentration is the study of nanotechnology, the science of matter near the atomic scale. Much of the current research focuses on understanding the toxicology of emerging nanomaterials as well as exposure assessment; very little research has been conducted on hazard control for exposures to nanomaterials. As we continue to research the health effects produced by nanomaterials, particularly as new materials and products continue to be introduced, it is prudent to protect workers now from potential adverse health outcomes. Controlling exposures to occupational hazards is the fundamental method of protecting workers. Traditionally, a hierarchy of controls has been used as a means of determining how to implement feasible and effective control solutions.

- Elimination
- Substitution
- Engineering Controls
- Administrative Controls
- Personal Protective Equipment

Following this hierarchy normally leads to the implementation of inherently safer systems, where the risk of illness or injury has been substantially reduced. Engineering controls are favored over administrative and personal protective equipment for controlling existing worker exposures in the workplace because they are designed to remove the hazard at the source, before it comes in contact with the worker. However, evidence of control effectiveness for nanomaterial production and downstream use is scarce. This document is a summary of available technologies that can be used in the nanotechnology industry. While some of these have been evaluated in this industry, others have been shown to be effective at controlling similar processes in other industries. The identification and adoption of control technologies that have been shown effective in other industries is an important first step in reducing worker exposures to engineered nanoparticles.

Our hope is that this document will aid in the selection of engineering controls for the fabrication and use of products in the nanotechnology field. As this field continues to expand, it is paramount that the health and safety of workers is protected.

John Howard, M.D.
Director, National Institute for
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Executive Summary

The focus of this document is to identify and describe strategies for the engineering control of worker exposure during the production or use of engineered nanomaterials. Engineered nanomaterials are materials that are intentionally produced and have at least one primary dimension less than 100 nanometers (nm). Nanomaterials may have properties different from those of larger particles of the same material, making them unique and desirable for specific product applications. The consumer products market currently has more than 1,000 nanomaterial-containing products including makeup, sunscreen, food storage products, appliances, clothing, electronics, computers, sporting goods, and coatings. As more nanomaterials are introduced into the workplace and nano-enabled products enter the market, it is essential that producers and users of engineered nanomaterials ensure a safe and healthy work environment.

The toxicity of nanoparticles may be affected by different physicochemical properties, including size, shape, chemistry, surface properties, agglomeration, biopersistence, solubility, and charge, as well as effects from attached functional groups and crystalline structure. The greater surface-area-to-mass ratio of nanoparticles makes them generally more reactive than their macro-sized counterparts. These properties are the same ones that make nanomaterials unique and valuable in manufacturing many products. Though human health effects from exposure have not been reported, a number of laboratory animal studies have been conducted. Pulmonary inflammation has been observed in animals exposed to nano-sized TiO_2 and carbon nanotubes (CNTs). Other studies have shown that nanoparticles can translocate to the circulatory system and to the brain causing oxidative stress. Of concern is the finding that certain types of CNTs have shown toxicological response similar to asbestos in mice. These animal study results are examples, and further toxicological studies need to be conducted to establish the potential health effects to humans from acute and chronic exposure to nanomaterials.

Currently, there are no established regulatory occupational exposure limits (OELs) for nanomaterials in the United States; however, other countries have established standards for some nanomaterials, and some companies have supplied OELs for their products. In 2011, NIOSH issued a recommended exposure limit (REL) for ultrafine (nano) titanium dioxide and a draft REL for carbon nanotubes and carbon nanofibers. Because of the lack of regulatory standards and formal recommendations for many nanomaterials in the United States, it is difficult to determine or even estimate a safe exposure level.

Many of the basic methods of producing nanomaterials occur in an enclosure or reactor, which may be operated under positive pressure. Exposure can occur due to leakage from the reactor or when a worker's activities involve direct manipulation of nanomaterials. Batch-type processes involved in the production of nanomaterials include operating reactors, mixing, drying, and thermal treatment. Exposure-causing activities at production plants and laboratories employing nanomaterials include harvesting (e.g., scraping materials out of reactors), bagging, packaging, and reactor cleaning. Downstream activities that may release nanomaterials include bag dumping, manual transfer between processes, mixing or compounding, powder sifting, and machining of parts that contain nanomaterials.

Hazards involved in manufacturing and processing nanomaterials should be managed as part of a comprehensive occupational safety, health, and environmental management plan. Preliminary hazard assessments (PHAs) are frequently conducted as initial risk assessments to determine whether more sophisticated analytical methods are needed. PHAs are important so that the need for control measures is realized, and the means for risk mitigation can be designed to be part of the operation during the planning stage.

Engineering controls protect workers by removing hazardous conditions or placing a barrier between the worker and the hazard, and, with good safe handling techniques, they are likely to be the most effective control strategy for nanomaterials. The identification and adoption of control technologies that have been shown effective in other industries are important first steps in reducing worker exposures to engineered nanoparticles. Properly designing, using, and evaluating the effectiveness of these controls is a key component in a comprehensive health and safety program. Potential exposure control approaches for commonly used processes include commercial technologies, such as a laboratory fume hood, or techniques adopted from the pharmaceutical industry, such as continuous liner product bagging systems.

The assessment of control effectiveness is essential for verifying that the exposure goals of the facility have been successfully met. Essential control evaluation tools include time-tested techniques, such as airflow visualization and measurement, as well as quantitative containment test methods, including tracer gas testing. Further methods, such as video exposure monitoring, provide information on critical task-based exposures, which will help to identify high-exposure activities and help provide the basis for interventions.

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List of Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
ANSI	American National Standards Institute
APF	assigned protection factor
ASHRAE	American Society of Heating, Refrigerating, and Air Conditioning Engineers
BSC	biological safety cabinet
BSI	British Standards Institute
CAV	constant air volume
CDC	Centers for Disease Control and Prevention
cfm	cubic feet per minute
CNF	carbon nanofiber
CNT	carbon nanotube
CPC	condensation particle counter
CVD	chemical vapor deposition
DMPS	differential mobility particle sizer
ELPI	electrical low pressure impactor
EPA	Environmental Protection Agency
FFR	filtering facepiece respirator
FMPS	fast mobility particle sizer
fpm	feet per minute
HEPA	high efficiency particulate air
HSE	Health and Safety Executive
IH	industrial hygiene
kg	kilogram
lbs	pounds
LEV	local exhaust ventilation
LPM	liters per minute
MPPS	most penetrating particle size
MSDS	material safety data sheet
MUC	maximum use concentration
NIOSH	National Institute for Occupational Safety and Health
nm	nanometer
OEL	occupational exposure limit
PEL	permissible exposure limit

PHA	preliminary hazard assessment
PM	preventive maintenance
PPE	personal protective equipment
PtD	prevention through design
R&D	research and development
REL	recommended exposure limit
SMACNA	Sheet Metal and Air Conditioning Contractors' National Association
SMPS	scanning mobility particle sizer
SOP	standard operating procedures
TEM	transmission electron microscopy
TEOM	tapered element oscillating microbalance
TLV®	threshold limit value
TWA	time- weighted average
VAV	variable air volume
VEM	video exposure monitoring
wg	water gauge
µg	microgram
µm	micrometer

Acknowledgments

This document was developed by the NIOSH Division of Applied Research and Technology (DART), Gregory Lotz, PhD, Director. Jennifer L. Topmiller, MS, was the project officer for this document, assisted in great part by Kevin H. Dunn, ScD, CIH. Other members of DART instrumental in the production of this document include Scott Earnest, PhD, PE, CSP; Liming Lo, PhD; Ron Hall, MS, CIH, CSP; Mike Gressel, PhD, CSP; Alan Echt, DrPh, CIH; and William Heitbrink, PhD, CIH (contractor). Elizabeth Fryer also provided writing and editing support in the initial stages.

The authors gratefully acknowledge the contributions of the following NIOSH personnel who assisted with the technical content and review of the document.

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The authors also wish to thank Cathy Rotunda, EdD, Brenda J. Jones, and Vanessa Williams for their assistance with editing and layout for this report. Cover photographs are courtesy of Quantum Sphere, Inc. and Bon-ki Ku, PhD, of NIOSH.

Special appreciation is expressed to the following who served as independent, external reviewers. Their input contributed greatly to the improvement of this document.

Keith Swain, DuPont, Wilmington, Delaware

Richard Prodans, CIH, CSP, Abbott, Abbott Park, Illinois

John Weaver, Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana

Gurumurthy Ramachandran, PhD, CIH, University of Minnesota, Minneapolis, Minnesota

Phil Demokritou, PhD, Harvard University, Boston, Massachusetts

CHAPTER 1

Introduction

The number of commercial applications of nanomaterials is growing at a tremendous rate. As this rapid growth continues, it is essential that producers and users of nanomaterials ensure a safe and healthy work environment for employees who may be exposed to these materials. Unfortunately, because nanotechnology is so new, we do not know or fully understand how occupational exposures to these agents may affect the health and safety of workers or even what levels of exposure may be acceptable. Given our current knowledge in this field, it is important to take precautions to minimize exposures and protect safety and health.

This document discusses approaches and strategies to protect workers from potentially harmful exposures during nanomaterial manufacturing, use, and handling processes. Its purpose is to provide the best available current knowledge of how workers may be exposed and provide guidance on exposure control and evaluation. It is intended to be used as a reference by plant managers and owners who are responsible for making decisions regarding capital allocations, as well as health and safety professionals, engineers, and industrial hygienists who are specifically charged with protecting worker health in this new and growing field. Because little has been published on exposure controls in the production and use of nanomaterials, this document focuses on applications that have relevance to the field of nanotechnology and on engineering control technologies currently used, and known to be effective, in other industries. This document also addresses other approaches to worker protection, such as the use of administrative controls and personal protective equipment.

1.1 Background

Nanotechnology is the manipulation of matter at the atomic scale to create materials, devices, or systems with new properties and/or functions. Around the world, the introduction of nanotechnology promises great societal benefits across many economic sectors: energy, healthcare, industry, communications, agriculture, consumer products, and others [Sellers et al. 2009].

Some nanoparticles are natural, as in sea salt or pine tree pollen, or are incidentally produced, as in volcanic explosions or diesel engine emissions. The focus of this document is engineered nanomaterials, those materials deliberately engineered and manufactured to have certain properties and have at least one primary dimension of less than 100 nanometers (nm). Nanomaterials have properties different from those of their bulk components. For example, many of these materials have increased strength/weight ratios, enhanced conductivities, and improved optical or magnetic properties. These new properties make nanomaterial development so exciting and are the reason they hold the promise of great economic potential.

Nanomaterials are often classified by their physicochemical characteristics or structure. The four classes of materials of which nanoparticles are typically composed include elemental carbon, carbon compounds, metals or metal oxides, and ceramics. The nanometer form of metals, such as gold, and metal oxides, such as titanium dioxide, are the most common engineered nanomaterials being produced and used [Sellers et al. 2009]. Nano-sized silica, silver, and natural clays are also common materials in use. The carbon nanotube is a unique nanomaterial being investigated for a wide range of applications. These tubes are cylinders constructed of rolled-up graphene sheets. Another interesting carbon structure is a fullerene (also known as a Bucky Ball). These are spherical particles usually constructed from 60 carbon atoms arranged as 20 hexagons and 12 pentagons. As shown in Figure 1, the structure resembles a geodesic dome (designed by architect Buckminster Fuller, hence the name). Nanomaterials are widely used across industries and products, and they may be present in many forms.

Significant international health and safety research and guidance concerning the handling of nanomaterials is underway to support risk management of commercial developments. Both risks and rewards are inherent in these new materials. Scientists around the world are conducting toxicological studies on these nanomaterials, and initial findings are concerning. Animals exposed to titanium dioxide (TiO_2) and carbon nanotubes (CNTs) have displayed pulmonary inflammation [Chou et al. 2008; Rossi et al. 2010; Shvedova et al. 2005]. Other studies have shown that nanoparticles can translocate to the circulatory system and to the brain and cause oxidative stress [Elder et al. 2006; Wang et al. 2008]. Perhaps the most troubling finding is that CNTs can cause asbestos-like pathology in mice [Poland et al. 2008; Takagi et al. 2008].

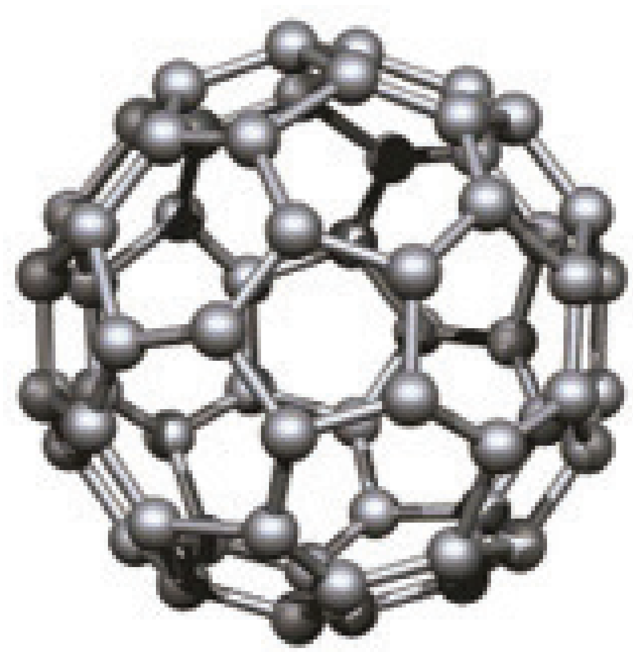

Figure 1. Atomic structure of a spherical fullerene