BOEING®
ENVIRONMENTAL TECHNOTES

ENVIRONMENTAL ASSURANCE

February 2005 Volume 10, Number 1

EHS*Aspects of Nanotechnology

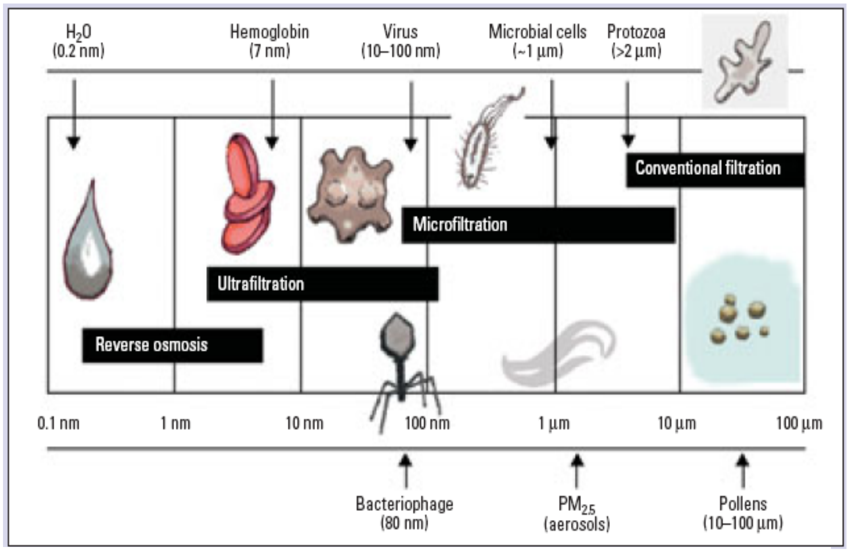
*(Environmental & Health Safety)

Background

With all of the recent attention given to atomic/molecular scale particles one might think they are a new phenomenon. Although that's not true, the terms being used to describe them are. Such particles have been produced by natural processes such as volcanic eruptions, forest fires, and dust storms for eons. They also are produced unintentionally by industrial age processes such as ore refining, smelting, welding, power plant and vehicle combustion and waste incineration. Such particles are called **"ultra-fine particles"**. The terms **"manufactured or engineered nanoparticles or nanostructures"** are reserved for particles created intentionally by manipulating atoms and molecules through a suite of technologies to produce new materials and products having desired novel physical, biological, mechanical, electrical or optical properties. "Nano" is coming and there's a need to be ready to use it appropriately and safely. Through this article Environmental Assurance (EA) provides some background to and briefing on significant recent events that we believe will clarify EHS requirements associated with applications of ultra fine particle technologies in industry.

Some occupational health specialists use the terms "ultra-fine" and "nano" interchangeably because both words refer to particles that are less than 100 nanometers in length or diameter, with a nanometer measuring one-billionth of a meter (Fig. 1). Nanotechnology is a set of tools and processes for manipulating matter that can be applied to virtually any manufactured goods. Economists predict that $2.6 trillion in products will incorporate emerging nanotechnology within 10 years.

It was not until the 1980s that instruments were invented with the capabilities needed to manipulate and measure the properties of these atomic/molecular scale -"nano"-structures. These instruments, including scanning tunneling microscopes, atomic force microscopes, and near-field microscopes, provide the "eyes" and "fingers" required for nanostructure measurement and manipulation (Fig. 2).



Bacteriophage; A parasitic bacterial virus capable of destroying the bacteria

Fig. 1.* ***"Small is Different"*** **Because nanoscale materials are in the same size range as hemoglobin and viruses and are even smaller than common irritants, such as particulate matter (<2.5 µm) and pollen, nanomaterials could pose serious health risks. Conventional air and water treatment techniques need to be evaluated for their efficacy to treat nanoscale pollutants**

But by the late '90s, industry leaders were concluding that nanoscience and technology might possibly change the nature of almost every human-made object before the end of the 21st century. The potential contribution of nanotechnology to future economic growth has attracted increased global attention. Nanotechnology has become a top research priority of the U.S. Government and was raised, in 2001, to the level of a federal program, the National Nanotechnology Initiative (NNI). To learn more about the initiative, see www.nano.gov.

For Boeing, its customers and suppliers, future nanotechnology applications in aeronautics & aerospace, and defense & homeland security are of foremost interest. Application possibilities in these areas are noted on pages 19 & 20 of the 2004 NNI Strategic Plan. See *www.nano.gov/NNI_Strategic_Plan_2004.pdf*

The engineering community commentators have advised that such nanotechnology advancements likely will require a 10 to 15 year lead time to achieve. As such, now is the time to consider the EHS implications of this new

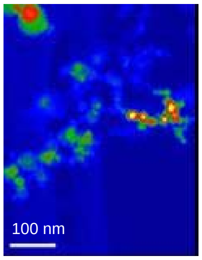


Fig. 2* Scanning Transmission Electron Micrograph of welding fume contaminated with lead (hot colors indicate higher concentrations of lead in the nanoparticles). High resolution analysis techniques such as this are being investigated for their ability to probe health-related characteristics of nanoparticles.

technology. An Institute of Medicine Conference, **"Technology and Environmental Health: Implications on Nanotechnology"**, given in 5/04, addressed both the potential benefits and risks. See downloads at ***www.iom.edu/Subpage.asp?id=19612***.

Potential EHS Benefits

Application of nanotechnology has been predicted to provide a variety of environmental benefits from waste and air emissions reductions. Recently, Phillip Bond, U.S. Undersecretary of Commerce for Technology, commented he expects that nanotechnology will provide **"freedom from pollution through clean (Green) production technologies."** Dave Whelan, Boeing Phantom Works General Manager, commented he believes that it will make possible **"specialized coatings so that planes don't need repainting".** Also, the use of POSS (polyhedral oligomeric silsesquioxanes) may result in zero volatile organic compound (VOC) coating development. Current semiconductor chip production may be replaced by use of environmentally benign biomolecular nanolithography. Nanoscale bimetallic particles may eliminate undesirable by products when used for *in situ* remediation of chlorinated hydrocarbons including, for example, trichlorethylene.

Scientists also have high hopes for Nano on the human health front. To reduce health hazards, a chrome-free, VOC-free bonding, and adhesion promoting sol-gel nanotechnology process has already been developed. Some applications of toxic poly brominated diphenyl ether (PBDE) flame retardants may be replaced by nanomaterials. Nontoxic corrosion control coatings may become possible by the use of nanoparticled substances to replace currently used toxic materials and electrolytically codeposited WC nanoparticles within a Ni-Co matrix may replace Cr+6 for non-line-of-sight applications.

As for improving security, nanomaterials may create faster response bio and chemical sensors for homeland security and precise sensors capable of detecting pollutants at the molecular level.

EHS Risk Potentials

On the other hand, certain risks from use of nanotechnology applications also are under discussion. Commenters have expressed concern that nanowaste passing through and being transformed in the environment may present future disposal concerns and deposition in water or soil could result in increased bio-uptake and accumulation along the food chain. In time, accumulated manufactured nanostructures may have adverse impacts on aquatic life and ambient air nanoparticle emissions may also be a concern.

Future worker exposure to free (aerosol) airborne engineered nanoparticles and nanostructured surfaces may pose unknown (today) inhalation, dermal absorption and oral ingestion risks. Although toxicity of nanoparticles is currently not well understood, however, high number concentration and surface area links to toxicity have been demonstrated. Some nanoparticles have raised health concerns due to an apparent ability to pass through cell membranes and cross the blood-brain barrier. Uniform nomenclature for nanomaterials is being studied, since without it regulative measures will be difficult to implement. The National Institute for Occupational Safety and Health (NIOSH) has advised, **"Workers within nanotechnology-related industries (will) have the potential to be exposed to uniquely engineered materials with novel sizes, shapes and physical and chemical properties, at levels far exceeding ambient concentrations. To understand the impact of these exposures on health, and how best to devise appropriate exposure monitoring and control strategies, much research is still needed. Until a clearer picture emerges, the limited evidence available would suggest caution when potential exposures to nanoparticles may occur."**

Another issue being investigated is whether reliable and valid methodology for measuring worker exposure to nanoparticles can be developed. Mass, the current metric for measuring exposure, may not be adequate for measuring nanoparticle exposure. Since Material Safety Data Sheets (MSDSs) are currently relying on voluntary nanoscale risk identification, any overlooked high surface area and increased reactivity in future nanomaterials may increase the risk of unexpected chemical reactions (catalytic effects), explosions and fires.

Ongoing Actions to Ensure Future Society & Workplace Nano Safety

Much study remains to be done before such time as machining nanomaterials may be required. Fortunately, given the plentiful research currently underway in governmental and industry research labs, by then, it appears likely answers will be available.

In 1/05, ASTM International announced the formation of a new Committee, E56, to cover Nanotechnology, ***www.astm.org/cgi-bin/SoftCart.exe/COMMIT/COMMITTEE/E56.htm?L+mystore+plpm4335+1107370479***. EA will represent Boeing on the E56.03 Subcommittee for Nano Environmental & Occupational Health & Safety. This committee intends to cover: 1) Best practices for Handling, 2) Medical surveillance of workers, 3a) Particle Penetration for Protective Clothing (through filters), 3b) Worker Safety, 4) Hazard Assessment and

Fig.3.* **The 1nm diameter Carbon-60 Buckyball (Buckminsterfullerene) is shaped like a soccer ball**

Classification for Nanoparticles, 5) (Test) Methodology for Toxicological Measurement, 6) Environmental Fate (E47), 7) Exposure Limits (what is safe for public/workplace?) and 8) Measurement of Airborne Nanoparticles/Exposure Assessment (critical need for tools).

Regarding relevant research, the 2004 NNI R&D funding for issues related to environment, health, and safety was $106M (11% of the total Nanotechnology R&D budget). These efforts, ***www.nano.gov/html/facts/EHS.htm***, were funded by several agencies, including National Science Foundation (NSF), EPA, National Institute of Health (NIH), DoE, NIOSH, U.S. Department of Agriculture, and DoD.

Three federal agencies have focused efforts to study the potential risks of exposure to nanomaterials: the National Toxicology Program (NTP) – a multi-agency effort established in the Department of Health and Human Services, NIOSH, and EPA.

The NTP studies are focusing on the potential toxicity of nanomaterials, beginning with titanium dioxide, several types of quantum dots, and fullerenes. The first studies will be of the distribution and uptake by the skin of titanium dioxide, fullerenes (buckyballs, Fig. 3), and quantum dots, (Fig. 4). For definitions, ***www.nanotech-now.com/nanotechnology-glossary-N.htm.*** NTP is considering conducting inhalation studies of fullerenes, and is exploring ways to assist NIOSH in the development of inhalation exposure capability for carbon nanotubes, (Fig. 5). NTP was also recently asked for a toxicological evaluation of nanomaterials & development of materials test protocols. It proposes to test for toxicity in animal models over the next five years

NIOSH provides research, information, education and training in the field of occupational safety and health, see ***www.nanoandthepoor.org/docs/Meridian_Maynard.pdf*** In 2004, NIOSH initiated several research projects focused on nanotechnology, including a five-year program to assess the toxicity of ultrafine and nanoparticles. They also co-hosted the 1st International Symposium on Nanotechnology & Occupational Health.. Held 10/12-14/04 in Great Britain, it was titled **"Nanomaterials – a risk to health at work?"**, see ***www.cdc.gov/niosh/topics/nanotech/confsumm-04.html.*** The 2nd International Symposium will be held 10/3-6/05 at Minneapolis, Minnesota, see ***www.cce.umn.edu/nanotechnology*.**

In late 12/04 EPA awarded more than $4M to a total of 12 universities. Six of the grants focus on potential toxicity of manufactured nanomaterials affecting human health or the environment. The other six grants focus on how manufactured nanomaterials will pass thru and transform in the environment and on the extent to which they may be found & bioaccumulate in the environment. Issues that will be studied include how lung cells respond to metals in nanoparticles, how skin reacts when exposed to nanoparticles, and whether nanoparticles harm microbes, algae, or other living organisms at the **"bottom of the food chain."** Results from these studies, some of which have already begun, are due in 2007. In addition, current and past work in ultra fine particulates at EPA labs and funded through the extramural program at EPA can help inform the effects of nanoparticles on human health. Scientists funded by the NIH are also studying the chemistry, biology, and physics of nanoscale material interactions at the molecular and cellular level addressed in vitro experiments and models. This research is creating a significant body of knowledge of nanoscale materials reactions with biological materials.

The NSF has focused on nanoscale processes in the environment and on societal implications in its programs since 8/00. NSF will have awarded about $16M in 2004 for grants with primary focus on environment and nanotechnology, and additionally about the same amount for multidisciplinary projects including the environmental issues. In 9/04, NSF awarded $12.4M to investigate the environmental impact of nanomanufacturing. Also in September, NSF, in concert with EPA and NIOSH, proposed spending $7M for investigating environmental and human health effects of nanomaterials.

In 10/04, the Center for Biological & Environmental Nanotechnology (CBEN) at Rice University announced the creation of the International Council on Nanotechnology (ICON). ICON's aim is to **"assess, communicate, and reduce potential environmental and health risks associated with nanotechnology."** See ***icon.rice.edu/about.cfm.***

An Air Force MURI (Multi-disciplinary University Research Initiative) recently announced funding of a new research effort whose goal is to develop a computational model that will predict toxic, salutary and biocompatible effects based on nanostructural features. The project is intended for five years at a total cost of $5.5 M. In addition, a United Nations University/Army co-sponsored survey, ***www.acunu.org/millennium/nanotech-rd2.doc*** seeks views about potential environmental pollution and health hazards from military use of nanotechnology, and research needed to address these risks. The Round 1 results are available and the Round 2 results are forecast to be available in several months.

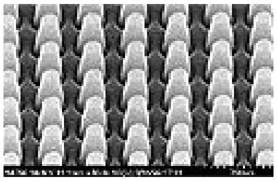


Fig. 4* **Quantum Dot (1-10 nm diameter) Nanoswitches**

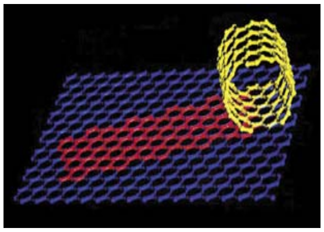


Fig. 5* **A carbon nanotube (1-100nm) is like a cylinder rolled up from a single sheet of graphite, whose atoms are arranged in hexagons. Depending on their "rolling" angle, nanotubes with different spirals have different electronic properties.**

EHS Regulatory Possibilities

(including Standards & Guidelines)

Nanotechnology also has attracted significant attention in the regulatory world. It has been reported that the Environmental Protection Agency (EPA) may suggest a pilot program for submitting voluntary information about nanoscale materials made with chemicals already on the Toxic Substances Control Act (TSCA) inventory. Those not on the inventory would be considered new chemicals subject to the TSCA PreManufacture Notice procedures. In any case, the TSCA Significant New Use Rule probably would apply. The industry could become subject to hazardous air pollutant standards promulgated by EPA under Section 112 of the Clean Air Act (CAA), but it would require EPA to go through a process of amending the hazardous air pollutant list to include nanomaterials not presently listed under Section 112 for their chemical structure. Resource Conservation and Recovery Act's waste identification criteria seems well suited to apply to the unknown hazards associated with "nanowaste." EPA may designate a specific listing under 40 Code of Federal Regulations (CFR) Section 261.32 (hazardous waste from specific sources) to capture waste from specific nanotechnology processes.

The Occupational Safety and Health Administration's (OSHA) General Duty Clause, Sec. 5 (a) (1) of the Occupational Safety and Health Act, which requires **"employers to provide a safe & healthy work environment"** (free from recognized hazards) should apply to working with nanoparticles. OSHA may establish a Permissible Exposure Limit (PEL) under 29 CFR, Section 1910, Subpart Z for nanoparticles in the workplace, issue hazardous communication measures (under Section 1910.1200) and prescribe the use of suitable Personal Protective Equipment (under Section 1910, Subpart I) to minimize risks to employees as more is learned about exposure pathways. OSHA would expect that potential hazards imposed by nanoengineered chemicals and materials would be reported on MSDSs under OSHA's Hazard Communication Standard. For two recent reviews of regulatory possibilities, see ***www.nanoandthepoor.org/docs/Perry_Nanotech_Primer_2.pdf*** &***www.schc.org/schcnewsite/events/2004fall/present/Lynn_Bergeson-Nanotechnology.pdf*** .

The American National Standards Institute's new Nanotechnology Standards Panel has been charged with devising consistent terminology for naming and classifying nanomaterials and nanostructures. See ***www.ansi.org/standards_activities/standards_boards_panels/nsp/overview.aspx?menuid=3*** This issue is particularly challenging since the properties exhibited at the nanoscale often differ depending on the size of the nanomaterials. This presents the possibility of hundreds of different entries by the Chemical Abstracts Service for a material that might otherwise be considered the same chemical.

NIOSH, ***www.cdc.gov/niosh/topics/nanotech***, plans to issue, early in 2005, **"best practice guidance"** for handling nanomaterials in the workplace. A preview is available from a 12/04 NIOSH presentation titled **"Working with engineered nanomaterials: Towards developing responsible work practices in an uncertain world."** It was given at **"Nanosafe":** a Workshop on EHS in Nanotechnology Research held at the Georgia Institute of Technology. See the available downloads at ***www.nnin.org/nnin_safetyworkshop.html.***.

Developing the Knowledge Base for Safety Management

Boeing faces this information explosion with established policies and procedures in place to develop, implement, and communicate workplace practices that will ensure safe new uses of nanotechnology. The Company's Safety, Health & Environmental Affairs, Engineering, and Research & Development professionals work together to implement a consistent strategy to facilitate introduction of new materials into the work place while protecting worker health and safety. Following these procedures, Boeing will ensure that any nanomaterials used or evaluated within Boeing will be used in a safe and efficient manner.

Conclusion

By the time nanotechnology has achieved its promise, we believe answers to most EHS issues will be available. The facts are clear- nanotechnology will be developed. We can be encouraged that relevant EHS research is gaining momentum. Better understanding of its significance isn't far off.

==

***Graphic credits (use Internet Explorer):**

Fig.1,***www.nano.gov/html/res/GC_ENV_PaperZhang_03-0304.pdf***

Fig.2,***www.cdc.gov/niosh/topics/nanotech/***

Fig.3,***www.science.doe.gov/Science_News/featurs_articles_2000/buckey_files/buckey.htm***

Fig.4,***www.nsf.gov/news/mmg/mmg_search.cfm*** (keywords "quantum dots & images")

Fig.5,***www.lbl.gov/Science-Articles/Research-Review/Magazine/2001/Fall/features/05Imagining2.html***

==