A Labor Perspective on the Assessment and Management of the Potential Risks of Nanotechnology

Darius D. Sivin, PhD
International Union, UAW
Health and Safety Department

What is New about Nanotechnology?

- **Nanomaterials have different properties from bulk chemicals because of**
  - **Scale**
  - **Surface area per unit of mass**
  - **Quantum effects**
- **The physical, chemical, and biological properties of materials at the nanoscale differ in fundamental and valuable ways from bulk matter.**
- **It is *our ability* to measure, manipulate and process at the nanoscale that is new**

Some Characteristics that Engineered Nanomaterials Share with Other Emerging Technologies

- Rapid introduction
- Broad distribution
- Complexity and range of materials
- Complex materials flows/multiple sources
- Hard to study and characterize risks
- Knowledge is limited, uncertain, and indeterminate regarding:
  - Cumulative and interactive effects
  - Potential effects from low level exposures

Penetration of Nanotechnology in Automobile and Automotive Parts Manufacturing

- Market for nano tire additives is already mature.
- Markets for nanoclay composites, wear and friction-resistant nanocoatings and mechanically enhanced nanocomposites are maturing.
- Many other nanomaterials are in the research and prototype stages, where occupational exposure, albeit to fewer workers, still occur.
  - Many of these are expected to enter the market within the next five years.

Nanomaterials that have already Entered the Automotive Market

- metal oxide nanopowder paint additives
- nanomagnetic fluid components
- anti-bacterial interior nanocoatings
- nanoclay polyurethane foams
- thermally conductive nanocoatings
- nanopowder catalysts and fuel cell additives
- carbon nanotube electrostatic paint
- nanofiber composites
- nanofluid coolants
- nanometal soldering additives
- anti-scratch nanocoatings
- anti-corrosion nanocoatings
- nanofiber engine filters and air filters

Problem

We don’t necessarily know whether a particular nanomaterial is in a particular product or process with which a worker is working.

Employer Obligations Under OSHA Hazard Communication Standard

- Prepare an inventory of chemicals.
- Ensure containers are labeled.
- Obtain a safety data sheet for each chemical.
- Make sheets available to workers.
- Conduct training of workers.

Obligations of Chemical Manufacturers and Distributors under OSHA Hazard Communication Standard

- Evaluate the hazards
- Prepare labels for containers and more detailed technical bulletins called safety data sheets.
- Provide the appropriate labels and material safety data sheets to the employers

Articles are Exempt from the Standard

Article means a manufactured item other than a fluid or particle: (i) which is formed to a specific shape or design during manufacture; (ii) which has end use function(s) dependent in whole or in part upon its shape or design during end use; and (iii) which under normal conditions of use does not release more than very small quantities, *e.g.*, minute or trace amounts of a hazardous chemical (as determined under paragraph (d) of this section), and does not pose a physical hazard or health risk to employees.

Problems

- *What if the manufacturer believes its product is an article, but does not know, the employer is cutting, grinding, welding, machining, brazing etc. with the item?*
- Safety data sheets are often poor for bulk materials and worse for nanomaterials.

Lippy Group reviewed NIOSH collection of nano SDSs

- N = 49 SDSs
- Reviewed all of the SDSs
- 33% did NOT identify the nano component
- 52% did NOT have any cautionary language
  - Large surface area in relation to particle size enhance physical and chemical properties (nanosilver)

NIOSH just completed a review of SDSs C. Crawford, L. Hodson, and C. Geraci, 2011, AIHce Poster

- **A total of 29 updated SDSs were reviewed from 22 manufacturers of engineered nanomaterials.**
- **The review revealed that only 5 had improved compared to the 2007-08 versions.**
  - **21 of the 29 (72%) were ranked as *not having any significant improvement*.**
  - ***3 of the 29 (10%) had not changed anything (including the date) since the original NIOSH study.***
  - ***Lack of recent toxicological data was main deficiency***

NIOSH looked at 26 new SDSs from 19 manufacturers

- **15 (58%) contained OELs for the bulk material without providing guidance that the OEL may not be protective for the nanoscale material.**

- ***18 (69%) of the 26 new SDSs* were classified as *in need of serious improvement* and**

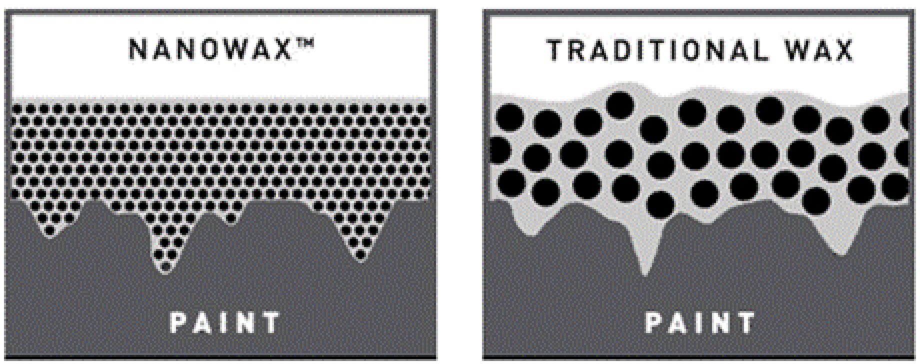
- **None were classified as good**

Example SDS: NanoWax

NanoWax® Story

Eagle One's NanoWax® is the most technologically advanced and best performing high-gloss wax formula on the market today.

Many people spend hours waxing their cars and still see scratches and swirl marks on the paint. NanoWax uses nano technology to fill in these scratches and conceal the swirl marks. This makes the surface of the car reflect light better, giving it a deeper, glossier shine. Nano technology also makes the wax easier to apply and remove without leaving behind any white residue.



What is Nano Technology?

Nano technology is a remarkable process that works at the molecular level to provide revolutionary benefits. Currently used in such cutting-edge industries as healthcare and electronics, Nano technology involves working with particles as small as one-billionth of a meter, or 1/75,000th of a human hair.

NanoWax SDS

Section 8: Exposure Controls/PPE

WAX EMULSION: No exposure limits established (NLE)

ALIPHATIC PETROLEUM DISTILLATES (64741-66-8): NLE

ALUMINUM SILICATE (66402-68-4): NLE

POLY(DIMETHYLSILOXANE) (63148-62-9): NLE

ALKYL QUATERNARY AMMONIUM BENTONITE (68953-58-2) : NLE

TETRAGLYCERYL MONOOLEATE (9007-48-1): NLE

GLYCOL (107-21-1)

OSHA PEL 50 ppm - Ceiling

ACGIH TLV 100 mg/m3 - Ceiling as an aerosol

No indication which component is nano-sized. Is it important in this application?

Lippy Group reviewed the use

- **62% used OSHA Permissible Exposure Limits or ACGIH TLVs for "macro" sized material**
- **32% percent indicated nothing**
- **Only 6% used conditional language about using PELs/TLVs**

SDS for Carbon Nanotube

Section 1 Product Identification

Chemical Name:	Carbon Fullerene
Formula:	Carbon
Chemical Family:	Synthetic Graphite
Synonyms:	Carbon Nanotubes
CAS Number:	7782-42-5 (Graphite)

"Nuisance" dust standard for synthetic graphite: 15 mg/m^3

Section 2 Composition and Information on Ingredients

Component	%	OSHA/PEL	ACGIH/TLV
Synthetic graphite	Up to 100%	15 mg/m^3 (total dust) 5 mg/m^3 (respirable fraction)	2 mg/m^3 TWA

“The MSDSs for carbon nanotubes treat these substances as graphite…but carbon nanotubes are as similar to pencil lead as the soot on my barbeque grill at home is to diamonds.”

Andrew Maynard, University of Michigan Risk Science Center

This MSDS for quantum dots of lead sulfide focuses on toluene

Section 1 - Chemical Product

Product Family #:	PbS Core EviDots
Substance:	Core EviDots packed in Toluene
Trade Names/Synonyms:	Core EviDots
Chemical Family:	Matrix: aromatic hydrocarbon Nanocrystal: IV-VI semiconductor compound

Section 2 - Composition, Information on Ingredients

Component	CAS#	EC#	% By Weight
Toluene	108-88-3	203-625-9	~ 99
Lead Sulfide (as nanocrystal compound)	1314-87-0	215-246-6	< 1

Exposure limit is for toluene, with **nothing** about PbS dots

Section 8 - Engineering Controls & Personal Protective Equipment

Exposure Limits	
Toluene	200ppm OSHA TWA PEL 300ppm ceiling OSHA 50ppm ACGIH TWA (skin) 100ppm (375 mg/m3) NIOSH TWA 10hour 190mg/m3 DFG MAK 50ppm (191 mg/m3) UK OES TWA

Nano language suggested by Dan Levine, Hazcom Expert
(PSS, 9-15-2006)

"Established exposure values do not address the small size of particles found in this product and may not provide adequate protection against occupational exposures."

PSS
Product Safety Solutions

Potential Hazards of Engineered Nanomaterials

- **Size, shape, and strength create new hazards – new distribution; higher surface to mass, higher reactivity**
- **Hazards depend on:**

- Small size	**- Surface area**
- Shape	**- Chemical composition**
- Purity	**- Aggregation**
- Solubility	**- Dissolution and degradation (during release)**

Potential Hazards of Engineered Nanomaterials

- **Greater surface areas means increased bioactivity**
- **Inhaled nanoparticles reach deeply into the respiratory tract**
- **Nanoparticles can pass the blood/brain barrier[1] and some evidence of passage of blood testis barrier[2]. These properties can be therapeutic or toxic**
- **Small size and shape leads to rapid uptake into cells and more effective transport to target organs.**
- **Nanomaterials may be "carriers" for other more toxic molecules.**

[1]JM Koziara, PR Lockman, DD Allen and RJ Mumper (2003). In Situ Blood–Brain Barrier Transport of Nanoparticles. Pharmaceutical Research: 20(11), 1772-1778
[2]Lan Z, Yang WX. Nanoparticles and spermatogenesis: how do nanoparticles affect spermatogenesis and penetrate the blood-testis barrier. Nanomedicine (Lond). 2012Apr;7(4):579-96.

Petrochemical Revolution

- **Produced many benign and beneficial substances.** ***The same can be expected for many nanomaterials.***
- **Also produced tetraethyl lead, DDT and Benzene.** ***We can expect that some nanomaterials will be bad actors as well***
- **Lesson: technological revolutions must be accompanied by regulatory regimes that can adequately distinguish between benign and harmful technologies and can restrict harmful technologies *before* exposure is widespread**

Reactive Policy: Making the Same Mistake Again

- **Develop technology without constraints and fix problems once they occur**
- **Wait until we have perfect evidence before establishing OELs**
- **Treat uncertainty and lack of information about harm as evidence of safety**
- ***This amounts to taking no action until the body count is indisputably large***

Lessons from Past Policy Mistakes

- Investigate potential hazards of a new technology before it gets widely introduced
- Assume that, when dealing with complex technologies, hazard information will always be incomplete
- Act on partial and/or accumulating knowledge
- Design technologies with an eye towards potential health, safety, environmental implications

Control Banding May Offer Methods for Dealing with Incomplete Information and Uncertainty

CB Nanotool Risk Level Matrix

Probability

Severity	Extremely Unlikely (0-25)	Less Likely (26-50)	Likely (51-75)	Probable (76-100)
Very High (76-100)	RL 3	RL 3	RL 4	RL 4
High (51-75)	RL 2	RL 2	RL 3	RL 4
Medium (26 -50)	RL 1	RL 1	RL 2	RL 3
Low (0-25)	RL 1	RL 1	RL 1	RL 2

RL 1: General Ventilation
RL 2: Fume hoods or local exhaust ventilation
RL 3: Containment
RL 4: Seek specialist advice

Paik, S, Zalk, D, and Swuste, P. (2008) Application of a pilot control banding tool for risk level assessment and control of nanoparticle exposures. *Annals of Occupational Hygiene* 52 (6): 419-428.

Livermore Probability Scores

- Estimated amount of material used (25 pts)
- Dustiness/mistiness (30 pts)
- Number of workers with similar exposure (15 pts)
- Frequency of operation (15 pts)
- Duration of operation (15 pts)

Livermore Severity Scores

- Nanomaterial: 70% of Severity Score
  - Surface Chemistry (10 pts)
  - Particle Shape (10 pts)
  - Particle Diameter (10 pts)
  - Solubility (10 pts)
  - Carcinogenicity (7.5 pts)
  - Reproductive Toxicity (7.5 pts)
  - Mutagenicity(7.5 pts)
  - Dermal Toxicity (7.5 pts)
- Parent Material: 30% of Severity Score
  - Occupational Exposure Limit (10 pts)
  - Carcinogenicity (5 pts)
  - Reproductive Toxicity (5 pts)
  - Mutagenicity (5 pts)
  - Dermal Toxicity (5 pts)

(Maximum points indicated in parentheses)

Handling Missing Information

- For a given hazard category, the Livermore group gave an unknown rating 75% of the value of a high hazard rating, which is higher than a medium rating
- The group assigned a risk level of 3 (second highest) to substance for which all hazards are unknown. Risk level 3 requires containment.
- If one risk category is high and all others are unknown, the substance was assigned to the highest risk level
- The authors indicated that this system was an incentive to seek information.

Summary

- Need better information about which products contain what nano-materials and bettter communication of those hazards about which information is available, especially on safety data sheets.
- Learn from pasts mistakes
- Act before there are countable bodies
- Reduce and prevent exposure while information is still incomplete
- Control banding may be a way of controlling exposures with incomplete information