Training Workers about Nanomaterials
WestON Conference, Denver
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Introductory Comments

Electron micrograph of a metal oxide nanoparticle
CPWR is a U.S. nonprofit funded by NIOSH and NIEHS

My comments are my own and not those of NIOSH or NIEHS
Who has used eLCOSH.org?
When we think of nanomaterials, we see this:

But not construction!

Center for Nanophase Materials Science, Oak Ridge, TN
Nanomaterials are bringing major changes to construction

CNTs bridging a gaps in OPC, with 100x tensile strength of steel

With approval from Hanus and Harris, Progress in Materials Science, 2013
No epi studies, but mesotheliomas have been produced in mice with MWCNTs (Takagi 08, Poland 08)

Multi-walled carbon nanotube penetrating the pleura of the lung. Courtesy of Robert Mercer, and Diane Schwegler-Berry, NIOSH
Here’s the questions we’ll tackle:

1. What do we know about use of nanomaterials in construction?
2. What is the state of hazard communication around nanomaterials?
3. How informed are workers?
4. How should workers be trained about nanomaterials?
What do we know about the use of nanomaterials in construction?

Question 1
Does any organization know how many nano-enabled products are in commerce?
Construction workers apply greater energy to nanomaterials
Construction exposures may be greater when the life cycle is considered

Production  Installation  Maintenance  Recycling/Demolition/

What happens with Hazcom?
TiO$_2$ self-cleaning windows can reduce worker fall exposures.

March 16, 2015
outside my office!
One prediction is by 2025, over 50% of building materials will contain nanomaterials.

That is a long way from where we are now!

Courtesy Dr. Wendy Jones
Our site currently features 545 commercial construction products reported to be nano-enabled

www.nano.elcosh.org
Three-quarters provide a U.S. address or export to U.S.

- Do not appear active in USA: 25%
- USA address or exports: 75%
Roughly 40% did **not** specify the composition

<table>
<thead>
<tr>
<th>Unspecified composition</th>
<th>Count</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanofibers</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>nanomaterials</td>
<td>15</td>
<td>3.3</td>
</tr>
<tr>
<td>nanoparticles</td>
<td>76</td>
<td>16.6</td>
</tr>
<tr>
<td><strong>Nanotechnology</strong></td>
<td>70</td>
<td>15.3</td>
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<tr>
<td>nanotubes</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>photocatalytic materials</td>
<td>5</td>
<td>1.1</td>
</tr>
<tr>
<td>reference to 'nano'</td>
<td>10</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Safety Data Sheets could not be confirmed for 55% of products
What is the current state of hazard communication for nano?
Using an car analogy, it would be a Yugo in this exact color.

Photo courtesy Wikimedia Commons
A 2008 review of the literature showed significant problems
Nicol et al. 2008, Am. J. Ind Medicine

“While MSDSs are still considered to be a mainstay of worker health and safety...there are significant problems with their accuracy and completeness. As such, they may be failing workers as a prevention tool.”
MSDSs were indicated as the preferred method of obtaining EHS info by nanotech firms

Lindberg and Quinn, 2007
A Survey of EHS risk management among nanotechnology firm in the Massachusetts Region
The new NIOSH REL for carbon nanotubes is 1 µg/m$^3$.

<table>
<thead>
<tr>
<th>Section 1</th>
<th>Product Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Name:</td>
<td>Carbon Fullerene</td>
</tr>
<tr>
<td>Formula:</td>
<td>Carbon</td>
</tr>
<tr>
<td>Chemical Family:</td>
<td>Synthetic Graphite</td>
</tr>
<tr>
<td>Synonyms:</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>CAS Number:</td>
<td>7782-42-5 (Graphite)</td>
</tr>
</tbody>
</table>

“Nuisance” dust standard for synthetic graphite:
- 15 mg/m$^3$ total
- 5 mg/m$^3$ resp

<table>
<thead>
<tr>
<th>Section 2</th>
<th>Composition and Information on Ingredients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>%</td>
</tr>
<tr>
<td>Synthetic graphite</td>
<td>Up to 100%</td>
</tr>
</tbody>
</table>
Workers may be at risk of lung lesions exposed to SWCNTs 20 days at 5 mg/m$^3$

NewLook International, Inc. Graf-X WB™

Material Safety Data Sheet

SDS

Section 1
PRODUCT & COMPANY IDENTIFICATION

Product Names: Graf-X WB™ Permanent Anti-Graffiti Coating
Manufacturer’s Name: NewLook International, Inc.
Manufacturer’s Address: 1525 South Gladiola Street, Suite 6, Salt Lake City, UT 84104
Information Phone: NewLook International, Inc. 877.763.9566 or 801.886.9495
Emergency Contact: For Emergency information, contact Chemtel, Inc. at 800.255.3924, Outside the USA at 813.248.0585

Section 2
COMPOSITION & INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>CHEMICAL NAME</th>
<th>CAS Number</th>
<th>Weight % is less than</th>
<th>TLV-TWA</th>
<th>TLV-STEL</th>
<th>PEL-TWA</th>
<th>Skin Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene Glycol Monoethyl Ether</td>
<td>111-90-0</td>
<td>10.0% to 20%</td>
<td>No Info</td>
<td>No Info</td>
<td>No Info</td>
<td>Yes</td>
</tr>
<tr>
<td>Zinc Ammonium Carbonate Compound</td>
<td>38714-47-5</td>
<td>25% to 30%</td>
<td>No Info</td>
<td>No Info</td>
<td>No Info</td>
<td>No</td>
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<tr>
<td>Titanium Nano Drivers</td>
<td>13463-67-7</td>
<td>5% to 10%</td>
<td>No Info</td>
<td>No Info</td>
<td>No Info</td>
<td>No</td>
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<tr>
<td>Tributoxy Ethyl Phosphate</td>
<td>78-51-3</td>
<td>5% to 10%</td>
<td>No Info</td>
<td>No Info</td>
<td>No Info</td>
<td>Yes</td>
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<tr>
<td>Polymeric Hybrid Nano Particles</td>
<td>25586-24-7</td>
<td>1.0% to 3%</td>
<td>No Info</td>
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<td>No Info</td>
<td>No</td>
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<td>Pluxi Acrylic Nano Fusion</td>
<td>9063-87-0</td>
<td>10% to 20%</td>
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<td>No Info</td>
<td>No Info</td>
<td>No</td>
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<tr>
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<td>No Info</td>
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<td>No Info</td>
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<td>CHEMICAL NAME</td>
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<tr>
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<tr>
<td><strong>Plexi Acrylic Nano Fusion</strong></td>
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<tr>
<td><strong>Polycarbonate Nano Drivers</strong></td>
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<tr>
<td>Hydrogen Hydroxide</td>
<td></td>
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</tbody>
</table>

*Courtesy Wikimedia*
Safe Work Australia found SDSs lacking (2010)

- Nano metals, metal oxides, silicates and carbon nanotubes
- (84%) were “not sufficient to fulfill an appropriate risk assessment”
- Many presented data for the bulk material
67% of SDSs NIOSH collected in 2010-2011 “still provided insufficient data for communicating the potential hazards of ENM.”

<table>
<thead>
<tr>
<th>Date collected</th>
<th>Satisfactory</th>
<th>In Need of Improvement</th>
<th>In Need of Significant Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007-2008, n = 32</td>
<td>7 (21.8%)</td>
<td>13 (40.6%)</td>
<td>12 (37.5%)</td>
</tr>
<tr>
<td>2010-2011, n = 21</td>
<td>7 (33.3%)</td>
<td>10 (47.6%)</td>
<td>4 (19.1%)</td>
</tr>
<tr>
<td>2007-2008, recollected in 2010-2011, n = 23</td>
<td>4 (17.4%)</td>
<td>8 (34.8%)</td>
<td><strong>11 (47.8%)</strong></td>
</tr>
</tbody>
</table>

Recent research into SDSs in the aerospace industry still paints a negative picture

Nayar et al.,

Photo of Virgin Atlantic A340-600, courtesy Adrian Pingstone and Wikimedia
Nayar et al. looked at 200 SDSs from 89 suppliers

- 98 of chemicals were hazardous, 102 weren’t (UK, COSHH regs 2002)
- Quality of SDS for hazardous was much lower
  - 46% had poor quality information
  - 1% had good quality
ISO has published a 2012 technical report for writing nano SDSs that is quite good and will be part of GHS!

ISO/TR 13329
Nanomaterials: Preparation of Material Safety Data Sheet (MSDS)
The ISO recommends a precautionary approach

Provide an SDS for nanomaterials and nanomaterial-containing products *regardless* of whether the material is classified as hazardous.
How informed are workers?

Question 3

1 2 3
NIOSH’s concept of responsible nanotechnology development hinges on hazard identification

CPWR surveyed 79 worker-trainers from 22 trades with an average of 30 years in the trade (2013-2014)

<table>
<thead>
<tr>
<th>Survey Respondent Characteristics</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Years in trade</td>
<td>78</td>
<td>30.5</td>
<td>9.4</td>
<td>9-55</td>
</tr>
<tr>
<td>Years as a trainer</td>
<td>79</td>
<td>13.3</td>
<td>7.8</td>
<td>1-34</td>
</tr>
</tbody>
</table>
Nearly half were not aware that nano had been applied to construction materials.

<table>
<thead>
<tr>
<th>Question</th>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aware that nanotechnology has been applied to construction materials?</td>
<td>41 (52%)</td>
<td>38 (48%)</td>
</tr>
<tr>
<td>Aware that construction products containing nanomaterials are commercially available in the USA?</td>
<td>38 (48%)</td>
<td>41 (52%)</td>
</tr>
</tbody>
</table>
Only 3 out of 79 had heard of NIOSH’s Nano RELs

<table>
<thead>
<tr>
<th>Nanomaterial</th>
<th>OEL (mg/m³)</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium dioxide</td>
<td>0.3 ultrafine</td>
<td>2011</td>
</tr>
<tr>
<td></td>
<td>2.4 fine</td>
<td></td>
</tr>
<tr>
<td>CNTs and nanofibers</td>
<td>0.001</td>
<td>2013</td>
</tr>
</tbody>
</table>
How should workers be trained about nanomaterials?

Question 4
NIEHS has the only guidance on training workers about nanotechnology risks
The guidance identified possible exposures among specific populations

<table>
<thead>
<tr>
<th>Worker Population</th>
<th>Type of Nanomaterial</th>
<th>Tasks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stationary engineers</td>
<td>Nanosilver biocides</td>
<td>Adding biocides to cooling tower water and drip pans</td>
</tr>
<tr>
<td>Cleanup workers</td>
<td>Nanoparticles in hazardous waste</td>
<td>Performing cleanup of waste sites</td>
</tr>
<tr>
<td>Nurses and physicians</td>
<td>Nanosiliver in disinfectants</td>
<td>Preparing intravenous liquids</td>
</tr>
</tbody>
</table>
The NIEHS guidance also provided:

1. Suggested learning objectives for a nanomaterials course for workers
2. Outline for 8-hour HAZWOPER refresher
3. Value of NIEHS Minimum Criteria in structuring nanoparticle training for workers
The NIEHS WETP Minimum Criteria provides guidance on key elements of worker training

- Worker training principles
- Characteristics of excellence
- Program design and QC

Available at the National Clearinghouse for Worker S&H Training
An 8-hour course is available for free at two locations

The GoodNanoGuide
www.goodnanoguide.org

OSHA Training Institute

Target audience was H&S professionals
The course has a nano-SDS exercise we continue to use for union trainers

1. Is nano mentioned?
2. Is there any cautionary language?
3. Is the OEL for the parent material?

Machinists doing SDS exercise, Aug 2016
Working with nano?
What you need to know and who to talk to

In every workplace using nanomaterials, it’s important to ensure appropriate risk evaluation for each nanomaterial used.

Help your safety representative answer these questions...

1. Are manufactured nanomaterials used in your workplace?
   Your employer is legally required to provide information on the specific substance used, like: titanium dioxide, nanosilver, carbon nanotubes, synthetic amorphous silica.

2. What shape is the nanomaterial? What chemical is it made of?
   1 dimension 2 dimensions 3 dimensions

3. Has your employer done a risk assessment on using the nanomaterial at your workplace?
   - Ask your employer for the Safety Data Sheet of the nanomaterial
   - Is the risk assessment complete?
   - What do you think is missing in the risk assessment?
   - Is the risk assessment useful to provide guidance on measures to prevent worker exposure

4. Could nanomaterials be released when you are working?
   - As a powder
   - As part of a solution or mixture
   - As part of a nano-enabled product (e.g. sawing, sanding, cutting, grinding or using a product containing nanomaterials)
What are Nanomaterials?

There are many kinds of nanomaterials, but they all share a remarkably small size (roughly 100,000 times thinner than a human hair). At this size, they can add new properties to many construction products.

Nanoparticles exist in nature and in man-made combustion sources, but this alert is about manufactured nanomaterials that are added to products. These products are called nano-enabled.

![A carbon nanotube lying across a human hair](image)

What are the risks?

Some nanomaterials may be safe, but others have been shown to be toxic in the lab. Of particular concern are respiratory exposures to long, thin fibers, such as carbon nanotubes (CNTs). Certain types of CNTs cause lung problems in rodents, similar to asbestos. Nanoparticles don’t seem to penetrate healthy skin but may get through damaged skin. Nanomaterials can be released from nano-enabled products, but the risks are not well understood.

The key is to limit exposure.

Are nanomaterials regulated?

OSHA does not have a regulation or Permissible Exposure Limit for any specific nanomaterial, but there are many existing OSHA standards, like the respirator standard, that would still apply.

NIOSH has set Recommended Exposure Limits for carbon nanotubes and nano-sized titanium dioxide that employers should follow. EPA has reporting requirements for nanoparticles under TSCA.

Learn more

- OSHA Nanotechnology: [http://tinyurl.com/OSHA9nano](http://tinyurl.com/OSHA9nano)
- NIOSH Nanotechnology: [http://tinyurl.com/NIOSH9nano](http://tinyurl.com/NIOSH9nano)
- EPA TSCA Regulations for Nanoscale

If you think you are in danger:

Contact your supervisor.
Contact your union.
Call OSHA 1-800-321-6742

Find out more about construction hazards.

To receive copies of this Hazard Alert and cards on other topics, call 301-578-6500.
It is electronically available in Spanish
What are the key messages for workers?

1. There are still questions about the health risks
2. Exposures to ENPs in construction appear to be below OELs
3. Local exhaust ventilation can greatly reduce construction exposures, including to nano-objects
4. Respirators can capture ENPs
5. SDSs for nano products are inadequate and shouldn’t be relied upon
6. NIOSH is your best source of info
The AIHA Nanotechnology Working Group could be a valuable resource.
Thanks! Questions?

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http://www.elcosh.org