Lawrence Livermore National Laboratory

March 19, 2010

DIRECTOR'S OFFICE
DEPT OF TOXIC SUBSTANCES CONTROL
MAR 25 2010
RECEIVED

Dr. Jeffrey Wong, Ph.D
Chief Scientist
Department of Toxic Substances Control
P.O. Box 806
Sacramento, CA 95812-0608

Subject: *Response to the Department of Toxic Substances Control "Chemical Information Call-In: Carbon Nanotubes" Lawrence Livermore National Laboratory*

References:
1. *DTSC letter dated January 22, 2009, "Chemical Information Call-in Carbon Nanotubes" from Jeffrey Wong, DTSC to George Miller, LLNL*
2. *LLNL letter dated January 21, 2010, "Response to the Department of Toxic Substances Control – Chemical Information Call-In: Carbon Nanotubes, LLNL" from George Miller, LLNL to Jeffrey Wong, DTSC*
3. *DTSC letter dated February 17, 2010, "Response to LLNL letter dated January 21, 2010" from Jeffrey Wong, DTSC to George Miller, LLNL*

Dear Dr. Wong:

In response to the January 22, 2009 request for chemical information call-in request letter and the follow up letter dated February 17, 2010, Lawrence Livermore National Laboratory (LLNL) submits the following information regarding carbon nanotubes (CNTs) research at LLNL. Listed below are DTSC questions followed by LLNL's response.

1. What is the value chain for your company? For example, in what products are your carbon nanotubes used by others? In what quantities? Who are your major customers?

CNTs are produced for research and development purposes only. LLNL advances and develops CNT technology that may be transferred to other governmental or private entities; however, LLNL is not involved in commercial manufacturing or distribution of CNTs.

LLNL is currently engaged in one CNT Project, which is briefly described as follows:

CNT growth:
A dense, vertically-aligned array of carbon nanotubes with sub-2.6 nm diameters is grown at 850 °C by atmospheric-pressure catalytic chemical vapor deposition (CVD) on the surface of a 1´1-cm, 300-mm thick, prepatterned silicon (100) chip using ethylene as a carbon source. The catalyst for CNT growth consists of 5Å Fe/2Å Mo bilayer deposited by electron beam evaporation and separated from the supporting Si wafer by a sputtered 30-nm Al2O3 barrier

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layer. After annealing the catalyst in a reducing environment (515-sccm argon, 400-sccm hydrogen) for 12-min at 850 °C, the hydrogen flow rate is reduced to 15-sccm and ethylene is introduced into the horizontal quartz tube reactor (22-mm inner diameter) at 100-sccm. SWNT/DWNT forests are grown to a height between 3-7 mm.

2. What sampling, detection and measurement methods are you using to monitor (detect and measure) the presence of your chemical in the workplace and environment? Provide a full description of all required sampling, detection, measurement and verification methodologies. If used, provide full QA/QC protocol.

Due to the challenges associated with workplace monitoring, LLNL has implemented a rigorous nanomaterials management program in order to prevent occupational exposures or releases to the environment.

The lack of international consensus on an exposure threshold, measurement standard (i.e., mass, total surface area concentration or particle number concentration) and sampling protocols diminishes the value of workplace monitoring. However, LLNL may use real-time condensation particle counters to evaluate baseline (or background) levels to work levels in progress.

3. What is your knowledge about the current and projected presence of your chemical in the environment that results from manufacturing, distribution, use and end-of-life disposal?

The existing body of evidence, obtained to date, strongly suggests that CNTs pose serious inhalation, dermal, absorption, and ingestion effects. LLNL research laboratory staff and Environment, Safety and Health (ES&H) support staff (e.g., certified industrial hygienists, heath and safety technicians and waste management technicians) receive formal on-site training, as well as professional off-site training.

LLNL ES&H staff also reference the following sources for CNT and nanomaterials worker safety and environmental management information:

DTSC:
http://www.dtsc.ca.gov/TechnologyDevelopment/Nanotechnology/nanocallin.cfm

National Institute of Occupational Safety and Health (NIOSH):
http://www.cdc.gov/niosh/topics/nanotech/

National Nanotechnology Initiative (NNI):
http://www.nano.gov/

Oak Ridge Institute for Science and Education (ORISE):
http://orise.orau.gov/ihos/Nanotechnology/nanotech_home.html

Department of Energy Notice 456.1: The Safe Handling of Unbound Engineered Nanoparticles. https://www.directives.doe.gov/directives/current-directives/456.1-CNotice/view

In addition to the above informational references, anyone who meets any one of the following criteria must take the "Engineered Nanomaterials Safety Awareness" training course.

1. Engage in or supervise work with engineered CNTs that are or could become dispersible.
2. Routinely spend significant time in areas where engineered CNTs are or could become dispersible.
3. Work on equipment that may be contaminated with or could release engineered CNTs during servicing or maintenance.
4. Handle dispersible engineered CNT-bearing waste.

Training course topics:

1. Identification of hazards associated with engineered CNTs.
2. Description of controls for safe handling and transport of engineered CNTs.
3. Identification of methods used to verify the effectiveness of controls for CNTs.
4. Explanation of safe clean up and disposal of engineered CNTs.

4. What is your knowledge about the safety of your chemical in terms of occupational safety, public health and the environment?

The knowledge base for occupational exposure, public health and environmental impacts is maintained by Certified Industrial Hygienists, medical staff (i.e., Medical Doctors, Registered Nurses and other medical staff), and environmental experts (i.e., waste management staff trained in hazardous waste "generator" requirements, as well as Resource Conservation and Recovery Act-permitted Treatment, Storage and Disposal Facility operations).

This support group ensures LLNL remains in compliance with all applicable legal and Department of Energy requirements, which also includes health and safety technicians and experts in radiation and construction safety.

The integrated review of all work activities by health and safety, environmental analysts, research staff and management forms the basis for LLNL's Integrated Safety Management System (ISMS). ISMS is LLNL's fundamental safety principle that is an iterative process consisting of defining the work, analyzing hazards, developing controls, performing work, obtaining feedback and improving the process.

Covered under the ISMS umbrella is LLNL's Environmental Management System (EMS), which is registered in conformance with the ISO 14000:2004 standard. The ISMS and EMS systems work together to ensure environmental, health and safety goals are communicated and actively implemented across LLNL to *all* employees for *all* work.

As a result of the ISMS multi-disciplinary work review process, project-specific work requirements are provided to research staff, ES&H staff, facility-responsible staff and line

management in a single, comprehensive, integrated work document. Prior to work commencing, all responsible individuals must approve the work document as required by LLNL's ISMS.

5. What methods are you using to protect workers in the research, development and manufacturing environment?

Worker protection in the R&D environment is addressed during the integrated work review process. Protection of all work-related staff is identified during the hazards analysis process. Depending on the hazard level, controls include, but are not limited to: worker medical surveillance and the standard of hierarchy of controls, which consists of engineered controls (e.g., fume hoods and negative pressure glove boxes), administrative controls (e.g., work procedures, labeling and signage) and the final line of defense, personal protective equipment.

LLNL developed and implemented the "Control Banding" approach for the safe handling of CNTs in the workplace. This approach is being evaluated as an internationally-accepted standard to assess exposure, hazards and risks and is used to identify appropriate control strategies when adequate scientific data are not available to develop specific exposure limits or when validated sampling methods have not been developed. The attached "Evaluating the Control Banding Nanotool: a qualitative risk assessment method for controlling nanoparticle exposures" paper was published in the Journal of Nanoparticle Research, 2009, 11:1685-1704. The URL is: http://www.springerlink.com/content/4t3241552m176137/fulltext.html. Two of the authors, Samuel Paik and David Zalk, are LLNL employees.

6. When released, does your material constitute a hazardous waste under California Health and Safety code provisions? Are discarded off-spec materials a hazardous waste? Once discarded, are the carbon nanotubes you produce a hazardous waste? What are your waste handling practices for carbon nanotubes?

LLNL is managing all discarded, off-spec and CNT meeting the definition of waste as hazardous waste pursuant to California Health and Safety Code, Division 20, Chapter 6.5, Hazardous Waste Control, and the California Code of Regulations, Title 22, Division 4.5, Environmental Standards for the Management of Hazardous Waste.

Specific waste handling practices are a function of the volume of waste, waste form, rate of waste generation, Land Disposal Restriction requirements, on-site RCRA-permitted Decontamination and Waste Treatment Facility requirements and the off-site RCRA-permitted Treatment, Storage and Disposal Facility.

If you have any questions or require additional information, please contact Bruce Schultz, Acting Department Head, Environmental Protection Department, at (925) 423-3978.

George H Miller
Director

Enclosure: Abstract

Copy:

Kao, Wen	(NNSA/LSO)	L-293
Liedle, Steve	(LLNL)	L-001
Schultz, Bruce	(LLNL)	L-626
Wuthrich, Steve	(LLNL)	L-510

Evaluating the Control Banding Nanotool: a qualitative risk assessment method for controlling nanoparticle exposures
[Journal of Nanoparticle Research 11(7):1685-1704 (2009)]

David M. Zalk, Samuel Y. Paik, Paul Swuste

ABSTRACT

Control Banding (CB) strategies offer simplified processes for controlling worker exposures in the absence of firm toxicological and exposure information. The nanotechnology industry is an excellent candidate for applying such strategies with overwhelming uncertainties of work-related health risks posed by nanomaterials. A recent survey shows that a majority of nanomaterial producers are not performing a basic risk assessment of their product in use. The CB Nanotool, used internationally, was developed to conduct qualitative risk assessments to control nanoparticle exposures. Nanotoxicology experts have requested standardization of toxicological parameters to ensure better utility and consistency of research. Such standardization would fit well in the CB Nanotool's severity and probability risk matrix, therefore enhancing the protection of nanotechnology industry workers. This paper further evaluates the CB Nanotool for structure, weighting of risk factors, and utility for exposure mitigation, and suggests improvements for the CB Nanotool and the research needed to bolster its effectiveness.

Application of a pilot control banding tool for risk level assessment and control of nanoparticle exposures
[Annals of Occupational Hygiene 52(6):419-428 (2008)]

Samuel Y. Paik, David M. Zalk, and Paul Swuste

ABSTRACT

Control Banding (CB) strategies offer simplified solutions for controlling worker exposures to constituents that are found in the workplace in the absence of firm toxicological and exposure data. These strategies may be particularly useful in nanotechnology applications, considering the overwhelming level of uncertainty over what nanomaterials and nanotechnologies present as potential work-related health risks, what about these materials might lead to adverse toxicological activity, how risk related to these might be assessed, and how to manage these issues in the absence of this information. This study introduces a pilot CB tool or 'CB Nanotool' that was developed specifically for characterizing the health aspects of working with engineered nanoparticles and determining the level of risk and associated controls for five ongoing nanotechnology-related operations being conducted at two Department of Energy (DOE) research laboratories. Based on the application of the CB Nanotool, four of the five operations evaluated in this study were found to have implemented controls consistent with what was recommended by the CB Nanotool, with one operation even exceeding the required controls for that activity. The one remaining operation was determined to require an upgrade in controls. By developing this dynamic CB Nanotool within the realm of the scientific information available, this application of CB appears to be a useful approach for assessing the risk of nanomaterial operations, providing recommendations for appropriate engineering controls, and facilitating the allocation of resources to the activities that most need them.

INSTRUCTIONS

<u>Severity Score:</u> Sum of all severity factors. Maximum score is 100. Out of the 100 pts, 70 points are based on characteristics of the nanomaterial and 30 points are based on characteristics of the parent material. Thus, more weight is given to nanoscale characteristics.
0-25: Low severity, 26-50: Medium severity, 51-75: High severity, 76-100: Very high severity.

1. Surface reactivity – Surface chemistry is known to be a key factor influencing the toxicity of inhaled particles. Particle surface free radical activity is the primary factor that influences the material's overall surface reactivity. Points will be assigned based on a qualitative judgment of whether the surface reactivity is high, medium, or low. Research studies will be consulted, when available, to make the judgment. High: 10 pts, Medium: 5 pts, Low: 0 pts, Unknown: 7.5 pts.

2. Particle shape – Studies have shown that exposure to fibrous particles like asbestos have long been associated with increased risk of fibrosis and cancer. Tubular structures, like carbon nanotubes, have also been shown to cause inflammation and lesions in rat lungs. Based on this information, the highest severity score is given to fibrous or tubular-shaped particles. Particles with irregular shapes (other than tubular or fibrous) are given a medium severity score because they typically have higher surface areas relative to isotropic (e.g. compact or spherical) particles. Tubular or fibrous: 10 pts, Anisotropic: 5 pts, Compact or spherical: 0 pts, Unknown: 7.5 pts.

3. Particle diameter – based on the ICRP curve, particles in the 1-10 nm range have a greater than approximately 80% chance of depositing in the lungs. Particles in the 10-40 nm range have a greater than approximately 50% possibility of depositing in the lungs and particles in the 41-100 nm range have a greater than approximately 20% possibility of depositing in the lungs. Based on this ability to deposit in the lungs (regardless of the region of deposition) and the fact that smaller particles have a higher overall surface area compared to larger particles for a given mass concentration, the following points are assigned to a given particle size range and used to determine the severity score. 1-10 nm: 10 pts, 11-40 nm: 5 pts, <41-100 nm: 0 pts, Unknown: 7.5. pts.

4. Solubility – several studies have shown that poorly soluble inhaled nanoparticles can cause oxidative stress, leading to inflammation, fibrosis, or cancer. Since soluble nanoparticles can also cause adverse effects through dissolution in the blood, severity points are assigned to soluble nanoparticles as well, but to a lesser degree than for insoluble particles. Insoluble: 10 pts, Soluble: 5 pts, Unknown: 7.5 pts.

5. Carcinogenicity – points are assigned based on whether the nanomaterial is carcinogenic or not. Yes: 6 pts, No: 0 pts, Unknown: 4.5 pts.

6. Reproductive toxicity – points are assigned based on whether the nanomaterial is a reproductive hazard or not. Yes: 6 pts, No: 0 pts, Unknown: 4.5 pts.

7. Mutagenicity – points are assigned based on whether the nanomaterial is a mutagen or not. Yes: 6 pts, No: 0 pts, Unknown: 4.5 pts.
8. Dermal toxicity – points are assigned based on whether the nanomaterial is a dermal hazard or not. Yes: 6 pts, No: 0 pts, Unknown: 4.5 pts.

9. Asthmagen – points are assigned based on whether the nanomaterial is an asthmagen or not. Yes: 6 pts, No: 0 pts, Unknown: 4.5 pts.

10. Toxicity of parent material – the bulk material of some nanoparticles have established occupational exposure limits. While it is known that the toxicity of particles at the nanoscale can differ significantly from their larger counterparts, this provides a good starting point for understanding the toxicity of the material. Points are assigned according to the OEL (occupational exposure limit) band of the bulk material. $< 1\ \mu gm^{-3}$: 10 pts, $1\ mgm^{-3} - 100\ \mu gm^{-3}$: 5 pts , $> 1\ mgm^{-3}$: 2.5 pts, Unknown = 7.5 pts.

11. Carcinogenicity of parent material – points are assigned based on whether the parent material is carcinogenic or not. Yes: 4 pts, No: 0 pts, Unknown: 3 pts.

12. Reproductive toxicity of parent material – points are assigned based on whether the parent material is a reproductive hazard or not. Yes: 4 pts, No: 0 pts, Unknown: 3 pts.

13. Mutagenicity of parent material – points are assigned based on whether the parent material is a mutagen or not. Yes: 4 pts, No: 0 pts, Unknown: 3 pts.

14. Dermal toxicity of parent material – points are assigned based on whether the parent material is a dermal hazard or not. Yes: 4 pts, No: 0 pts, Unknown: 3 pts.

15. Asthmagen of parent material – points are assigned based on whether the parent material is an Asthmagen or not. Yes: 4 pts, No: 0 pts, Unknown: 3 pts.

Probability Score: Sum of all exposure factors. Maximum score is 100. These factors determine the extent to which employees may be potentially exposed to nanoscale materials, primarily through inhalation, but also through dermal contact.
0-25: Extremely unlikely, 26-50: Less likely, 51-75: Likely, 76-100: Probable.

1. Estimated amount of chemical used during task. >100 mg: 25 pts, 11-100 mg: 12.5 pts, 0-10 mg: 6.25 pts, Unknown: 18.75 pts.

2. Dustiness/mistiness – points are assigned according to dustiness/mistiness level of material. Until further guidance is provided on quantifying dustiness/mistiness levels, points will assigned based on an estimate of relative dustiness/mistiness level. When "None" is chosen for dustiness/mistiness level, this automatically causes the overall probability score to be "Extremely Unlikely", regardless of what the other probability factors are. High: 30 pts, Medium: 15 pts, Low: 7.5 pts, None: 0 pts, Unknown: 22.5 pts.

3. Number of employees with similar exposure – points are assigned according to the number of employees authorized for the activity. >15: 15 pts, 11-15: 10 pts, 6-10: 5 pts, 1-5: 0 pts, Unknown: 11.25 pts.

4. Frequency of operation – points are assigned according to the frequency of the operation. Daily: 15 pts, Weekly: 10 pts, Monthly: 5 pts, Less than monthly: 0 pts, Unknown: 11.25 pts

5. Operation duration – points are assigned according to the duration of the operation. >4 hours: 15 pts, 1-4 hours: 10 pts, 30-60 min: 5 pts, Less than 30 min: 0 pts, Unknown: 11.25 pts.

Overall Risk Level

Based on the severity score and probability score, the following table is used to determine the overall risk level of the activity:

Severity \ Probability	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