Unidym

January 21, 2010

Jeffery Wong, PhD
Department of Toxic Substances Control (DTSC)
1011 "I" Street
PO Box 806
Sacramento, CA 95812-9806

Re: DTSC Chemical Information Call-in, Carbon Nanotubes
Unidym, Inc.

Dear Dr. Wong:

Unidym respectfully submits its response to the DTSC Chemical Information Call-in dated January 22, 2009.

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 (e.g., polymer industry, electronics industry, etc.)?**

Unidym provides carbon nanotube (CNT) enabled products and specialized CNT materials to a wide range of customers and business partners. Unidym's primary product line includes Double Walled Carbon Nanotubes (DWNT) materials and Hipco™ Single Wall Carbon Nanotubes (SWNT). Unidym currently has one facility in Sunnyvale, California involved in the use and handling of CNT materials.

The SWNT product is provided to academic and research institutions for Research and Development (R&D) purposes only. Although we are not aware of the specifics associated with our customer's use of our SWNT, we do know that our SWNT customers utilize the nanomaterials for R&D work related to Polymers, Photovoltaics, Electronics, Molecular Biology, Toxicology, Pharma, LED lighting and Electrophoretics (EPD).

Unidym is involved in the manufacture and application of CNT based Transparent Conductive Films (TCF) and Ink products derived from our DWNT product line. In order to streamline our DWNT manufacturing process and better serve our customers, we closed our Texas CNT manufacturing facility in early 2009 and partnered with another company to manufacture our specialty CNT materials for us. This partner is located outside the State of California. We will receive these DWNTs in our Sunnyvale facility and convert them to water soluble, coat-able ink dispersions. Unidym may either supply our ink product directly to our customer for coating onto their substrate or supply finished film manufactured by Unidym to our customer. For Unidym manufactured film products, we send our ink dispersion a toll coater and in turn, this coater manufactures coated film and supplies the coated film directly into our supply chain. The toll coaters are/will be geographically located in close proximity to our end-use customer(s). The market for our transparent conductive film product is international; therefore our supply chain terminates at various locations throughout the world.

The CNT concentration and substrate selections used by both Unidym and our customers are based on customer specifications for their product. Our film and ink market includes Touch Panel (TP), EPD, Liquid Crystal Display (LCD), and Organic Light Emitting Diode (OLED). Future markets may include Thin Film Solar applications. The manufacture of Unidym DWNT ink and film products do not involve environmentally adverse manufacturing processes such as the acid etch processes currently used in these market sectors. The use of CNT TCF as a replacement for current technologies will result in a significantly "greener" product.

Both SWNT and DWNT products are highly specialized, expensive to produce and are used by Unidym and our customers in gram quantities. The maximum annual quantity manufactured, distributed, used and/or handled by Unidym is estimated to be 10 kilograms (~22 pounds).

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

Unidym works with CNT materials in four distinct formats.

- Dry, powder CNT materials
- Wet, mud form comprised of CNTs in a dilute ethanol water based media
- Liquid, ink dispersions comprised predominantly of water
- CNT based film or coated substrates

In order to better understand the hazards associated with these various formats, Unidym conducted two monitoring evaluations at our facility. Dry, powder CNT materials were chosen for monitoring as these materials are thought to potentially create the greatest workplace hazard due to their airborne mobility and tendency to adhere to work surfaces. The hazard evaluations were designed to identify the behaviors of our CNT materials in "uncontrolled" work environments as this is the most "severe" hazard scenario. "Uncontrolled" workplace events are defined as those occurring without the benefit of mechanical air ventilation and closed reactors/containers. Wipe sampling and air monitoring were conducted during two separate events in August 2008 and December 2008, respectively. Please note that employees and third party contractors participating in the monitoring events utilized the appropriate (as defined under response to question 5 in this document) Personal Protective Equipment (PPE) and were not exposed to CNT material as a result of this test.

In August 2008, surfaces were sampled to determine if visual appearance could be used to differentiate areas with extensive, moderate or no accumulations of CNTs in the workplace. A statistically significant number of sample locations were identified throughout various work areas. The sample locations were grouped into three categories, "heavy accumulation of CNTs", "moderate accumulation of CNTs" and "clean or no visible CNT material present". Samples sizes were 100 square centimeters

each. Sample collection was performed by a Certified Industrial Hygienist (CIH) and all samples were analyzed by an AIHA Accredited Laboratory.

Each location to be sampled was identified and a sample identification number was assigned to each sample. A plastic transparency film with a 10 centimeter by 10 centimeter square cut out of the center was used as a sampling template. The template was placed on the area to be sampled, and the sample ID card was placed on a corner of the template, away from the sampling opening. A digital photograph was taken of the template and the sample ID card to document the exact location and condition of each sample. The 100 square centimeter area was completely wiped vertically and then horizontally with the inside of a polyethylene double zipped bag. The sampling bag was turned right side out, sealed, labeled with a sample identification code which did not indicate to the analyst the presumed degree of accumulation. The template and the latex examination gloves used during the collection of the sample were immediately discarded, and a new template and pair of gloves were used for collecting the next sample. The card indicating the sample identification number was attached to the sample bag, and then the sample bag and ID card were sealed inside another double zipper lock bag for shipment to the laboratory. The collected samples along with a reference sample of known CNTs were examined in the laboratory by polarized light optical microscopy (PLM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to determine whether CNTs were present on the wipes. Energy dispersive X-ray spectrometry (EDS) was used in conjunction with SEM and TEM to determine the elemental composition of metal catalyst particles used in nanotube synthesis. The CIH and analytical laboratory developed an analytical strategy of initially isolating particulate from the sample bag in a clean room and performing a screening examination by polarized light optical microscopy (PLM). Depending on the amount and nature of the material seen in the optical images, the sample would be further examined by high resolution scanning electron microscopy (SEM) or transmission electron microscopy (TEM). PLM magnifications were at 100 times and 200 times while SEM and TEM magnifications ranged from 5,000 to more than 130,000 times the original scale length. Certain samples were also subjected to energy dispersive X-ray spectrometry (EDS) to determine if a chemical "signature" characteristic of the metals used for catalysts in the manufacturing process could be identified so that rapid classification of samples as CNT containing could be made in the future.

The results of the microscopic examination were compared to the presumed classification of the sample areas by arranging the results in a 3 x 3 contingency table. Chi Square analysis demonstrated that there is a statistically significant relationship among the presumed classification versus the analytical results. The calculated Chi Square statistic was 11.80 compared to the Chi Square statistic for $p<0.05$ and 4 degrees of freedom of 9.488, indicating that similar agreement would be expected to occur at random less than 5 percent of the time if many similar trials were conducted.

The visual and SEM examination during this study also showed that free individual CNTs are not extensively present, and are probably rare. CNTs exhibited morphology with filaments of CNTs attached to clumps or mats of larger particles or agglomerates.

Based on the results of this study, it was concluded that the visual and presumed determinations were accurate, and can be relied on for monitoring workplace activities. After careful examination of the reference material and review of a initial set of samples, it was determined that clean room isolation was rarely necessary, and that EDS confirmed the catalyst particles consisted mainly of iron, which is ubiquitous in most environments, and no other more exotic or unique material was present which could be used as a surrogate for CNT presence.

In the absence of established OSHA permissible air exposure limits (PELs) for CNTs available, several reference publications were consulted in order to design sampling protocol for workplace monitoring protocol in December 2008.

- ASTM E 2535-07 Standard Guide for Handling Unbound Engineered Nanoscale Particles in Occupational. This ASTM standard recommends that in the absence of definitive occupational exposure limits, it is prudent to control exposures to "as low as reasonably practicable." This standard describes "practicable measures" as those that are both feasible, in the sense of being capable of being done in practice at a given location, and practical, in the sense of being demonstrably useful in achieving a particular exposure minimization or other program goal. This standard also describes "reasonable efforts" as those that follow from a rational (logical) evaluation and selection process, and excluding both considerations and measures that are extreme or excessive. The standard recommends following an approach to selecting precautionary actions considering proportionality, cost-effectiveness, consistency with actions in similar circumstances, and openness to change with new information or refined analysis.

- Approaches to Safe Nanotechnology: An Information Exchange with NIOSH, July 2006

- Draft NIOSH Current Intelligence Bulletin: Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide, November 22, 2005.

- "Occupational Risk Management of Engineered Nanoparticales," Schulte, Paul et al., Journal of Occupational and Environmental Hygiene, Vol. 5, pages 239-249, April 2008.

- "Measurement of the Physical Properties of Aerosols in a Fullerene Factory for Inhalation Exposure assessment," Fujitani, Yuji, et al., Journal of Occupational and Environmental Hygiene, Vol. 5, pages 380-389, June 2008.

- "Filtration Performance of NIOSH-Approved N95 and P100 Filtering Facepiece Respirators Against 4 to 30 Nanometer-Size Nanoparticles, Rengaswamy, Samy et al., Journal of Occupational and Environmental Hygiene, Vol. 5, pages 556-564, September 2008.

- "Evaluation of Aerosol Release During the Handling of Unrefined Single Walled Carbon Nanotube Material," Paul A. Baron, Andrew D. Maynard, and Michael Foley, NIOSH DART-02-191 Rev. 1.1 April 2003.

Inititally, the 2008 American Conference of Govermental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for respirable synthetic graphite of 2 milligrams per cubic meter was planned as air monitoring criteria. Based on the microscopic examination of Unidym CNTs during the wipe sampling event, it was shown that our CNTs aggregate and are present as rough-edged clumps of material and would be more accurately described as particulates with a graphite crystalline microstructure instead of fibrous in shape. Therefore the OSHA PEL for respirable dust (not otherwise classified) of 5 milligrams per cubic meter was used as air monitoring criteria.

In the absence of existing methodologies for the air monitoring/sampling of airborne, powder CNT materials, several areas of investigation were pursued to qualitatively and quantitatively measure the exposure of employees in the workplace. It was originally estimated that the CNT particle diameter size range was 20 nm to greater than 300 nm. This estimate was based on a CNT molecular weight of 12×10^3 to 10×10^6. After review of Unidym's August 2008, wipe sample results it was suggested that the 300 nm diameter is more likely at the smaller extreme of the scale range. Aggregates and agglomerates of Unidym CNTs extend in size into the micrometer or tens of micrometer size range.

Qualitative analytical techniques for air sampling included polarized microscopy (PLM) and field emission scanning electron microscopy (SEM). Quantitative analytical methods included the collection of air samples on filter media for chemical and gravimetric laboratory analysis, and real-time detection and quantitation of particles larger than 300 nm by a Lighthouse Model 3016 IAQ hand-held optical particle counter. Workplace air filter samples were collected on site by a CIH and then sent to an AIHA accredited laboratory. The air samples were analyzed for respirable dust, respirable synthetic graphite, and various metals associated with CNT catalyst residuals. A summary of sampling and analytical methodologies are included below:

Analyte	Sampling Equipment	Analytical Method
Respirable Particulate	SKC Air Chek 52 personal sampling pump at 2.5 liters per minute with SKC aluminum cyclone and 37 mm, 5 µm pore size or 0.8 µm pore size polyvinyl chloride (PVC) filter	NIOSH 0600
Respirable Synthetic Graphite	SKC Air Chek 52 personal sampling pump at 2.5 liters per minute with SKC aluminum cyclone and 37 mm, 5 µm pore size or 0.8 µm pore size PVC filter	OSHA ID 142
Selected Metals (catalyst)	SKC Air Chek 52 personal sampling pump at 2.5 liters per minute with 37 mm Mixed Cellulose Ester 5 µm pore size filter.	OSHA ID 125
Graphite	SKC Air Chek 52 personal sampling pump at 2.5 liters per minute with 25 mm silver membrane 0.8 µm pore size filter in open-face conductive cowl	OSHA ID 142
Carbon Nanotube Aggregates	SKC Air Chek 52 personal sampling pump at 1.5 liters per minute with 25 mm polycarbonate 0.8 µm pore size filter in open-face conductive cowl	PLM, SEM, TEM
Real-time Particulate in six size ranges (0.3 to 10 micrometers)	Lighthouse 3016 IAQ optical particle counter calibrated to each size range with NIST traceable polystyrene latex particles and calculated mass loadings with a particle specific gravity of 2.500 gram/cubic centimeter (carbon)	Differential Mode for PM 0.5 to PM 10

More recent publications were also reviewed to ensure that the techniques used are state-of-the-art. These references included:

- "Relationships Among Particle Number, Surface Area and Respirable Mass Concentrations in Automotive Engine Manufacturing," Heitbrink, William A., et al, Journal of Occupational and Environmental Hygiene, Vol. 6., pages 19-31, January 2009.

- "Airborne Monitoring to Distinguish Engineered Nanomaterials from Industrial Particles for Environmental Health and Safety," peters, Thomas M. et al., Journal of Occupational and Environmental Hygiene, Vol. 6, pages 73-81, February 2009.

The results of personal air samples collected during this monitoring event indicated that personnel were not exposed to respirable dust exceeding the OSHA PEL of 5 milligrams per cubic meter as an 8-hour Time Weighted Average (TWA) or respirable synthetic graphite exceeding the ACGIH TLV of 2 milligrams per cubic meter as an 8-hour TWA.

The results of samples collected for metal analysis associated with CNT catalyst indicate that personal participating in the monitoring study were not exposed to airborne concentrations of iron, chromium, cobalt, magnesium, molybdenum or zinc in excess of the respective OSHA PELs or ACGIH TLVs. Real-time particle counting supported the filter based monitoring results during this study.

The examination of samples taken indicated that CNT aggregates consistent with the CNT reference material were present in 4 out of 5 air samples. Microscopic examination of surface wipe samples by PLM, followed as necessary by SEM or TEM, should be used to confirm the relative presence of CNT materials in the workplace. Sampling methods to assess airborne concentrations of CNT material should utilize methods, such as respirable dust sampling by cyclones, to characterize particulate, rather than fiber type aerosols.

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

Based on current available information, it is our understanding that we can effectively control and monitor the presence of CNTs in the workplace. The implementation of workplace occupational safety controls such as mechanical ventilation with HEPA filtration, Personal Protective Equipment and the use of controlled environments are effective in the prevention of occupational exposures and environmental release at/from the Unidym facility.

Our SWNT products are distributed to various academic and research institutions for research and development purposes. We provide available Environmental, Health and Safety (EHS) information to all end users through our Material Safety Data Sheet (MSDS) but do not have any direct knowledge as to how these materials are distributed, used or disposed of once they leave Unidym.

During the manufacture of our film product, we communicate extensively with our CNT manufacturing partner and our toll coaters to ensure that they are informed of the potential hazards associated with CNT materials; however we do not have control over their manufacturing processes and procedures. Unidym does not have any direct knowledge of the presence of our CNTs in their manufacturing environments.

Our DWNT film product is intended to be part of a consumer market. Based on toxicity data currently available on this product, we do not believe that a significant hazard exists for End-of Life (EOL) disposal of this product. Our CNT product would initially be incorporated into devices containing other materials that require recycling/reclamation under existing statues. As markets and CNT industries grow and technology advances, additional testing would be prudent to understand any new consumer product type.

4) What is your knowledge about the safety of your carbon nanotubes in terms of occupational safety, public health and the environment?

Based on the data we obtained from our workplace monitoring events and the toxicity characteristic analysis, we believe that our CNT materials can be managed safely in the workplace to mitigate risk to employees and prevent release to the environment. We do not have direct knowledge pertaining to the toxicological effects nor the fate and transport effect of our CNT materials on the environment.

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

Unidym takes a very active approach to the protection its employees in the work environment. Based on analytical results outlined in question 2, Unidym developed and implemented a CNT Safe Handling Procedure for use in its Manufacturing and Research and Development environments. Additionally, due to the potential of some light powder CNT formats to become airborne, we amended our internal handling procedure to convert these materials into a wet, mud format. This practice prevents light, dry powder CNT material from becoming airborne, thus removing any inhalation risk. This procedural change included both materials used internally and those purchased by our customers.

The Unidym CNT Safe Handling procedure is a conservative approach to the protection of employees while working with CNT materials and products in both controlled and uncontrolled environments. The procedure is based on current Best Manufacturing Practices for the handling of materials of unknown hazard, Workplace Risk Assessment analysis and the results obtained from Unidym workplace monitoring events.

The purpose of the procedure is to document recommended safe handling practices for Carbon Nanotube (CNT) Products manufactured by Unidym and provide our employees with a framework for the safe handling of CNT materials. At the time of the development of this procedure, it had not been determined that the CNTs covered under this procedure constitute a safety hazard, therefore the procedure outlines a "Best Safe Practices" approach for the handling of CNT material.

The procedure includes the following sections:

- Spill Notification and Response for CNT dry powders, wet muds and inks/dispersions.
- Training requirements for all employees, contractors and consultants that handle CNT materials in Unidym facility.
- Record Keeping
- General Work Practices
- Specific Work Practices for material type and environment

Specific work practices for CNT products are grouped by type. The types are defined as:

1. Dry, powder CNT and unknown materials
2. Wet CNT muds or slurries
3. Inks and dispersions containing CNTs
4. Conductive films/coatings containing CNTs

Specific workplace environments are identified as controlled and uncontrolled. A controlled environment is defined when CNTs are handled in closed reactors or vessels, closed containers, inside a glove box that ventilates to an approved HEPA filtration system with a capture efficiency of ≥ 99.5% or an enclosed area serviced by mechanical ventilation system that ventilates to an approved HEPA filtration system with both a capture efficiency of ≥ 99.5% and a uniform face velocity of ≥ 80 feet per minute (fpm). An uncontrolled environment designation is assigned in the absence of controls defined above.

Personal Protective Equipment (PPE) requirements each material and environment scenario are grouped into three levels, Standard Lab, PPE Level M and PPE Level Z.

Unidym Standard Lab PPE includes the following:

- Safety Glasses with side shields, ANSI Z87.1 approved
- Long sleeved uniform or lab coat
- Nitrile gloves or equivalent

Unidym Level M PPE includes the following:

- N100/P100 Half Face HEPA respirator or HEPA Face Mask rated for dusts
- Safety Glasses with side shields, ANSI Z87.1 approved
- Long sleeved uniform or lab coat
- Nitrile gloves or equivalent

Unidym Level Z PPE includes the following:

- NIOSH-approved full-face respirator with N-100 HEPA cartridges or appropriate powered air purifying respirator (PAPR), such as 3M BE-10
- No safety glasses are required for eye protection as full-face respirator provides eye protection
- Long sleeved uniform or lab coat or Tyvek coverall
- Nitrile gloves or equivalent

Unidym specific work practices as outlined in our CNT Safe Handling Procedure are summarized below.

Product Type	Controlled or Uncontrolled	Standard Lab PPE Protocol	Unidym Level M PPE required	Unidym Level Z PPE required
Dry, powder CNT and unknown materials	Controlled		X	
Dry, powder CNT and unknown materials	Uncontrolled			X
Wet CNT muds or slurries	Controlled	X		
Wet CNT muds or slurries	Uncontrolled		X	
Inks and dispersions containing CNTs	Controlled	X		
Inks and dispersions containing CNTs	Uncontrolled		X	
Conductive films/coatings containing CNTs	Controlled	X		
Conductive films/coatings containing CNTs	Uncontrolled		X	

6) When released, do your carbon nanotubes constitute a Hazardous Waste under California Health & Safety Code provisions? Are discarded off-spec carbon nanotubes a hazardous waste? Once discarded are the carbon nanotubes you produce a hazardous waste? What are your waste handling practices for carbon nanotubes?

Unidym may generate up to five waste streams potentially containing CNT materials. The possible air, water and solid waste scenarios are:

1. Water based ink/dispersion materials and water generated by the wash process after coating
2. Dilute acid waste generated by CNT purification process
3. Off-spec CNT dry powders
4. Plastic substrates coated with CNT ink/dispersion materials
5. Air emissions from process activities

Due to the potential hazard and high value assigned to CNT materials, we manage our waste streams accordingly.

Water based waste materials generated as a result of coating activities are either recycled and may be reused for future coating activities. Water based CNT materials that cannot be recycled or reused are disposed of along with other laboratory waste streams as a California regulated "Laboratory Waste", California waste code 551. These materials are not regulated as a hazardous waste under Federal RCRA statues.

California state regulations do not specifically regulate waste materials containing CNT materials.

Dilute acid waste solutions are collected and disposed of as hazardous waste under both Federal RCRA and California hazardous Waste regulations due to the pH of the waste stream. This waste stream is classified as corrosive and disposed of as a D002 RCRA waste and a 791 California hazardous waste.

Due to the high value of Unidym CNT materials, no materials have been characterized as off-spec, therefore none have been profiled for waste disposal at this date.

During and after the coating process, off-spec CNT coated plastic substrates may be generated as a result of normal processing. These substrates are not specifically regulated as a "listed" (40CFR261 and 22CCR66261) hazardous waste under both Federal and State guidelines. In order to determine if this waste material may still be considered a hazardous waste by exhibiting any ignitability, reactivity, toxicity, or corrosivity "characteristics", the waste stream was further evaluated. The waste material did not meet criteria for ignitability, reactivity or corrosivity characteristic properties. The CNT substrate waste material was evaluated for toxicity characteristic properties. The waste stream does not contain any components covered by Toxicity Characteristic Leaching Procedure (TCLP); therefore it was appropriate to determine the Acute Aquatic Toxicity of the waste material. The methodology used for this analysis is outlined in CCR Title 22, Fathead Minnow Hazardous Waste Screen Bioassay (Polisini & Miller, 1988). Three sample types were chosen for analysis:

- Bare substrate without CNT coating (control sample)
- Substrate with CNT coating
- Substrate with CNT coating and additional encapsulation

None of the samples evaluated, exhibited the toxicity characteristic. The analytical results for all samples were an acute aquatic 96-hour LC50 greater than 750 milligrams per liter when measured in soft water (total hardness 40 to 48 milligrams per liter of calcium carbonate) with fathead minnows (*Pimephales promelas)* according to procedures described in Part 800 of the "Standard Methods for the Examination of Water and Wastewater (16th Edition)," American Public Health Association, 1985 and "Static Acute Bioassay Procedures for Hazardous Waste Samples," California Department of Fish and Game, Water Pollution Control Laboratory, revised November 1988 (incorporated by reference, see 22CCR section 66260.11).

Based on results of the Aquatic Toxicity Test, our CNT coated substrates do not exhibit the toxicity characteristic and are classified as a non-hazardous waste stream.

Response prepared and submitted by on January 21, 2010:
Mary Beth Miller
Vice President, Operations
Unidym, Inc.