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**Nanomaterial Risk Assessment Worksheet**  
**Incorporation of Single and Multi Walled Carbon Nano Tubes (CNTs)**  
**into Polymer Nanocomposites by Melt Processing**

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APPENDIX: OUTPUT WORKSHEET

**Nanomaterial Risk Assessment Document —  
Incorporation of Single and Multi Walled Carbon Nano Tubes (CNTs)  
into Polymers by Melt Processing**

**Step 1 - Describe Material and Its Applications**

Develop basic descriptions — general overviews — of the nanoscale material and its intended uses.

**General Overview:<sup>1</sup>**

Carbon nanotubes are cylindrical carbon molecules with novel properties that make them potentially useful in a wide variety of applications (e.g. nano-electronics, optics, materials applications, etc.). They exhibit extraordinary strength and unique electrical properties and are efficient conductors of heat. Nanotubes have also been synthesized with other inorganic materials.

A carbon nanotube (also known as a “buckytube”) is a member of the fullerene structural family, which also includes “buckyballs”. Whereas buckyballs are spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure. The diameter of nanotubes is on the order of a few nanometers, while they can be up to several centimeters in length. There are two main types of carbon nanotubes: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

The chemical bonds in carbon nanotubes are similar to those of graphite. This bonding structure, stronger than the bonds found in diamond, provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by weaker Van der Waals forces. Under high pressure, nanotubes can bond together, potentially enabling the formation of strong wires of unlimited length through high-pressure nanotube linking.

**Material Description:**

*Material Source or Producer:* Single-wall (SWCNT) and multi-wall (MWCNT) carbon nanotubes were supplied in powder form by two manufacturers in the U.S. and one in China. In this case study, DuPont evaluated both SWCNTs and MWCNTs from these suppliers. Monitoring tests did not discriminate between the CNTs used, since all three materials were compounded in the same experiment. These externally sourced nanotubes were incorporated into DuPont polymers to form CNT-polymer composites.

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<sup>1</sup> The general overview should contain descriptions sufficient to guide development of more detailed profiles of the material's properties related to hazard and exposure potential at various lifecycle stages (such as manufacture, use, and end-of-life). This overview should be developed from information in the possession of the user or available in the literature.

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*Manufacturing Process:* Today, CNTs are available from a wide variety of sources, using a range of manufacturing methods with widely varying compositions, structures and properties. DuPont is not synthesizing CNTs for use in the applications envisioned by this case study, but incorporates externally sourced CNTs into a polymeric matrix by one of the following routes:

a) CNT powder melt compounded into a polymer using conventional batch mixers (Banbury, Haake, etc.) or continuous extrusion equipment (twin screw, single screw, multi-screw, co-kneader, etc.) Incorporation may be by direct addition as a powder into the compounder to create the final composition for the intended application (typically 0.5 to 5% by weight). Alternatively, CNTs can be incorporated into the polymer at high concentrations (5% - 50% by weight) to create a masterbatch with a desired dispersion, in which the CNTs are encapsulated into the polymer for use in subsequent processing steps. In either case, the product would normally be in a pellet form.

b) Addition of a pre-compounded CNT masterbatch in pellet form into a melt compounding process or a shaping or forming process. This is referred to as a letdown step.

c) Addition of CNT powders into monomers, solvents or other carrier liquids for addition to polymerization, compounding or shaping or forming processes. This operation typically requires intensive mixing by rotor-stator, ultrasound, ball mill or other grinding and milling equipment in either the final composition or to form a concentrate for subsequent re-dispersion.

d) Shaping/forming operations (injection molding, film or fiber forming, blow molding, stock shape extrusion, etc.). In this step, CNTs that are contained in pellets at the desired concentration are added as a masterbatch concentrate, or introduced in a solution, slurry or paste and mixed in the processing equipment (distributive mixing).

*Appearance:* black powder (highly agglomerated visible fibrils with less dusting potential than carbon black) or pellets (concentrates of CNTs encapsulated in a polymer matrix)

*Chemical composition:*

Chemical analysis was not performed by DuPont. According to the CNT supplier, the “as produced” material used was >95% MWCNT. The composition of the impurities was not disclosed.

*Physical Form:*

All CNTs were received from the suppliers as a dry powder in research quantities. Nanocomposite samples were prepared by weighing dry powders and pellets into a

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formulation, followed by melt compounding in a batch mixer and injection molding on laboratory equipment for internal research purposes only.

If the research program were successful, DuPont would deliver commercial nanocomposite products containing CNTs encapsulated in a matrix polymer in pellet form to customers who would perform an additional melt processing step, such as injection molding or film casting. Potential customers could be large in number and may be spread geographically in most States in the U.S. or globally, typically in North and South America, Europe and the Asia-Pacific region. In this instance, the research project ended prior to commercialization, for business reasons, so such downstream customer operations were not involved.

*Concentration:*

Powder from supplier: ~100% (from ~0% to 4% impurities)

Masterbatch: 5 – 50 wt. %, typical: 10-25%.

Nanocomposite Product: 0.1 – 10 wt. %, typical: 1 – 5%

According to the CNT supplier, the “as produced” material provided to DuPont has purity greater than 95% (MWCNT).

*Size distribution:* Nanotube diameters range from ~0.4 to > 3 nm for single-walled nanotubes (SWCNT) and from ~1.4 to at least 100 nm for multi walled nanotubes (MWCNT). Nanotube lengths vary from 100nm to several millimeters, depending on type and supplier.

The CNTs used were reported by the typical supplier to have a diameter of  $10\pm 5$ nm with a surface area BET  $230\pm 50$  m<sup>2</sup>/gm.

*Solubility:*

Typically, MWCNTs are not soluble in H<sub>2</sub>O without ionic surfactant addition. Certain “as produced” CNTs used in this study exhibit an affinity for certain surfactants and other organic solvents, polymer additives and monomers.

*State of Aggregation or Agglomeration:*

The materials used in this research were highly aggregated or agglomerated into entangled, rope-like bundles. Visible particles are fibril-like structures. Little or no visible dusting was observed as compared to fine carbon blacks (for example, Ketjenblack). Monitoring of small-scale, lab batch mixing operations detected very low levels of particles relative to the background during sample preparation and melt blending operations (see Attachment 1).

*Material CAS Number (if applicable):*

At present, the materials are supplied to DuPont utilizing the CAS Number for graphite, as illustrated below:

Material	CAS Number	Composition
MWCNT	7782-42-5 (Graphite)	Carbon (> 95%)

**Main applications (current or expected):**

For the products envisioned by this research project, applications of interest to DuPont customers include molded shapes and forms. Typically, DuPont would provide materials to customers in the form of pellets that would then be formed or molded. Of greatest immediate interest is injection molded parts for automotive applications. A typical first tier customer is an automotive original equipment manufacturer (OEM) supplier. DuPont would sell resins to an injection molding parts and sub-assembly manufacturer as the first tier customer, who would then sell the parts to the automotive OEM. In many instances, the OEM specifies and certifies the resins to be used in the parts, so DuPont would interact with the OEM and parts manufacturer during design, specification and testing steps.

- CNT composite materials of this kind are expected to find the following applications:
  - Lighter, stronger, tougher materials
    - Lighter automobiles with improved safety
    - Composite armor for aircraft, ships and tanks
  - Conductive polymers and coatings
    - Antistatic or EMI shielding
    - Improved process economics for coatings, paints
  - Thermally conductive polymers
    - Waste heat management or heat piping
  - Multifunctional materials, with combinations of two or more of these properties.

**Stage of development:**

**Research:** In this study, CNTs were consumed in sub-kilogram quantities. Material consumption is typically 1 – 100gms per set of experiments to make nanocomposites by direct compounding, masterbatch-letdown or in-situ polymerization approaches. Polymer nanocomposite products and applications are at the proof-of-concept stage in DuPont. That is, tensile and flexural bars or film samples are produced in polymer composite formulations using laboratory-scale batch processing equipment. Mechanical, electrical and thermal properties are measured on small sample sets (3 – 5 bars per composition or process state).

**General physical and mechanical properties of this material:**

The goal was to prepare composite materials with enhanced properties as measured by the following methods:

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Mechanical: Increased stiffness/strength (tensile and flexural stress-strain properties including modulus) , toughness (% elongation at break) and impact strength (IZOD, falling dart impact, etc.)

Thermal: DSC (differential scanning calorimetry), DMA (dynamic mechanical analysis), HDT (heat deflection temperature), thermal conductivity

Electrical: Surface and bulk conductivity or resistivity (2 and 4-point measurements)

**Past experience with this material or a similar material:**

DuPont has practiced the initial handling and processing of CNT's in a research environment from 2004 until the present time. DuPont has a long history of working with similar materials such as carbon black and graphite (over 15 years for the primary author of this report). The laboratory in which this work was conducted has also worked with other nano-particles and ultra-fine powders since 2003. DuPont history with certain nanoscale materials dates to the 1950's (Ludox® colloidal silica).

**Potential benefits/positives of the material:**

The expected benefits in this application include the following: Lighter, stronger, tougher materials, electrical and thermal conductivity increases, wear resistance, novel combinations of mechanical, electrical and thermal properties, potential novel appearance and surface properties. CNTs are one of the highest modulus, stiffness and strength materials per unit weight with very high aspect ratios. CNTs have very high thermal and electrical conductivities. CNTs are unique engineered nano materials.

**Potential risks/negatives of the material:**

This work was limited to research and development within DuPont facilities. However, DuPont considered future commercial scenarios, as follows. The product transfers for such materials will typically be limited to a few tiers (CNT – supplier – DuPont – OEM parts maker – auto assembler – consumer). Currently, first generation automotive parts have a marker showing product identity code; hence tracking of materials back to the source would be feasible. In such applications, we would see relatively limited potential for exposure in use.

At the other extreme, pellets could be sold to a distributor who sells to a wide array of downstream customers for applications we could not track. Materials transfers in this case could have multiple intermediate steps: distribution, further compounding, molding, shaping, machining, recycling operations, toll operators, etc.

The type of CNT, manufacturing processes and subsequent processing might affect the toxicity and other risk-relevant characteristics in ways that are not easily be predicted based on present scientific knowledge. At this R&D stage, a general overview of the toxicological literature on CNTs is provided, with full recognition that the available studies may not directly apply to the specific CNTs that are or may become of interest to DuPont. The value of the literature review is to recognize the available published literature and the potential issues to be considered as the potential product moves forward.

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*Health:* A recent literature review on CNT toxicity cites a number of in vivo studies that indicate that pulmonary exposure to CNTs in sufficient quantities could result in adverse health effects (Helland et al. 2007).

That review also includes summaries of in vitro studies that demonstrate uptake of CNTs in numerous cell types, in some cases with evidence of oxidative stress and decreased cell viability (Shvedova et al. 2003; Kagan et al. 2006). It should be noted that both studies indicate that the iron catalyst used in production of the CNTs may be in whole or in part responsible for the observed effects. This re-asserts the observation (made just above) for CNTs, of the potential for residual catalysts or surface treatments to significantly influence the toxicology of a specific CNT material. Thus far, the evidence for oxidative stress to cells exposed to CNTs is unclear. Stress could be due to the CNT system, the residual catalyst or other factors.

As product development advances, Life Cycle Assessments for potential exposure will need to consider dry bulk handling by suppliers, safety in DuPont manufacturing facilities, handling and recycle or disposal of defective material, clean-up of operating areas, normal waste disposal, customer operations such as grinding, machining, or sanding, and final product disposition at end-of-life.

*Environmental:* Less information is available regarding potential environmental impacts, but a recent paper by Smith and colleagues demonstrate that CNT exposure of rainbow trout to CNTs solubilized using sodium dodecyl sulfate (SDS) resulted in respiratory toxicity and possibly neurotoxicity (Smith et al. 2007). Because it is known that treatment or modification of the surface of CNTs can alter toxicity (e.g., see Sayes et al 2006), the use of SDS to solubilize the CNTs may have contributed to the observed results. While it has generally been assumed that CNTs would aggregate and be unavailable in aqueous environments, a study by Hyung et al. (2007) determined that naturally occurring organic matter in river water can serve a surfactant function to keep individual MWCNTs stabilized in the aqueous phase.

Composites manufacturing process will determine how much waste is generated (e.g. cutting of sheets generates wastes; plops, yield – off quality parts, etc.). Additional research will be needed for the determination of risks to ecological receptors, the potential for indirect human exposures, and the handling of such wastes to mitigate risks.

**Sources of additional information:** See references section and Attachment 1.

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**Section 2 —Profile Lifecycles**

Define and catalog the known and anticipated activities in a material’s lifecycle in the following table, detailing both the product form and the operations and activities that occur at that stage of the product lifecycle. Include activities within the user’s control as well as those activities upstream or downstream of the user.

The lifecycle projections in the table below are for multiple applications and manufacturing scenarios.

<b>Lifecycle Profile</b>		
<b>Material Lifecycle Stage</b>	<b>Material Form(s)</b>	<b>Operations and Activities</b>
<b>Material Sourcing</b> Particle Manufacture (synthesis, packaging) Particle shipping Warehousing	Dry particles or slurries	Synthesis Separations /recycling Packaging/Shipping Storage Waste disposal
<b>Manufacturing Level I</b> Masterbatch processors, compounding companies or resin producers	Dry particles or slurries "In process" particle/resin mixtures Resin pellets	Shipping/Receiving Handling and mixing operations (dispersion into polymer) Clean up Storage Waste disposal
<b>Manufacturing Level II</b> Distributors of pellets	Resin pellets	Storage Handling and shipping of pellets
<b>Manufacturing Level II</b> Resin molders Fabricators	Resin pellets; molded parts Forms (sheets, tubes, rods) Forms	Further compounding Polymer molding (forming, extruding) Cutting, shaping, machining, surface finishing Recycling of waste Grinding, machining, recycling, disposal, handling of defective/off quality parts
<b>Manufacturing Level III</b> OEM Customers for shapes and parts	Molded Part Molded or formed materials	Grinding, cutting, machining, recycling, disposal, handling of defective/off quality parts
<b>Distribution</b> (e.g., retailer)	Parts sold to OEM’s or retailers	Assembly into final products and packaging. Some machining or part alteration possible.
<b>Use/Reuse/Maintenance</b> Consumer / End User	Assembled system (e.g., autos)	Wear and tear during use
<b>End of Life</b> Recyclers Landfill	Recovered parts Un-recovered parts and/or assembled systems	Separating, cleaning, grinding, chopping, milling, re-melting, mixing, re-pelletizing,

Incineration		compounding, and other downstream operations Disposal Burning
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### Section 2A — Develop Lifecycle Properties Profile

Identify and characterize the nanoscale material's physical and chemical properties, including property changes, throughout the full product lifecycle.

#### *Summary:*

Presently CNTs in powder form are of a concentration approaching 100%, typically with 0% to 4% impurities. Masterbatch concentrations may range from 5 – 50 wt. %, with 10-25% being typical. Nanocomposite products may contain 0.1 – 10 wt. % CNTs, with 1 – 5% being typical.

Nanotube diameters range from ~0.4 to > 3 nm for single-walled nanotubes (SWCNT) and from ~1.4 to at least 100 nm for multi walled nanotubes (MWCNT). Nanotube lengths vary from 100nm to several millimeters, depending on type and supplier.

In the air monitoring tests conducted (Attachment 1), MWCNTs were used “as produced” (impurities from manufacturing were not removed). The chemical composition was not characterized and supplier information was limited.

#### *Data needs and actions:*

If DuPont pursues CNT nanocomposites in commercial applications, the necessary information will be obtained or generated to complete the following table for the specific CNT material used in each application, including the identification and quantification of any impurities.

<b>Lifecycles Properties — Summary Table</b>			
<b>Lifecycle Stage*</b>	<b>Manufacturing Level I: Dry Ingredients</b>		
<b>Technical or Commercial Name</b>	R&D Sample: Polymer Nanocomposite/Masterbatch		
<b>Common Form</b>	CNT: Powder feed		
	<b>Result</b>	<b>Method</b>	<b>Remarks***</b>
<b>Chemical Composition</b> (including surface coatings)			
Component 1: MWCNT	Carbon (> 95%), residual catalyst (Fe, Mo, Ni) and other impurities	TOF-Sims, ESCA	Specific composition not provided by supplier
Component 2:			
Component n:			
<b>Crystal Phase/Molecular Structure</b>	Graphite/ Graphene (mostly		Not measured or provided by

	conducting)		supplier
<b>Physical Form/Shape</b>	Dry solid	Visual observation, supplier information	
<b>Particle Size and Size Distribution</b>	10 ± 5nm (diam.) 1-2mm (length)	TEM	Diameter provided by supplier
<b>Surface Area</b>	230±50 m <sup>2</sup> /gm	BET	Supplier info
<b>Particle Density</b>	1.8 – 2.6 gm/cc		Estimates for CNTs from various literature and product information sources
<b>Solubility</b>	Insoluble in water	Not disclosed by supplier	Provided by supplier
<b>Bulk Density</b>	50 kg/m <sup>3</sup>	Not disclosed by supplier	Provided by supplier
<b>Agglomeration/Aggregation State</b>	Agglomerated rope-like structures 5-70µm in diameter	Visual observation, optical microscopy, TEM	Provided by supplier
<b>Porosity</b>			Not measured or provided by supplier
<b>Surface Charge</b>			Not measured or provided by supplier
<b>Lifecycle Stage*</b>	<b>Manufacturing Level I: Nanocomposite</b>		
<b>Technical or Commercial Name</b>	R&D Sample: Polymer Nanocomposite/Masterbatch		
<b>Common Form</b>	CNT: Powder feed, Compounded pellet product		
	<b>Result</b>	<b>Method</b>	<b>Remarks***</b>
<b>Chemical Composition</b> (including surface coatings)			
Component 1: MWCNT	0.1 – 50 wt. %	TGA - ashing	Composition determined by pre-blend weights
Component 2: Polymer matrix (various thermoplastic resins)	50 – 99.9 wt. %		Composition determined by pre-blend

			weights
Component n: Standard plastics additives (plasticizer, heat stabilizer, mold release agent, etc.)	0.1 – 30 wt. %		Composition determined by pre-blend weights
<b>Crystal Phase/Molecular Structure</b>	Not applicable: semi-crystalline or amorphous polymer with no change in CNT microstructure		Not measured
<b>Physical Form/Shape</b>	Solid pellets or injection molded shapes	Visual observation	CNTs encapsulated and dispersed in polymer matrix
<b>Particle Size and Size Distribution</b>	10 ± 5nm (diam.) 1-500µm (length)	TEM	CNTs dispersed in polymer matrix
<b>Surface Area</b>	Not applicable		CNTs dispersed in polymer matrix
<b>Particle Density</b>	1.8 – 2.6 gm/cc		Estimates for CNTs from various literature and product information sources
<b>Solubility</b>	Insoluble in water (polymers used and CNTs)		CNT and resin supplier information
<b>Bulk Density</b>	Not applicable		
<b>Agglomeration/Aggregation State</b>	Qualitative dispersion: agglomerates and individual CNTs	TEM	CNTs dispersed in polymer matrix
<b>Porosity</b>	Not applicable		
<b>Surface Charge</b>	Not applicable: tensile or flex bar surface resistivity: 10 <sup>3</sup> – 10 <sup>14</sup> Ohm-sq	2 point surface resistivity	Depending on concentration, surface conductivity of pellets or molded bars

			varies
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*\*Repeat table entries for each lifecycle stage if properties change.*

*\*\*User may create rows for data on additional properties, if available.*

*\*\*\* E.g., reference, source of data, degree of certainty.*

**Additional Notes:**

General comment: DuPont will purchase nano-fillers, like CNTs from external material suppliers for its research and development applications within the scope of this case study. Many of these suppliers are small companies or start-ups who may not have the resources or capabilities to characterize materials. More nano-filler suppliers are located overseas. It is more difficult to obtain information from such sources when the information is not explicitly required by regulations or import rules. Furthermore, many suppliers will not disclose any chemical analysis and the supply terms may prohibit purchasers from analyzing samples. Finally, many materials are new and may represent experimental research and development samples, and thus are not characterized by the supplier. Certainly, as such projects progress towards commercialization, this information is necessary, and mechanisms would need to be developed in cooperation with the suppliers to obtain this information.

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## **Section 2B — Develop Lifecycle Hazard Profile**

Gather information and characterize the material's potential health, environmental, and safety hazards over the entire lifecycle.

### ***Summary:***

Limited CNT toxicity testing has been conducted by DuPont on materials other than those used in this test case. Because different manufacturing processes result in CNTs with different physical and chemical properties, toxicity is expected to be CNT-specific and generalizations likely cannot be made.

A number of *in vivo* mammalian toxicity studies on CNTs have been published, as well as a larger number of *in vitro* assays (see review by Helland et al., 2007), including a study by David Warheit (DuPont Haskell Laboratory, Newark, DE, USA) involving pulmonary exposures in rats via intratracheal instillation. Much less is known about potential hazards to ecological receptors and fate and transport in the environment. One recent study indicates that exposure of rainbow trout to CNTs in water (solubilized using sodium dodecyl sulfate) results in respiratory toxicity and indications of neurotoxicity (Smith et al. 2007). It is not clear that the results of these early studies can be readily generalized. The methods used for solubilization, surface treatment, and functionalization can affect toxicity (Sayes et al. 2006). Cheng and Cheng (2007) reported a slight delay in zebrafish hatching rate when incubated with SWCNTs. The US Environmental Protection Agency's recent Nanotechnology White Paper (EPA 2007) identifies important testing issues for both human and ecological receptors.

The very low volumes being used by DuPont currently solely for R&D purposes, measures taken to mitigate user exposure potential and uncertainty of project success at this time do not justify development of further toxicity data. CNT suppliers did not provide toxicity data, and usually only provide generic MSDS sheets. Thus, the laboratory practices used for handling ultra-fine powders and nanoparticles cited in this case study were developed to contain and control potential exposure. As any specific project becomes successful and the volume increases, DuPont will develop relevant toxicology data appropriate to the specific exposure scenarios with those nanomaterials to be used in the product formulation.

Additional information is provided in the references section of this document.

### ***Data needs and actions:***

If this CNT application progresses beyond the R&D stage, toxicology data will be obtained from the literature and in-house studies conducted by DuPont's toxicology group (Dr. David Warheit et al.) to address the components of this table for the specific materials selected for further development. Data are not entered into these tables, since toxicology studies were not conducted on the CNTs used in this research program. Engineering controls were put in place to minimize potential for environmental release of CNTs used in small quantities and incorporated into thermoplastic resins. See references section for more information on toxicology studies of other CNTs that may serve as bridge materials.

Nanomaterial Lifecycle Hazard Profile — Base Set		
Route	Hazard (characterization, e.g., low, moderate, high, and quantification if available, e.g., LOEL=x mg/kg)	Source of Information (e.g., report number)
<b>Health Hazard Data</b>		
<b>1. Short-term Toxicity</b>		
a. Pulmonary	Not addressed as yet by DuPont due to early stage of R&D with these materials	
b. Oral toxicity		
2. Skin sensitivity		
3. Skin penetration		
<b>4. Genotoxicity</b>		
a. Gene mutation in prokaryotic cells		
b. Chromosomal aberration		
<b>Environmental Hazard Data</b>		
<u>Aquatic Toxicity</u>		
1. Fish (fathead minnow or trout)	Not addressed as yet by DuPont due to early stage of R&D with these materials	
2. Invertebrate (Daphnia)		
3. Aquatic Plant (algae)		
<b>Terrestrial Toxicity (if significant release to terrestrial environments)</b>		
1. Earthworms		
2. Plants		
<b>Environmental Fate Data</b>		
Water Solubility		
Vapor Pressure		
Adsorption/Desorption Coefficients in Relevant Medium* (Soil/Sediment)	Not addressed by DuPont due to early stage of R&D with these materials	
Persistence potential		
Bioaccumulation potential screen		

Base Set of Safety Hazard Data		
Flammability	Ignition in air is not expected, but may occur above 600°C. Carbon dioxide and monoxide and carbon could be released.	Supplier information (MSDS)
Explosivity	Not known to present an explosion hazard	Supplier information (MSDS)
Incompatibility	Incompatibility with strong oxidizing and reducing agents is expected	Supplier information (MSDS)
Reactivity	Non-reactive (stable) under ambient conditions	Supplier information (MSDS)
Corrosivity	Not known to be corrosive under ambient conditions	Supplier information (MSDS)

**Additional information:**

**HAZARDOUS MATERIALS IDENTIFICATION SYSTEM (HMIS)**

Health	Flammability	Reactivity	BASIS
1	0	0	Synthetic graphite powder

**NATIONAL FIRE PROTECTION ASSOCIATION (NFPA)**

Health	Flammability	Reactivity	BASIS
1	0	0	Synthetic graphite powder

**Additional tests on an “as needed” basis**

Nanomaterial Lifecycle Hazard Profile — Additional Tests		
Route	Hazard (e.g., low, moderate, high)	Source of Information (e.g., report number)
<b>Health Hazard Data — Additional tests as needed</b>		
Biological fate and behavior		
Chronic inhalation studies		
Chronic oral studies		
Chronic dermal irritation/skin sensitization	Not addressed by DuPont due to early stage of R&D with these materials	
Reproductive development		
Neurotoxicity Studies		
More extensive genotoxicity studies		
Focused toxicity studies		
<b>Environmental Hazard Data — Additional tests as needed</b>		
ADME studies on aquatic organisms		
Chronic toxicity to aquatic microorganisms and soil dwellers	Not addressed by DuPont due to early stage of R&D with these materials	
Further testing for acute toxicity		
Avian Toxicity		
Population/ecosystem level studies		
<b>Environmental Fate Data — Additional tests as needed</b>		
Activated sludge respiration inhibition		
Microorganism growth inhibition	Not addressed by DuPont due to early stage of R&D with these materials	
Persistence potential in various media		
Potential for transformation via oxidation-reduction reactions		

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*\*\*User may create rows for additional data, if available.*

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**Section 2C — Develop Lifecycle Exposure Profile**

Assess potential for exposure from direct human contact or release to the environment at each stage of the lifecycle. The key deliverable from Step 2C is the *Exposure Characterization* — a summary and synthesis of the gathered exposure information.

**Summary:**

DuPont conducted area and employee exposure monitoring in a batch melt compounding operation using small quantities of representative MWNT's. The air monitoring results are described in Attachment 1. The results show that the samples were below the established OSHA permissible exposure level (PEL) guidelines for Total Dust (PEL 15mg/m<sup>3</sup> for 8 hour TWA) and Respirable Dust (PEL 5mg/m<sup>3</sup> for 8 hour TWA). At the time of this work, there were no established exposure limits for carbon nanotubes. Also, there are currently no established exposure guidelines for particles in the nano-sized range (less than 100 nm or 0.1 μm). Since an arbitrary PEL could not be established for CNT's, the engineering controls developed, PPE used and operating procedures adopted were designed to reduce exposure as low as reasonably achievable. The air monitoring tests showed that exposure potential near the equipment ranged between the non-detection (ND) limit of the measurement and a maximum ND level of 0.65 mg/m<sup>3</sup>. Because CNT use is limited to R&D, DuPont has not, at this time, conducted studies on potential environmental releases that could lead to human or ecological exposures.

**Data needs and actions:**

All laboratory areas will conduct a full Laboratory Process Hazards Review, or the equivalent, working with DuPont experts. Similarly, procedures and controls used in manufacturing area workplaces will be reviewed as appropriate to the particular situation as any specific project becomes successful and the volume increases, with particular attention to the drying, trimming, packaging and waste disposal areas.

If these CNT applications progress beyond the R&D stage, in addition to the better characterization of workplace exposures, the potential for environmental releases that could lead to human and ecological exposures will need to be evaluated.

<b>Potential for Direct Human Contact — Summary Table</b>			
<b>Lifecycle Stage*</b>	<b>Manufacturing Level I (Nanocomposites process)</b>		
<b>Material Form</b>	<b>MWCNT – Powder</b>		
<b>Material</b>	<b>MWCNT (as produced, unpurified)</b>		
<b>Step (e.g. process step, transfer step, ...)</b>	<b>Engineering Controls</b>	<b>Personal Protection Equipment (PPE)</b>	<b>Exposure Potential</b>
Decanting CNT powder from supplier double-bagged packaging into sample pan	Ventilated enclosure (inward airflow into exhaust	Dust mask (N100 HEPA filtering respirator), disposable lab	Potential for short-term inhalation or

	system), Exhaust system fitted with bag-in, bag-out HEPA filter, portable HEPA filter unit to collect localized dust generated	coat, Tyvek® gauntlets, Nitrile gloves	dermal exposure
Pre-blending solid ingredients in sample pan	Ventilated enclosure (inward airflow into exhaust system), Exhaust system fitted with bag-in, bag-out HEPA filter, portable HEPA filter unit to collect localized dust generated	Dust mask (N100 HEPA filtering respirator), disposable lab coat, Tyvek® gauntlets, Nitrile gloves	Potential for short-term inhalation or dermal exposure
Adding sample to batch mixer	Hot process vapor ventilation trunks (building exhaust system), Exhaust system fitted with bag-in, bag-out HEPA filter, portable HEPA filter unit to collect localized dust generated	Dust mask (N100 HEPA filtering respirator), Tyvek® gauntlets, Nitrile gloves, Nomex lab coat (melt processing), leather gloves (melt processing)	Potential for short-term inhalation or dermal exposure
Transferring Nanocomposite sample to molding machine	Sample transferred directly from mixer to hot-sample cylinder, then placed in injection molding machine – no	Dust mask (N100 HEPA filtering respirator), Tyvek® gauntlets, Nitrile gloves, Nomex lab coat (melt processing), leather gloves (melt processing)	De minimus exposure potential

	exposure to operator). Hot process vapor ventilation trunks (building exhaust system), Exhaust system fitted with bag-in, bag-out HEPA filter		
Removing molded nanocomposite sample bar		Nomex lab coat (melt processing), leather gloves (melt processing)	De minimus exposure potential
Transferring sample bars for physical property testing	Sample bars in plastic bags or paint cans	Nomex lab coat (melt processing), leather gloves (melt processing)	De minimus exposure potential
Testing bars (analytical)			De minimus exposure potential
Cleaning batch mixer	Hot process vapor ventilation trunks (building exhaust system), Exhaust system fitted with bag-in, bag-out HEPA filter, Portable HEPA filter unit to collect localized dust generated (if necessary)	Nomex lab coat (melt processing), Leather gloves for brushing, etc.	Potential for short-term inhalation or dermal exposure
Cleaning sample preparation area	Wet wipe with multi-purpose liquid cleaner applied to paper towels (or similar disposable wipes)Wet wipe wipes bagged.	Dust mask (N100 HEPA filtering respirator), Tyvek® gauntlets, Nitrile gloves, Nomex lab coat (melt processing), leather gloves if	Potential for short-term inhalation or dermal exposure

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	Ventilated enclosure (inward airflow into exhaust system), Exhaust system fitted with bag-in, bag-out HEPA filter, portable HEPA filter unit to collect localized dust	needed (melt processing)	
Disposing clean-up waste	Bagged during cleanup, incineration		De minimus exposure potential
Disposing test samples	Incineration or landfill		De minimus exposure potential

*\*Repeat table entries for each lifecycle stage.*

**Elaboration: Direct Human Contact**

**Lifecycle Stage: Manufacturing Level I**

Step Name: Nanocomposite synthesis by melt compounding

Material Form: MWCNT – Powder from supplier. Output of process: polymer nanocomposite pellets or injection molded test bars (in product research and development phase in laboratory environment)

Number of People Potentially Exposed: 2 laboratory technicians

Potential Routes for Exposure (e.g., inhalation, ingestion, eye, dermal): Dry powder in open bags, jars and sample pans – inhalation, dermal and eye.

Personal Protection Equipment: Fitted dust mask (N100 filtering face piece - 3M 8233), rear-tie disposable lab coat (Tyvek® or Sontara®) or Tyvek gauntlets, Nitrile gloves, Nomex® lab coat (required for melt processing, not disposable – i.e. gauntlets and disposable lab coat worn over Nomex lab coat) and leather gloves (required for melt processing).

Engineering Controls: HEPA ventilation system (mobile vacuum unit), ventilated enclosure for sample weighing and preparation. Addition of HEPA filter in exhaust system to trap powder particles that may escape into ventilation trunks required for vapor removal from molten polymers.

Procedures: Written Standard Operating Procedures (SOPs) covering all ultra-fine powder handling and cleanup steps at sub-kilogram quantity level used in the product and process research and development stage. No additional controls were applied for CNTs. DuPont

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laboratory personnel applied a standard Process Hazards Review process to identify potential hazards in the lab for a broad class of nanoparticle and nanocomposite sample handling and processing experiments. A standard DuPont Management of Change process was applied for handling CNTs. SOPs were written, modified and signed-off by line management, the principal investigators and laboratory research technicians involved in the work. The SOPs include step-by-step operational instructions, what PPE to wear, when and how to apply localized engineering controls, and how to clean up and dispose of waste and disposable PPE.

Exposure Potential: Qualitative: Overall exposure potential is low, due to localized isolation of material during each processing stage (HEPA filter unit and sample preparation in ventilated enclosure). Exposure potential to CNT agglomerates is greatest in the sample preparation stage (decanting material from bag or jar), sample transfer stage (adding material from metal pans into the mixing equipment) and during cleanup of the sample preparation enclosure and around the equipment. Conductive CNTs may also have an electrostatic dispersal potential. Since they are stored in plastic containers or bags, they may accumulate a static charge and be attracted to metal surfaces (for example, the ventilated enclosure used to prepare samples was constructed of metal and is grounded by design).

Estimated Exposure and Dose: See Attachment 1. The established OSHA permissible exposure guideline (PEL) for Total Dust is PEL  $15\text{mg}/\text{m}^3$  for 8 hour TWA, and Respirable Dust is PEL  $5\text{mg}/\text{m}^3$  for 8 hour TWA. Currently, exposure limits have not been established for CNTs. Also, there are no established exposure guidelines for particles in the nano-sized range (less than 100 nm or  $0.1\ \mu\text{m}$ ). Since an arbitrary PEL could not be set for CNTs, the engineering controls developed, PPE used and operating procedures adopted were designed to reduce exposure to as low a level as reasonably achievable. The air monitoring tests showed that exposure potential near the equipment ranged between the non-detection limit of the measurement and a maximum of  $0.65\text{mg}/\text{m}^3$ . Current work practices and controls appear to be adequately controlling the exposures. Actual exposure through inhalation or skin contact is estimated to be well below the detection limit, assuming that the PPE is effective. DuPont is testing the effectiveness of dust masks using other nanoparticles and laboratory equipment as a part of the Nanoparticle Occupational Safety and Health consortium effort.

Unknowns and Uncertainties: Globally, considerable effort is underway to recognize the potential hazard, evaluate the hazard and exposure potential, and safely control the use of nano-scale materials. As the development of new products using CNT's progresses through later stages, DuPont will take the appropriate steps to address these unknowns.

The potential for direct human contact with CNTs throughout the value chain and in non-occupational contexts resulting from the handling or use of CNTs or associated products is an additional uncertainty that would need to be addressed if material or product development were to proceed beyond the R&D stage.

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If DuPont should decide to move toward commercialization of such CNT nanocomposite products, these issues will be addressed. Such a program will involve experts from the businesses (engineers, chemists, manufacturing, and product stewards), the research community (materials science and process engineering), the DuPont toxicology organization, and safety, health and environmental consultants and practitioners. In the interim, DuPont is playing a proactive role with government regulatory agencies and leading universities in this area to begin to address these unknowns.

<b>Potential for Environmental Release — Summary Table</b>			
<b>Lifecycle Stage*</b>	Manufacturing I: R&D – Nanocomposite evaluation		
<b>Material</b>	Carbon nanotubes		
<b>Step (e.g. process step, transfer step, ...)</b>	<b>Potential Release Medium (e.g., Air, Water, Soil)</b>	<b>Engineering Controls</b>	<b>Release Potential</b>
Dry Sample preparation	Air	Localized HEPA filter, ventilated enclosure w/ HEPA line filter	Low discharge potential to ambient air
Sample transfer to mixer	Air	Localized HEPA filter	Low discharge potential to ambient air
Area cleanup	Air, Waste	Wet wipe with multi-purpose liquid cleaner applied to paper towels (or similar disposable wipes), Localized HEPA filter, bagging of wastes	Low discharge potential to ambient air
PPE removal	Air, Waste	Removal and bagging of disposable garments and PPE. Wet wipe local area where PPE was removed with multi-purpose liquid cleaner applied to paper towels	Low discharge potential to ambient air

*\*Repeat table entries for each lifecycle stage.*

**Elaboration: Potential for Environmental Release**

Lifecycle Stage: Manufacturing I – Nanocomposites Research and Development

Step Name: Nanocomposite sample preparation and evaluation

Potential Release Medium (i.e., routes of entry): Air

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Engineering Controls: PPE, Localized HEPA filter, ventilated enclosure w/ HEPA line filter as described above.

Procedures: SOPs specify how and where to open CNT source bag or jar and decant into weigh pans in a ventilated enclosure. Local HEPA ventilation applied during sample prep. Same basic procedure is used to transfer samples from weigh pans or jars into melt mixing equipment. Ventilation trunks can extract CNTs (if somehow released into the air) into the exhaust system, but they are trapped in in-line HEPA filter. Area cleanup, waste removal and PPE removal may generate airborne particulates, but potential is expected to be low.

Release Potential: Low with localized containment as described above. Potential spill cleanup would use the same basic procedures with localized containment and HEPA extraction.

Map Fates of the Material (e.g., degradation, transformations, or transfers to other media): Estimated Exposure and Dose: No detection of CNTs as per monitoring study (Attachment 1).

Unknowns and Uncertainties: Globally considerable effort is underway to recognize the potential hazard, evaluate the hazard and exposure potential, and safely control the use of nano-scale materials.

There are few studies evaluating the fate of CNTs in the environment. While it has generally been assumed that CNTs would aggregate and be unavailable in aqueous environments, a study by Hyung et al. (2007) determined that naturally occurring organic matter in river water can serve a surfactant function to keep individual MWCNTs stabilized in the aqueous phase. Additional information would need to be gathered regarding the environmental fate and transport and subsequent exposures prior to any use of CNTs by DuPont. The following questions have not been addressed due to the current early stage of research into these applications:

- What is the ultimate environmental fate of the material?

- Does it accumulate in a particular environmental sink?

- What are the populations (human and ecological) that may be exposed via environmental releases?

- What is the bioaccumulation potential?

If DuPont should decide to move toward commercialization of such CNT nanocomposite products, these issues will be addressed. Such a program will involve experts from the businesses (engineers, chemists, manufacturing, and product stewards), the research community (materials science and process engineering), the DuPont toxicology organization, and safety, health and environmental consultants and practitioners. In the interim, DuPont is playing a proactive with government regulatory agencies and leading universities in this area to begin to address these unknowns.

<b>Environmental Fate and Transport — Summary Table</b>		
<b>Characteristic</b>	<b>Information</b>	<b>Source of information</b>
<b>Distribution among media (partition coefficients)</b>		
Adsorption-desorption to media subject to exposure (e.g., soil, sediment, or sludge)	N/A	
Persistence (including identification of breakdown products)	N/A	
Biodegradability (only for organic-based materials)	Not addressed by DuPont due to early stage of R&D with these materials	
Photodegradability/Phototransformation		
Stability in water (Hydrolysis)	N/A	
<b>Bioaccumulation potential</b>		
Octanol-Water Air/Water Partition Coefficient	N/A	
Bioconcentration Factor	N/A	
* N/A — information not available		

Exposure Data — Summary Table					
Nanomaterial Manufacture (Nanocomposite Sample Preparation)					
Information					
Stage of Development	R&D				
Number and Location of Manufacturing Sites	No Manufacturing sites – 1 Research facility, 1 laboratory				
Annual Production Volumes (current & expected)	Research samples: 1-2kg CNT consumption into 50kg polymer				
Manufacturing Site's NAICS code					
Manufacturing Method	Melt processing				
Number of workers handling nanomaterials at the manufacturing site	CNTs – 4 research technicians in the nanocomposites laboratory used in this case study				
Industrial Functions (e.g., adhesive, coloring agent)	Percent of Production	Physical Form & Concentration			
Function 1: Masterbatch concentrate	25	Plastic pellets with <50% CNTs encapsulated in thermoplastic polymer matrix			
Function 2: Nanocomposite for mechanical reinforcement and electrical/thermal conductivity	75	Plastic pellets, molded test bars or films with <10% CNTs encapsulated in thermoplastic polymer matrix			
Material Processing					
Type of downstream industrial product	This is an internal R&D Program. Downstream applications have not yet being established				
Number of commercial products					
NAICS code					
Industrial Functions	Percent of Production	Number of Sites	Numbers of Workers at Site	Number of Workers Exposed	
Function 1:					
Function 2:					
Function 3:					
Function n:					
Material Use					
Product Type	Percent of Production	Setting for Use (homes, outdoors)	Concentration in Product	Released During Use?	Est. Number of Exposed Users
Product Type 1:	This is an internal R&D Program. Downstream applications have not yet being established				
Product Type 2:					
Product Type 3:					
Product Type n:					

<b>Distribution/Storage</b>		
Methods of Delivery and Storage		
Manufacturer	CNT supplier – plastic containers or bags (double bagging) inside cardboard boxes, some with packing material. Standard shipment.	
Processors	DuPont – CNT nanocomposites in pellet form – CNT encapsulated in polymer matrix. Pellets (~ 2 – 5 mm spheres or cubes) in sealed bags or plastic containers. For research samples, material in bags transported in secondary containers (plastic pails) to prevent spills. Commercially, DuPont would package pellets in sealed bags, lever packs, tote bins or in large rail car shipments.	
Distributors	sealed bags, lever packs, tote bins	
Retailers	Molded, packaged parts, films or assembled goods	
Consumers	Molded, packaged parts, films or assembled goods	
<b>Post-Use Management</b>		
	Expected disposal methods	Expected Recovery/Reuse/Recycle Methods
Manufacturer	Incineration, landfill or (preferably) recycling	Filtration in incineration, recycle by melt processing and compounding
Processors	Recycling of plastic parts	
End-Users	Recycling of plastics	

The following questions are most appropriately addressed in later stages of development and commercialization, when there is greater certainty regarding application scenarios:

Elaborate on the types of employees, handling practices, and environmental containment and control equipment used to mitigate exposure potential at the manufacturing site(s) and the downstream processing site(s).

Elaborate on the use the material in commercial and consumer products. Is there potential for exposure to the nanomaterial? If so, describe the circumstances. Describe any recommended controls for use. Describe recovery or recall techniques. Are the products intended for use by children or other sensitive populations?

Elaborate on the post-use management of the material across the lifecycle:

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### Section 3 — Evaluate Risks

A synthesis of information collected in Step 2 to produce a **Risk Evaluation** — estimates of the nature, likelihood, and magnitude of adverse effects on human health and the environment.

**Summary:** A systematic assessment of risk was not considered appropriate at this stage of development, because of the very low volumes of CNTs being used by DuPont currently solely for R&D purposes, the diverse range of materials being evaluated, the uncertainty about the specific nature of probable applications and their associated user exposure scenarios, and the uncertainty of project success at this time. As any specific future project enters later stages of development, program leaders will work with DuPont experts to assess risks appropriate to the materials of choice and the specific exposure scenarios.

**Data needs and actions:**

<b>Risk Evaluation — Summary Table*</b>		
<b>Risk Type</b>	<b>Nature, Magnitude, and Probability</b>	<b>Source(s) of Risk Assessment</b>
<b>Human</b>		
<b>Respiratory</b>	Nature: Inhalation of airborne material in a research setting Magnitude: Low Probability: Potential for risk to receptors is low	Attachment 1 air monitoring of process operations. Reference section for studies with other CNTs.
<b>Dermal</b>	Nature: Worker contact with material in a research setting. Magnitude: Low Probability: Potential for risk to receptors is low	Attachment 1 air monitoring of process operations. Reference section for studies with other CNTs.
<b>Ingestion</b>	Nature: Worker contact with material in a research setting. Magnitude: Low Probability: Potential for risk to receptors is low	Attachment 1 air monitoring of process operations. Reference section for studies with other CNTs.
<b>Eye irritation</b>	Nature: Worker contact with material in a research setting. Magnitude: Low Probability: Potential for risk to receptors is low	Attachment 1 air monitoring of process operations. Reference section for studies with other CNTs.
<b>Other health</b> (e.g., reproductive, developmental, neural)	Nature: Worker contact with material in a research setting. Magnitude: Low Probability: Potential for risk is low	Attachment 1 air monitoring of process operations. Reference section for studies with other CNTs.
<b>Environmental</b>		

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<b>Aquatic</b>	Nature: Worker use of water in laboratory. Magnitude: Low Probability: Potential for risk to receptors is low	Attachment 1 air monitoring of process operations. CNTs contained within laboratory environment designed for nanocomposites processing. Lab procedures for preparation, cleanup and disposal does not generate waste water.
<b>Avian</b>		
<b>Mammalian</b>		
<b>Soil</b>	Nature: Land Magnitude: Low Probability: Potential for exposure and risk to receptors is low	Attachment 1 air monitoring of process operations. CNTs contained within laboratory environment designed for nanocomposites processing.
<b>Other</b> (e.g., sludge)	Nature: Incineration ash Magnitude: Low Probability: Potential for exposure and risk to receptors is low	Bottom ash is contained and stored in special landfill. No data on ash composition from CNT nanocomposite incineration.

*\*Information contained in this table is based on existing studies. Where no information is available, a reasonable worst case assumption may be made.*

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**Section 4 — Assess Risk Management**

Determine how to minimize or eliminate any potential adverse impacts throughout the product’s lifecycle. The key deliverable from Step 4 is the *Plan for Risk Management* — a summary of the gathered exposure information and a plan for risk management, monitoring, compliance, and reporting.

**Summary:** DuPont is handling CNTs as if they are potentially hazardous materials. DuPont will establish a PEL as more monitor data are collected in laboratories using CNTs for different applications. For example, should DuPont’s businesses support the development of a nanocomposite product requiring a continuous compounding process using CNTs, new engineering controls and air monitoring evaluations will be conducted to establish a PEL.

Improvements may be required of CNT suppliers in packaging to prevent accidental spillage during shipping or when received and opened for use. Many ultra-fine powders are shipped in sealed bags and boxes, with no special consideration for containing nanoparticles. Storage of CNTs may also require improvement by using secondary containment in dedicated areas. Specific monitoring and sampling tests should be conducted.

**Data needs and actions:** While CNT compounding and molding experiments in the DuPont nanocomposites laboratory environment were tested for potential exposure, other equipment and operations should be monitored as well. Reproducibility data are needed and improvements made to the facility, PPE and operating procedures should be verified with follow-up tests. An action plan depends on the resumption of the research in this area.

**Review cycle and conditions:**

**Plan and timeline for risk management, monitoring, compliance and reporting:** Additional risk management steps are contingent upon resumption of project support and funding from DuPont. At this time, research for this CNT application has been suspended.

No entries are made in the following table for the nanomaterial manufacturing stage. DuPont purchased MWCNTs from a supplier.

<b>Material Safety and Handling (manufacturer of nanomaterial)</b>		
<b>Material Hazard Event</b>	<b>Recommended Precaution/Action</b>	<b>Expected effectiveness of recommended action (e.g., what level of exposure will be achieved)</b>
<b>Receipt</b>	DuPont is not the manufacturer of these materials	
<b>Process</b>		
<b>Storage</b>		
<b>Handling</b>		

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<b>Spills</b>		
<b>Transport</b>		
<b>Packaging</b>	DuPont is not the manufacturer of these materials	
<b>Use</b>		
<b>Disposal (materials)</b>		
<b>Other:</b>		

<b>Material Safety and Handling (nanomaterial user)</b>		
<b>Material Hazard Event</b>	<b>Recommended Precaution/Action</b>	<b>Expected effectiveness of recommended action (e.g., what level of exposure will be achieved)</b>
<b>Receipt</b>	Secondary containment, perhaps in re-usable conductive plastic containers	Prevent accidental spills in shipment and handling. Contain potential residual CNTs on outside of packages. Potential to eliminate release or exposure under normal operations.
<b>Processing</b>	PPE, localized engineering controls and operating procedures applied for ultra-fine powders and nanoparticulate solids	Exposure levels documented in the monitoring test Attachment 1.
<b>Storage</b>	Secondary containment, perhaps in re-usable conductive plastic containers	Prevent accidental spills in transfer and handling. Potential to eliminate release or exposure under normal operations.
<b>Handling</b>	PPE, localized engineering controls and operating procedures are applied for ultra-fine powders and nanoparticulate solids	Exposure levels documented in the monitoring test Attachment
<b>Spills</b>	A wet wipe down approach is specified in the operating procedures. Vacuuming is prohibited. PPE, localized engineering controls and operating procedures are applied for ultra-fine powders and nanoparticulate solids.	Cannot estimate exposure levels. Spill simulation was not conducted (material is expensive and only small quantities available)
<b>Transport</b>	Secondary containment, perhaps in re-usable conductive plastic containers	Potential to eliminate release or exposure under normal operations, and minimize potential for spills in the event of an accident or high-impact event.
<b>Packaging</b>	Secondary containment, perhaps in re-usable conductive plastic containers. Dual plastic bags may be	Potential to eliminate release or exposure under normal operations, and minimize potential for spills in the event

	inadequate to prevent puncture-type spillage.	of an accident or high-impact event.
<b>Use</b>	Test samples or nanocomposite pellets are used with no special controls.	Exposure risk should be extremely low. Post processing of nano-TiO <sub>2</sub> nanocomposite articles showed that micron particles were created during machining (grinding) and that nanoparticles remained encapsulated in the host polymer. CNT nanocomposite post machining tests were not performed. Research samples were limited to in-house analytical testing.
<b>Disposal</b> (including packaging materials)	PPE and localized engineering controls and operating procedures applied for cleanup of powders. A wet wipe down approach is used to collect powder waste. Waste and disposable PPE are bagged, sealed and sent for incineration or landfill as designated by site policy.	Exposure risk should be low, since SOPs are in place for bagging waste, packaging materials and used PPE, then disposing via incineration.
<b>Other:</b>	<p>Portable and exhaust HEPA filter systems filter exchange and cleanout procedure: PPE and localized engineering controls are employed. Filters are bagged for incineration or landfill.</p> <p>Laboratory access is restricted to the research technicians and principal investigators during processing operations.</p>	Risk of exposure is the same as that during normal processing, since the same preventative and containment methodology is applied.

This project was an in-house research evaluation. CNT nanocomposite samples were prepared and tested in DuPont laboratories. End use handling of ASTM tensile and flex bars is described below. At this stage, CNTs are dispersed and encapsulated in the polymer.

<b>Material Safety and Handling (end-product user)</b>		
<b>Material Hazard Event</b>	<b>Recommended Precaution/Action</b>	<b>Expected effectiveness of recommended action</b> (e.g., what level of exposure will be achieved)
<b>Receipt</b>	Bars are stored in plastic bags or air-tight cans, consistent with standard practice of handling polymer test bars. No special handling was used.	Exposure risk should be extremely low and nanoparticles in the air were not measurable (see Attachment 1 for handling of bars)
<b>Storage</b>	Bars are stored in plastic bags or air-tight cans, consistent with standard practice of handling polymer test bars. No special handling was used.	Exposure risk should be extremely low and nanoparticles in the air were not measurable (see Attachment 1 for handling of bars)
<b>Handling</b>	Bars are removed from bags or cans and handled without additional PPE or precautions	Exposure risk should be extremely low and nanoparticles in the air were not measurable (see Attachment 1 for handling of bars)
<b>Spills</b>	No special precautions, since bars are stored in plastic bags.	Exposure risk should be extremely low and nanoparticles in the air were not measurable (see Attachment 1 for handling of bars)
<b>Transport</b>	Bars are stored in plastic bags or air-tight cans and transported in this state (carried by hand)	Exposure risk should be extremely low and nanoparticles in the air were not measurable (see Attachment 1 for handling of bars)
<b>Packaging</b>	Bars are stored in plastic bags or air-tight cans	Exposure risk should be extremely low and nanoparticles in the air were not measurable (see Attachment 1 for handling of bars)
<b>Use</b>	Bars are removed from bags or cans and handled without	Exposure risk should be extremely low and

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	additional PPE or precautions during testing (conductivity or mechanical)	nanoparticles in the air were not measurable (see Attachment 1 for handling of bars)
<b>Disposal</b> (including packaging materials)	Bars are bagged and sent for disposal in secondary containment (plastic buckets). Bars and bags are incinerated.	Exposure risk should be extremely low.
<b>Other:</b>		

End of life safety and handling were not covered in this research evaluation program. Test samples were stored or disposed of as described above.

<b>Material Safety and Handling (end of life)</b>		
<b>Material Hazard Event</b>	<b>Recommended Precaution/Action</b>	<b>Expected effectiveness of recommended action</b> (e.g., what level of exposure will be achieved)
<b>Receipt</b>		
<b>Processing</b>	Not addressed by DuPont due to early stage of R&D with these materials	
<b>Storage</b>		
<b>Handling</b>		
<b>Spills</b>		
<b>Transport</b>		
<b>Packaging</b>		
<b>Use</b>		
<b>Disposal</b> (including packaging materials)		
<b>Other:</b>		

*User may add tables for additional steps in the value chain as appropriate*

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### **Step 5. Decide, Document and Act**

Cross-functional review team critically examines compiled information, analyzes the options, documents the resulting analysis, makes decisions, and takes appropriate actions.

Go/no-go/redirect decision and rationale: Research from a safety, health and environmental perspective can proceed based on test results and processes put in place. However, business circumstances caused this project to be suspended. Should DuPont decide to resume research, an improved infrastructure is in place to proceed.

For nanocomposite synthesis at the research scale, a laboratory was designed to process small quantities (typically less than 1kg) of ultra-fine powders and nanoparticles in order to minimize potential exposure of personnel and the environment during sample preparation, melt blending, cleanup and waste disposal stages. Engineering controls, PPE and special operating procedures were implemented as preventative measures. The air monitoring tests described in this example documents and validates the effectiveness of the approach taken. As a result of these and other nanoparticle air monitoring tests, significant capital improvements were made in 2006 and 2007. A new nanocomposites process lab was constructed and a bag-in/bag-out HEPA filtration system was installed in the ventilation system to trap aerosolized powders. Disposable Tyvek® rear-tied gowns are being evaluated as additional PPE.

Additional data needs: 1) chemical analysis of CNTs used, 2) Comprehensive safety and health information from CNT suppliers, government agencies or academia on the specific CNTs (or equivalent types and forms), 3) Monitoring of operations at the next level (continuous melt compounding).

Additional data-collection assignments: To be defined if project is resumed

Product steward: To be defined if project is resumed

Review team: To be defined if project is resumed

Product review cycle: To be defined if project is resumed

Needed actions and responsible persons: To be defined if project is resumed

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### **Step 6. Review and Adapt**

User implements a series of periodic and as-needed reviews to ensure that the information, evaluations, decisions, and actions of the previous steps are kept up-to-date.

List of reviews held (dates): Initial process hazards reviews of the laboratory were held in 2004, with reviews in 2005 and 2006 as laboratory systems were upgraded or modified. All lab equipment and SOPs are reviewed and signed off by line management, the principal investigators and the laboratory research technicians involved in the work.

Conditions that triggered review(s): Comprehensive annual safety reviews are held. Anytime a new piece of equipment is procured or modified, or a new material is to be processed, a hazards review is conducted using DuPont's Management of Change (MOC)

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process. Any new information (peer-reviewed articles or regulatory actions) that elevates concerns over CNTs will prompt a safety and health review.

Changes made in report and rationale (e.g., changes to lifecycle profiles):

Actions taken and rationale (e.g., revised risk management practices):

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### **Additional References:**

#### **CNT Toxicology:**

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## **Attachment 1: Safety, Health and Environmental: Small-scale Processing of Carbon Nanotubes**

### **DuPont FS&RE Industrial Hygiene Group**

*The following report illustrates the SH&E process monitoring efforts conducted by the ESL Industrial Hygiene Group. This test monitored technician and local area particle concentrations in the Rapid Prototyping Center during sample preparation, DSM and Brabender mixer loading, molding and sample post handling operations.*

## **Industrial Hygiene Monitoring Report – Air Monitoring**

**Site:** Experimental Station

**Area:** E323/162

**SBU:** ENGR/DuET

**Date:** December 19 & 20, 2005 and February 8 & 9, 2006

**File #:** ES 06-64

### **1. PURPOSE:**

Air monitoring was conducted to evaluate potential exposure to carbon nanotubes (CNT) while performing extrusion and molding of a mixture of a thermoplastic polymer and CNT. Industrial Hygiene Evaluation was requested perform sampling to help determine if exposure potential is being adequately controlled. Monitoring was performed on representative employees performing the tasks and area samples were collected from various positions in the room. Sample results are listed in the following report.

### **2. DISCUSSION:**

Personal samples were collected from the worker's breathing-zone each day for the duration of the tasks involving the use of CNT and area samples were collected at various positions shown in the attached photos and as described in the results table. Air monitoring and sample analysis was conducted in accordance with NIOSH method 0500 for Total Dust. Samples were analyzed by an American Industrial Hygiene Association (AIHA) accredited laboratory. Also a TSI P-Trak Ultrafine particle counter was used to measure increases in airborne particle levels in order to assess containment and control.

The work being performed involves the use of various types of equipment to perform extrusion, molding and compounding of material. On 12/19/2005 and 12/20/2005 the work involved extrusion and molding of 1% and 3% CNT with the polymer. The steps involved weighing material in the ventilated enclosure. Powder was added to the DSM Micro-compounder by pouring from an aluminum dish. A small metal plunger located below the opening was used to push the material into the DSM. Some dust generation was observed during this part of the procedure. The run temperature was 200 degrees C. After compounding, the

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material was collected in the mold transfer cylinder. Cylinder was then moved to the molding machine. After completion, the molded part was then removed using an air gun. This procedure was performed multiple times.

On 2/8/2006, the procedure performed was very similar with the exception of the final product. Instead of molding the material into bone shapes, material was extruded directly into a water bath and cut pieces were placed into bags. 4 runs were performed. The first 2 were controls and the second 2 were 5% CNT.

On 2/9/2006, the work being performed was on the Brabender (Plasti-corder). Material was weighed and poured from glass jars into Brabender. After processing front plate was removed and material was manually scraped from the block and equipment was cleaned up with a wire brush. Processed material appeared to be highly viscous in consistency.

PPE worn:

- N100 HEPA filtering respirator
- lab coat and Tyvek® disposable gauntlets (or rear-tied disposable gown)
- Nitrile and leather gloves
- Safety glasses with side-shields

Engineering Controls:

- Portable HEPA filtered vacuum cleaner
- Ventilated enclosure for weighing /mixing
- Local exhaust trunk
- Local exhaust canopy

**3. EXPOSURE GUIDELINES:**

**\* There are currently no established exposure limits for carbon nanotubes.**

DuPont Acceptable Exposure Limits (AEL):

**Total Dust:**

**Established OSHA permissible exposure level (PEL) guidelines for Total Dust (PEL 15mg/m<sup>3</sup> for 8 hour TWA) and Respirable Dust (PEL 5mg/m<sup>3</sup> for 8 hour TWA).**

NOTE: The PEL is a standard, and is not specific to CNT's. There was little data available at the time to support the establishment of a CNT-specific PEL. DuPont treats CNTs as potentially hazardous materials, and the engineering controls, PPE used and procedures employed reduce the potential exposure significantly as documented in this report.

**4. RESULTS:**

Table 1. E323/162 Carbon Nano-tube Monitoring, 12/19/2005

<b>Sample #</b>	<i>Type / Name or Location</i>	<b>Time (min)</b>	<b>Vol (liters)</b>	<b>Analyzed for</b>	<i>Results (mg/m<sup>3</sup>)</i>
NANO-051219-01	Personal / Technician (BZ)	130	351	<b>Total Dust</b>	ND < 0.28
NANO-051219-05	Area / right side of DSM	134	331	<b>Total Dust</b>	ND < 0.30
NANO-051219-07	Area / top of hood enclosure	132	317	<b>Total Dust</b>	ND < 0.32
NANO-051219-08	Area / base of the enclosure	135	320	<b>Total Dust</b>	ND < 0.30
NANO-051219-10	Blank	N/A	N/A	<b>Total Dust</b>	--

Table 2. E323/162 Carbon Nano-tube Monitoring, 12/20/2005

<b>Sample #</b>	<i>Type / Name or Location</i>	<b>Time (min)</b>	<b>Vol (liters)</b>	<b>Analyzed for</b>	<i>Results (mg/m<sup>3</sup>)</i>
NANO-051220-01	Personal / Technician (BZ)	155	461	<b>Total Dust</b>	ND < 0.22
NANO-051220-05	Area / right side of DSM	157	377	<b>Total Dust</b>	ND < 0.27
NANO-051220-07	Area / top of hood enclosure	156	348	<b>Total Dust</b>	ND < 0.29
NANO-051220-08	Area / base of the enclosure	156	386	<b>Total Dust</b>	ND < 0.26
NANO-051220-12	Blank	N/A	N/A	<b>Total Dust</b>	--

Table 3. E323/162 Carbon Nano-tube Monitoring, 02/08/2006

<b>Sample #</b>	<i>Type / Name or Location</i>	<b>Time (min)</b>	<b>Vol (liters)</b>	<b>Analyzed for</b>	<i>Results (mg/m<sup>3</sup>)</i>
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BC020806-01	Personal / Technician (BZ)	145	289	<b>Total Dust</b>	ND < 0.35
BC020806-02	Area / top of hood enclosure	224	451	<b>Total Dust</b>	ND < 0.22
BC020806-03	Area / right side of DSM	146	294	<b>Total Dust</b>	ND < 0.34
BC020806-04	Area / 5' from DSM bench 56.5" high	221	449	<b>Total Dust</b>	ND < 0.22
BC020806-08	Blank	N/A	N/A	<b>Total Dust</b>	

Table 3. E323/162 Carbon Nano-tube Monitoring, 02/09/2006

<b>Sample #</b>	<i>Type / Name or Location</i>	<b>Time (min)</b>	<b>Vol (liters)</b>	<b>Analyzed for</b>	<i>Results (mg/m<sup>3</sup>)</i>
BC020906-01	Personal / Technician (BZ)	77	153	<b>Total Dust</b>	ND < 0.65
BC020906-02	Brabender – top right	77	156	<b>Total Dust</b>	ND < 0.64
BC020906-03	Brabender – top left	78	157	<b>Total Dust</b>	ND < 0.64

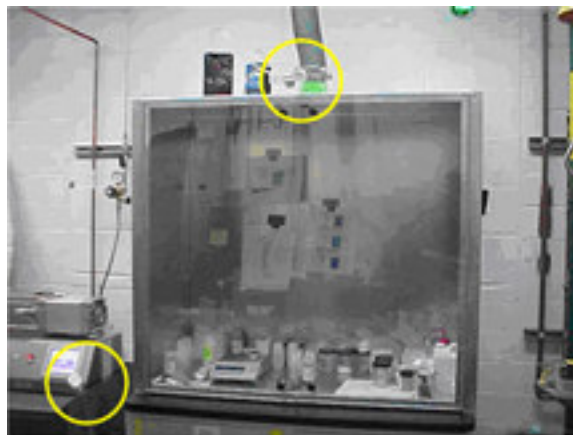
- For non-detects (ND) the results indicated with a '<' value represents the reporting limit for that analysis.

- Breathing Zone (BZ): Limit of Quantification (LOQ) = 0.1 mg / sample

The files below contain all logged data collected using the TSI model 8525 P-Trak Ultrafine Particle counter. The P-Trak (condensation particle counter) direct reading instrument was used to measure particle concentrations emitted from processes performed. This unit can measure particles in the range of 20 to 1000 nanometers. The sample probe was placed in close proximity to the point where material was poured in and around the DSM Microcompounder. Particle count readings quickly rose and fell when material was added to the DSM indicating that particulate was being generated in the size range listed above. Subsequently, counts quickly fell to background levels indicating that engineering controls were effectively collecting airborne particulate matter. Particle count readings were taken at the Portable HEPA filter exhaust (filtered air). Levels dropped to below background levels indicating that HEPA filter was removing airborne particles. At the time of the writing of this report, the P-Trak was a new instrument that had not been validated with aerosolized nanoparticles of known size in a controlled environment. Thus, the measurement response was used qualitatively in this test.

**5. CONCLUSIONS/RECOMMENDATIONS:**

Results show that the samples were below the established exposure guidelines listed in section 3 for Total Dust. There are currently no established exposure guidelines for particles in the nano-sized range (less than 100 nm or 0.1  $\mu\text{m}$ ). Current work practices and controls appear to be adequately controlling the exposures. Continue to use current PPE, including respiratory protection.

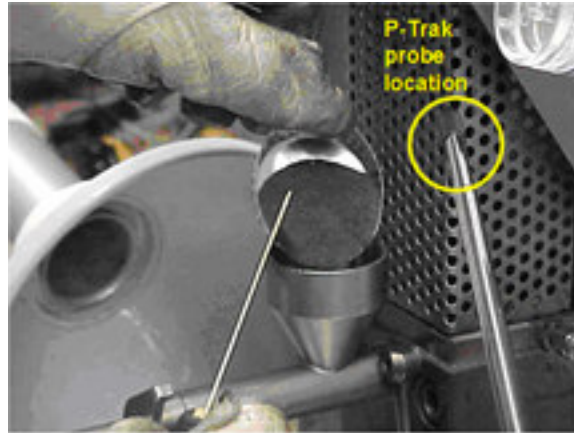


**Figure 1. Ventilated Enclosure/Weigh-up with air sampling devices (12/20/05)**



**Figure 2. Ventilated Enclosure/Weigh-up with CNTs in pans (12/20/05)**

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**Figure 3. Pouring polymer + CNT blend into compounder (12/20/05)**



**Figure 4. Batch melt with air sampling device and HEPA ventilation system in place for loading material (12/20/05)**

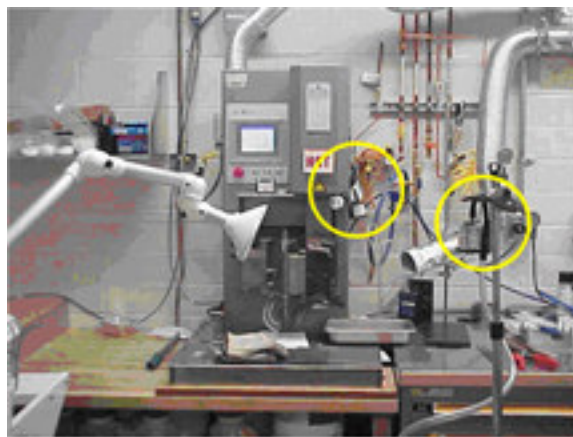


**Figure 5. Injection molding Unit (12/20/05)**

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**Figure 6. Ventilated Enclosure/Weigh-up with air sampling device (2/8/06)**



**Figure 7. Batch melt compounder with air sampling devices (2/8/06)**



**Figure 8. Batch melt compounder extruded material sample (2/8/06)**

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**Figure 9. Brabender Plasti-corder Batch Mixer with air sampling device (2/8/06)**