CASE STUDIES

# GOOD PRACTICE HANDLING CARBON NANO TUBES

## 1. Case metadata

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## 2. Organisations involved

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- Nanocyl s.a., Rue de l'Essor, 4, B-5060, Sambreville, Belgium

## 3. Description of the case

### *3.1. Introduction*

***Carbon Nano Tubes***

Among the various nanomaterials being currently developed multi wall carbon nano tubes (MWCNT) are often of interest due to their great commercial possibilities resulting from their specific properties and the potential benefits they can deliver in many industrial applications.

Three properties of MWCNTs that are especially interesting for industry are:

- electrical conductivity,
- mechanical strength
- thermal conductivity

In order to exploit these properties it is essential for industry to ensure sustainable development of these materials, particularly with respect to managing potential health and safety risks to workers. Workers are after all the first group to be exposed to the carbon nano tubes (CNT).

***Potential Health Risk***

As with any material being developed, scientific data on the health effects in exposed workers are largely unavailable. In the case of nanomaterials the uncertainties are even greater because the characteristics of nanoparticles may be different from those of larger particles with the same chemical composition. Potential hazardous properties of CNT are a matter of ongoing research but there are indications that certain types of CNT may be hazardous if workers or users are exposed through inhalation pathways (Poland et al., 2008). Until the results from research studies can fully elucidate the hazard to human health, precautionary measures are warranted.

Therefore current good practice for the handling of CNT is to minimise potential exposition of workers particularly via inhalation.

***Case study***

This document describes the various risk management measures (RMM) introduced by a commercial scale producer of MWCNT (~40 tons/year) to minimise CNT exposure for workers handling these products. The RMM applied by this company could serve as a good practice advice for handling CNT in general.

## 3.2. Aims

The main aim was to minimise Carbon Nano Tube exposure to workers by the application of various RMM in the production of MWCNT.

## 3.3. What was done, and how?

First, the lifecycle of the MWCNT was analysed in order to identify the potential exposure moments.

The company uses a chemical vapour deposition (CVD) based process for industrial scale production. In chemical vapour deposition a hydrocarbon feedstock is reacted with a cobalt catalyst in a hot furnace to 'grow' the nano tubes, which are subsequently removed from the substrate and catalyst by a simple acid wash. The following steps in the life of MWCNT are either compounding into a polymer matrix or blending with liquid products before being incorporated into a polymer matrix.

The production processes are performed in a closed system. Therefore, exposure to nanoparticles is more likely to happen after the manufacturing process. However, once the MWCNT are encapsulated in the polymer the exposure potential to workers and consumers is expected to be very low. Transfer activities, during the packaging of the material and when introducing the material into the extruder, thus have the highest exposure potential of all activities with the MWCNT.

In line with the hierarchy in the Chemical Agents Directive (the reduce-to-a-minimum principle-article 6 of Chemical Agents Directive 98/24/EC) various RMM were implemented by the company manufacturing MWCNT in order to minimise exposure to these MWCNT while transferring these products.

This was done by implementing:

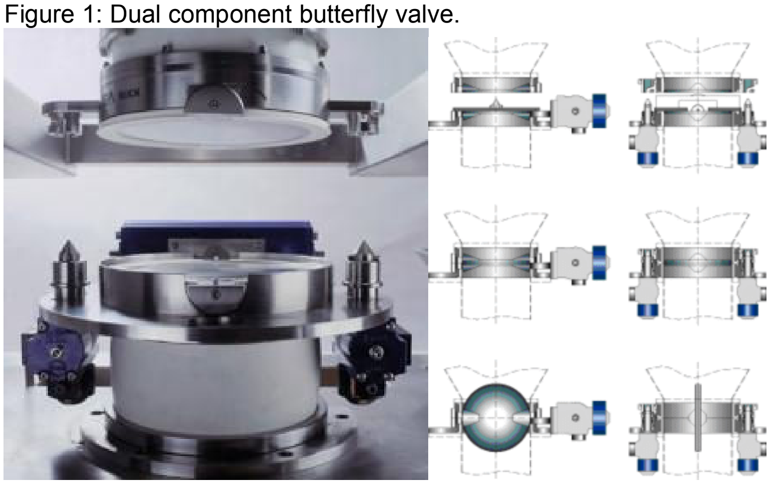
- technical measures at process level (source) to prevent release
- application of collective protection measures at the source,
- appropriate organisational measures,

- measures related to personal protection

In more detail:

At process level, the transfer system is designed to minimise the surface area which comes into contact with the material. The transfer equipment is entirely enclosed within a  high containment area by the introduction of a butterfly valve that can be separated in two closed parts (see Figure 1).

Figure 1: Dual component butterfly valve.



The valve systems consist of an active and a passive valve that are able to seal (dustproof) two different container systems independently of each other. The active (lower part) ‘split valve’ is located on the fixed production unit. The passive split valve is fixed with a collar to a mobile receptacle like a bag or container and has an additional mechanical lock that prevents it from opening on its own without the active unit. The docking of the complementary split-valves results in an effective seal. When the valve is opened the CNT can flow under gravity from one container to the other. A safety device does not allow the opening of the valve when the two parts are separated or not correctly linked.

Collective protection measures applied in this company in order to limit potential emission of CNT from surfaces after disconnection.

- The air is extracted by a dust extraction systems installed on the top of the transfer unit and in the hood where the mobile receptacle is separated from the valve part. To avoid the emission of CNT dusts in the external air, appropriate filter are placed on the outlet of the air extraction system.
- To prevent possible spreading of the material via the shoes an adhesive mat is placed in front of the MWCNT preparation room door.

Personal protection equipment (PPE). To further limit exposure, workers have to wear PPE when they separate the valves and when they remove/install the valve to a new mobile receptacle

- Adequate protection from airborne CNT is obtained by using a filtering face piece respirator type FFP3.
- Dermal exposure is minimised by using disposable protective overall suit covering the head and disposable protective gloves with cuff.
- The protective suits and gloves have to be changed every day. An appropriate procedure of dressing, undressing and the disposal of the suits and gloves has been established.

Appropriate organisational measures are recognised as an essential part of implementing RMM in order to minimise exposure to these MWCNT.

- All workers receive specific information and instructions on the materials and processes, the risks involved, training on the use of collective and personal protective equipments, and training on the use of control systems in place.
- Work processes are clearly described. The work processes include proceedings to reduce potential exposure like: the 'bottom part of butterfly valve is wet-wiped to eliminate possible MWCNT accumulation between both parts of valve'. Any alterations are always carefully documented and approved before putting them into practice.
- Compliance with the instructions, particularly the compliance with required protective measures, is routinely monitored.

Additional
This MWCNT manufacturer also provides guidance to downstream users on how to manage health and safety risks associated with use of the MWCNT. The processes used by the downstream users are most likely very similar to the process in company producing MWCNT. Therefore the guidance to downstream users is closely related to the RMM applied in the production facility described above. The guidance strongly advises on the use of the butterfly valve and gives a procedure of proper use. The guidance also includes strong recommendations regarding the use of local exhaust ventilation, personal protection equipment and a high standard of personal hygiene after handling CNT.

## *3.4. What was achieved?*

By introducing various RMM in the company manufacturing MWCNT, MWCNT exposure has been reduced to a minimum.

This was confirmed by measurements of airborne nanoparticles taken at a number of locations at the MWCNT production site. The data obtained enables CNT concentration to be compared with the 'no effect level' defined on the basis of inhalation toxicological studies. In an inhalation study carried out on rats using commercial samples of MWCNT produced on the specific production site, a Low Observed Adverse Effect Concentration (LOAEC) of 0.1 mg/m³ has been determined (Ma-Hock *et al*. (2009)). By applying a conservative safety factor of 40, it is possible to estimate an internal Occupational Exposure Level (OEL) of 2.5µg/m³.
In the offices, the measured respirable CNT concentration in air of 0.25 µg CNT/m³ is then 10 times lower than the OEL. At the transfer sites; near the extruder and near the packaging unit the respirable CNT concentration was 1.0 µg CNT/m³ and 1.4 µg CNT/m³ respectively. This level is also lower than the OEL.
If we consider that operators do not stay near the packaging unit or in the extrusion room more than one quarter or one half of their working time, the actual exposure dose is 3 to 6 times lower than the OEL even without personal protective equipment. Therefore, according to the measurements made, the exposure to CNT at the plant is below the defined safety limit. However, as we can not exclude the possibility of having concentration peaks from time to time, on the basis of the precautionary principle the use of personal protective equipment at the transfer sites should stay implemented to ensure that the risk is negligible.

### *Success factors*

The main success factors have been the training an instructions of the workers in this company and the inhalation toxicity study.

The training and instructions of the workers results from the goal in the company to prevent or reduce risks related to the use of CNT to their employees and their customers. Therefore, the companies corporate policy is to communicate with employees, customers, suppliers and authorities about its products, processes, and new learning from industry-wide initiatives on health, safety and environment (HS&E).

In order to do so they continuously improve their knowledge about the possible adverse effects linked to the production and use of CNT by:

- collaboration with international experts
- participation in joint regional and global studies,
- maintenance of good relationships with local and regional governments.
- contribution and sharing general HS&E learning through the Producer Association of Carbon Nano Tubes in Europe (PACTE).

Their processes and practices are in keeping with Product Stewardship programs and the Responsible Care® Global Charter that was developed by the chemical industry to help ensure and improve health, safe handling of products, and care for the environment. The guidelines, organisation and training ensure a high standard of safety.

The inhalation toxicity study is an important success factor as the results create the opportunity for quantitative comparison between exposure levels and the company OEL.

By also sharing their knowledge with downstream users this company reduces potential health risks not only for its employees, but for everyone working with its MWCNT. This means that potential worker exposure to MWCNT can be well-managed in other companies as well.

## *3.5. Further information*

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## *3.6. Transferability*

Most of the RMM can be adopted successfully by other companies working with CNT or comparable powdery (nano) products, e.g. the butterfly valve is commercially available.[1]

Guidelines and training material for workers is available in Dutch.

[1] Buck Valve® from GEA Pharma Systems,Keerbaan 70, Wommelgem, Belgium

## 4. References, resources:

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