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Single Wall Carbon Nanotubes—Health, Safety and Environmental Status

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Abstract: SWCNTs (single wall carbon nanotubes) are a universal additive that improves the properties of numerous base materials. Their exceptional physical and chemical characteristics, such as superior conductivity to weight ratio, high flexibility, excellent temperature resistance, ultimate strength, and high length to diameter ratio (about 3,000 times) have been known for several decades since their discovery in 1991 by Japanese physicist Sumio Iijima. However, due to the previous lack of industrial approvals and independent researchers, only recently have extensive and significant data on health, safety and environment aspects been collected. In 2014, OCSiAl debuted the world's first—and currently the only—facility for industry scale production of high-purity TUBALL™ single wall carbon nanotubes at an economically viable price. The unprecedented 10 tons production capacity developed SWCNTs into a technologically and economically feasible product for many industries, such as composites, plastics, coatings, elastomers, and batteries. OCSiAl is also the first company to initiate a variety of single wall carbon nanotubes certification procedures, helping to blaze a trail to further their widespread use. This paper amasses the significant knowledge based on health, safety and environmental aspects of SWCNTs grounded on OCSiAl internal research findings, revealed results of industrial partners and various tests conducted by independent researchers. Among the latter are tests on themorphology and non-cytotoxicity of the TUBALL™ SWCNT substance, as well as the results of the Buehler sensitizing assessment test and Ames test.

Key words: Nanotubes, CNT, nanomaterial, toxicity, nano-safety.

1. Introduction

Nanomaterial is a broad term encompassing a vast number of nanoscale materials, including quantum dots, fullerenes, multi wall carbon nanotubes, single wall carbon nanotubes, and more. Engineered nanoscale materials often have unique electrical and mechanical properties that have made them particularly useful in commercial industries in recent years. The focus of this article is on single wall carbon nanotubes (SWCNTs) and their unique properties, which may have differing environmental, health and safety ramifications than other nanoscale materials.

These nanoscale materials, such as SWCNTs, continue to undergo testing and research regarding their impact on the health and safety of humans, as well as the environment, when in use—especially as they have moved beyond the laboratory and into consumer products in many industries.

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As there is a strong need from the market side to use more and more different nanomaterials, SWCNTs constitute an important part. There is a growing amount of research on the health and safety of conventional nanomaterials (fibers, multi wall carbon nanotubes, etc.). However, there is a lack of research on SWCNTs, which are a very different material, possessing many unique properties, even from morphology side. It should be noted that in contrast to multi-wall carbon nanotubes, carbon fibers or other conductive carbon-based additives, single wall carbon nanotubes demonstrate high flexibility, and consequently reveal several radically different features in terms of health, safety and environmental issues.

There are many tests that will need to be completed as materials continue to develop, and the tests shown in this paper are only the first stage. Sharing the preliminary results as the overall plan moves forward is beneficial to the scientific and commercial

community.

Being the world's largest producer of SWCNT with a 10-ton annual production capacity, OCSiAl is taking the lead in raising transparency of the nature and approach to responsible management of SWCNTs. The company constantly initiates numerous internal and independent tests and research, and has accumulated a significant knowledge base in this field. This paper explores results on health, safety and environmental studies of only TUBALL™ nanotubes and the current status of SWCNTs compliance with the national requirements of the EU, USA and other regions.

2. Health and Safety of Carbon Nanotubes

With the continued development of products containing carbon nanotubes concerns come about the health and safety of the substance to humans and the environment. Many studies have been completed regarding the occupational safe use of carbon nanotubes, as well as in end-use products.

2.1 Exposure to Nanoparticles

As products manufactured using carbon nanotubes move beyond the research and development stage and into end-use applications, human exposure to carbon nanotubes increases. However, research conducted suggests fear of exposure via inhalation, dermal, and GI, as well as systemic translocation, may be premature [1].

Single wall carbon nanotubes are revolutionizing many industries ranging from electric vehicle batteries to engineering and from wearable technology to biomedicine. Thus, the potential risk of exposure to nanoparticles in the development, manufacture, use, and post-consumer stages of these products was evaluated.

Research is being conducted by companies who manufacture carbon nanotubes, like OCSiAl with their TUBALL™ substance, and independent researchers and universities to determine the risks and potential exposure levels.

2.1.1 Exposure via Inhalation

Concern regarding inhalation exposure remains at the forefront of researchers' studies. Nanoparticles, when airborne, can cover expansive distance and lodge in the lungs [2] when inhaled. Studies completed measuring the levels of airborne particles found low levels of exposure [3]. In addition, nanoparticles tend to agglomerate and form larger particles, which settle in the upper airways or Ref. [1]. That seems to indicate a low potential risk of exposure via inhalation.

Inhalation exposure depends on the make-up of the nanomaterials related to their rigidity. TUBALL™ SWCNTs, for instance, are supposed to benot rigid in nature, and therefore currently not classified as a carcinogen to humans, as noted in sections below.

2.1.2 Exposure via Dermal Contact

Wearable technology, stain-resistant clothing and cosmetics made with nanoparticles has increased awareness of dermal exposure more recently. And, as mentioned above, the agglomerations of nanoparticles that settle from the air then become dermal absorption opportunities.

In several studies conducted on human volunteers and animals using sunscreen made with nanoscale material, the particles did not appear to penetrate beyond the stratum corneum of the skin [4]. Considering these studies and others (conducted on penetration of quantum dots and fullerenes), it suggests that certain nanoparticles do not fully penetrate healthy skin. The test results on the exposure of TUBALL SWCNTs can be found in Section 3.3 of the current paper.

3. Health, Safety and Environmental Aspects of TUBALL™ Nanotubes

TUBALL™ nanotubes have already passed a number of various tests providing some clear and essential conclusions about nanotubes nature and safety methods for handling them.

3.1 TUBALL™ Nanotubes Morphology

An SWCNT is an extremely thin, single-layer sheet of graphene that is rolled into a tube. The morphology of TUBALL™ SWCNTs is exceptional, measuring at more than 5 μm in length with a diameter of 1.6 (+/- 0.4) nm. SWCNTs provide a number of unique characteristics, such as superior electrical conductivity, high flexibility and strength, and extraordinary temperature resistance. TUBALL™ are high-purity SWCNTs that consist of ≥ 80% w/w ≤ 94% w/w nanotubes.

The morphology—the form and structure—of TUBALL™ nanotubes makes them distinct in the marketplace. They are 100 times stronger than steel, have the highest length-to-diameter ratio, are one of the best conductors in the world (5 times lighter than copper), and can provide thermal stability up to 2,800 ^{o}C in a vacuum.

TUBALL™ nanotubes have a unique geometry in their structure—one layer of rolled-up graphene—paired with high purity and low moisture. The carbon content is > 99±1 wt%, the moisture is < 5 wt%, and metal impurities of purified TUBALL™ nanotubes are < 1 wt%.

The European Chemicals Agency Board of Appeal published a decision in June 2017 regarding nanomaterials (Board of Appeal A-15-2015). They found that being a nanomaterial is insufficient on its own to justify as a potential concern and mentioned that there is no consistent, causal link yet established between a material's size and hazardous properties.

In a recent IARC publication (IARC Monographs, Vol. 111), the carcinogenic risks of nanomaterials were evaluated. They concluded that there was inadequate evidence in experimental trials on animals to consider SWCNTs as carcinogenic to humans.

Due to their entanglement, TUBALL™ SWCNTs are strongly suppost to be non-rigid fibers—as a result, they do not behave as asbestos-like fibers.

In consequence of the absence of any related indications, TUBALL™ nanotubes are currently not classifiable as to their carcinogenicity to humans. There is no indication for any carcinogenic risk associated with this material today.

3.2 Non-cytotoxicity of TUBALL™ SWCNT

Cytotoxicity focuses on the cell level rather than an organ overall (e.g. lung). In independent testing completed for OCSiAl, several discoveries were made regarding TUBALL™ SWCNTs:

SWCNTs are non-cytotoxic. They do not decrease the survival rate of cells. The rate is close to 100% at 100 μg/mL (compared to MWCNT, which kills almost half of the cells with a low concentration 10-25 μg/mL %). In line with additional data, there is no indication that SWCNTs are more toxic than MWCNT. On the contrary, SWCNT shows a lower toxicity in certain *in vitro* experiments (cytotoxicity in THP cells).

The MWCNTs and SWCNTs in the involved paper show similar properties regarding their effect on inflammatory pathways [5].

3.3 TUBALL SWCNT Exposure via Dermal Contact

TUBALL™ nanotubes tests for skin corrosion and irritation, as well as the Buehler sensitizing assessment test, showed no negative effects. The Reverse Mutation Assay "Ames Test" was completed using Salmonella typhimurium and Escherichia—showing it was not mutagenic. This test is the most widely used initial screen for determining mutagenic potential of chemicals, according to the National Institute of Biology. It is often required by regulatory agencies for registration or acceptance of the product.

3.4 Environmental Aspects of TUBALL SWCNT

The Algal Growth Inhibition Test and Acute Toxicity Test with Daphnia Magna confirmed the non-toxicity of TUBALL™ nanotubes to the environment. Both tests are standard toxicity screenings completed for compliance with regulatory

agencies.

There is no indication that dissolved TUBALL™ single wall carbon nanotubes have any intrinsic ecotoxic properties at all when tested in solution as stipulated by the testing guideline [6].

More tests results, information on ongoing studies and further plans can be found in Tables 1-3.

3.5 Utilization of Materials Improved with Nanotubes

In March 2017, nano-safety testing of different polymer samples containing TUBALL™ was completed. Tests were conducted by VITO, a leading European independent research and technology organization (Fig. 1). Simulation experiments on blank and TUBALL™-nanoaugmented epoxy, high density PE and elastomer (natural rubber, tire type) materials were carried out inside a test chamber and any possible aerosol release was captured and measured with a TEM microscope.

Hardly any micron sized particles were released during the abrading of the TUBALL™ containing epoxy, polyethylene and elastomer material. As shown by the results of the real time measurements, limited nano and micron sized particles were released during Taber abrading, resulting in a low deposition efficiency on the grids. TEM analysis showed some micron sized particles, but no protruding or free standing SWCNTs were found (Fig. 2). Another significant finding was the significant decrease in the number of micro-sized particles released from the TUBALL™-nanoaugmented materials in comparison with the blank materials, depending on the type of material, the range was up to 35%. The results are yet another demonstration of the bonding power of SWCNTs that enable a 3D nanotube network to greatly strengthen the material's structure. This enhancement of a material's physical properties is the subject of ongoing research.

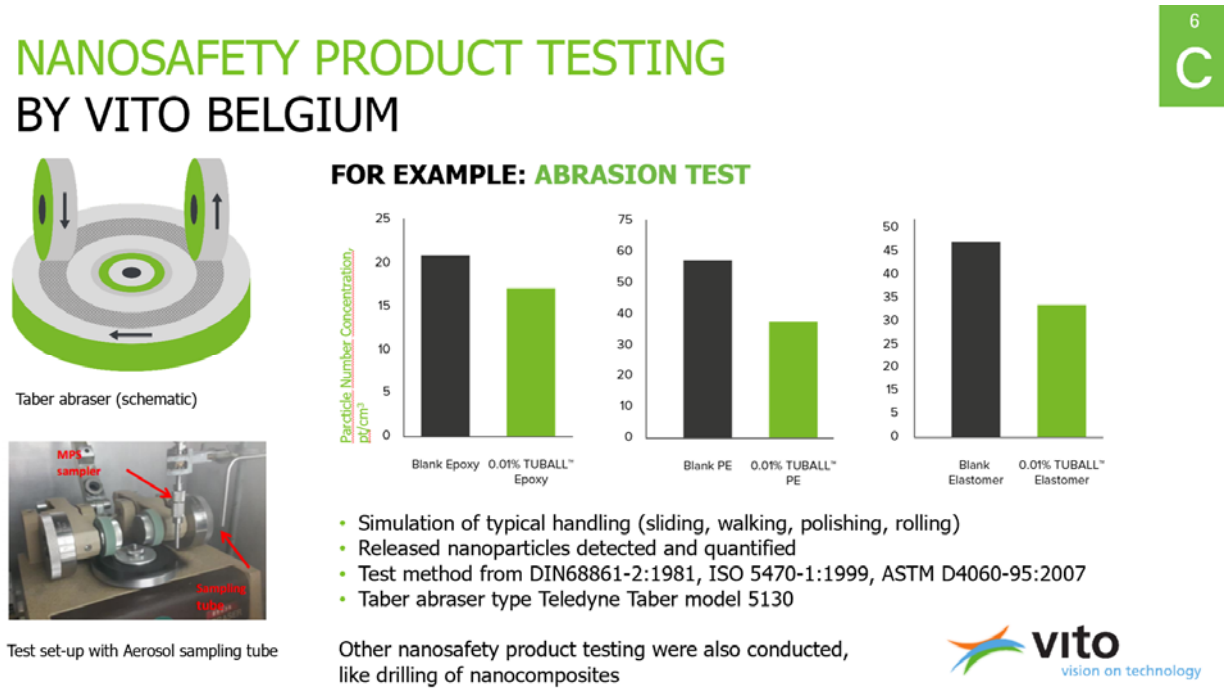

Fig. 1 VITO Belgium testing of TUBALL™ nanotubes.

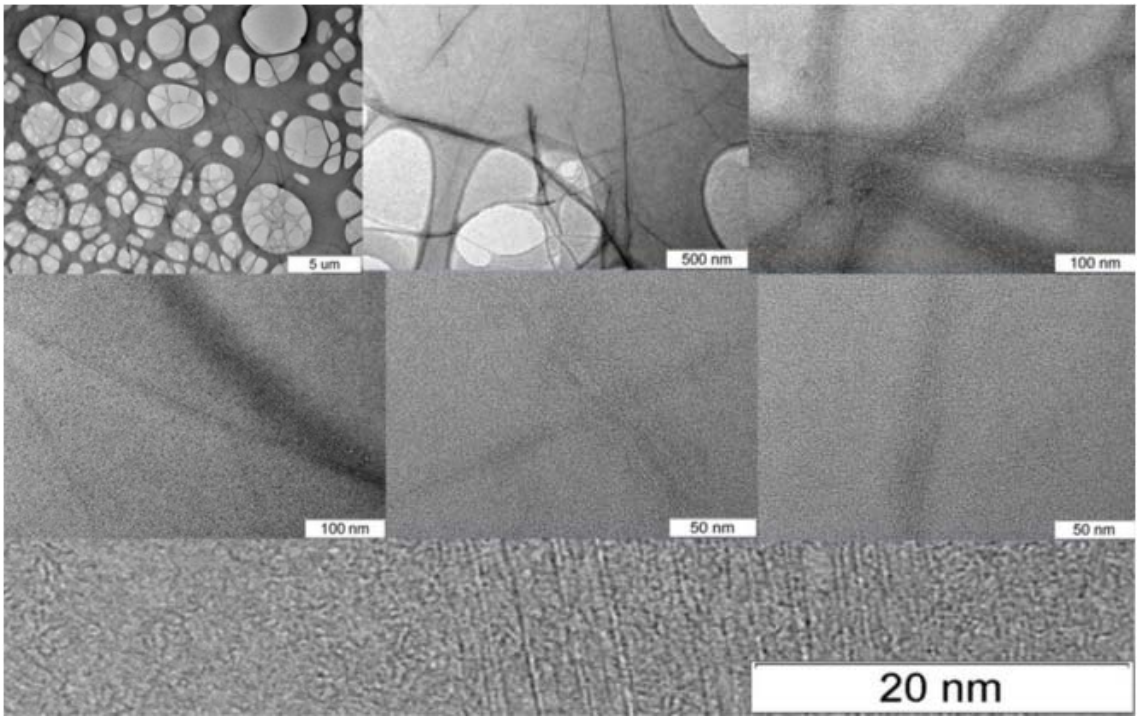

Fig. 2 TEM images of dispersed TUBALL™ nanotubes.

Table 1 List of testing completed on TUBALL™ nanotubes in 2016.

TEST ITEM	CIRCUM-STANCES	TEST	TEST CONCLUSION
TUBALL™	H.A.	PHYSICO CHEMICAL TESTING	**OK AVAILABLE RESULT**
	H.A.	HAZARDOUS PHYSICO CHEMICAL TESTING	**OK AVAILABLE RESULT**
		OECD 420 ACUTE ORAL TOXICITY (FIXED DOSE PROCEDURE)	**NOT PERFORMED**
	IN VITRO	OECD 431 IN VITRO SKIN CORROSION: MATTEK EPIDERM	**NO SKIN CORROSION**
	IN VITRO	OECD 439 DETERMINATION OF SKIN IRRITATION POTENTIAL USING THE EPISKIN TM	**NO SKIN IRRITATION**
	IN VITRO	OECD 492 IN VITRO OCULAR EYE IRRITATION HUMAN EPIOCULAR TM EYE MODEL TEST	**EYE IRRITATION**
		OECD 471 REVERS MUTATION ASSAY "AMES TEST" USING SALMONELLA TYPHIMURIUM & ESCHIRICHA	**NO MUTAGENIC**
	H.A.	OCED 201 ALGAL GROWTH INHIBITION TEST	**NO TOX.**
		OECD 202 ACUTE TOXICITY TO DAPHNIA MAGMA	**NO TOX.**
	IN VIVO	OECD 406 BUEHLER SENSITISING ASSESSMENT	**NO SKIN SENSITISING**

Table 2 List of testing completed on TUBALL™ nanotubes in 2017.

TEST SUBSTANCE / PRODUCT	ASSISTANCE OF	TEST	TEST CONCLUSION
POLYMER MATRICES CONTAINED TUBALL™	VITO	PRODUCT TEST — MECHANICAL ABRASION ON EP/HDPE/RUBBER (TYRE)	NO EFFECT
	VITO	PRODUCT TEST — DRILL ON EP/HDPE	NO EFFECT
	VITO	PRODUCT TEST — SPILL OF WATER-BASED SUSPENSION	NO EFFECT
TUBALL™	OCSiAl — STATPEEL	TUBALL™ HANDLING & PROCESS SIMULATIONS – 1ST SERIES	NO EFFECT

Table 3 List of testing completed on TUBALL™ nanotubes in 2018.

TEST SUBSTANCE/ PRODUCT	ASSISTANCE OF	TEST	TEST CONCLUSION
TUBALL™	BAuA	TOXICITY STUDY BY INHALATION	ONGOING
	BAuA	DUSTINESS TESTING TUBALL™ SUBSTANCE	NOT SELECTED BECAUSE OF TOO LOW DUSTINESS
POLYMER MATRICES CONTAINED TUBALL™	OCSiAl STATPEEL	TUBALL™ HANDLING & PROCESS SIMULATIONS – 2nd SERIES	NO EFFECT
	OCSiAl – STATPEEL	TUBALL™ CONTAINING PRODUCT HANDLING & PROCESS SIMULATIONS – 3rd SERIES	NO EFFECT
	OCSiAl – STATPEEL	TUBALL™ CONTAINING PRODUCTS HANDLING & PROCESS SIMULATIONS – 4th SERIES	TO BE STARTED IN 2019
TUBALL™ PAPER	INERIS	PRODUCT TEST – SLITTING PROCESS DURING PRODUCTION OF TUBALL™ PAPER	ON HOLD
TUBALL™	BASF SE	90 DAYS INHALATION TOXICITY IN VIVO STUDY – OECD 413	ONGOING
TUBALL™	CEA France	DUSTINESS TESTING TUBALL™ SUBSTANCE (requested by EPA)	LOW DUSTINESS INDEX (DI_{RM})
POLYMER MATRICES CONTAINED TUBALL™	VITO	LIFE CYCLE ASSESSMENT	TO BE STARTED 2019
	INERIS	WEATHERING TESTING	TO BE STARTED 2019
	INERIS	ECO-TOXICOLOGIC STUDY – ALGAE & DAPHNIA ON NEW/AGED EP/HDPE/RUBBER	ONGOING
	INERIS	INCINERATION ON EP/HDPE/RUBBER (TYRE)	TO BE STARTED Q1 2019
	INERIS	COMBUSTION ON EP/HDPE/RUBBER (TYRE)	TO BE STARTED Q1 2019

4. TUBALL™ Nanotubes Compliance with Health & Safety Regulations

OCSiAl continues its responsible approach to health, safety and environmental issues by initiating the registration of TUBALL™ nanotubes in accordance with global standards, assuring TUBALL™ compliance with them. In order to provide its customers with more comprehensive information on nanotubes and boost their wide application, the company permanently invests in various tests and research conducted by external laboratories (Tables 1-3). As a leader in the space, it shows a proactive attitude toward EH&S questions and concerns.

4.1 Authorization Compliance

OCSiAl is the first company to be authorized to start large-volume commercial shipments of SWCNTs in Europe, the US and other areas.

The company is the first SWCNTs producer to be registered in accordance with the EU's REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulations. In September 2016, TUBALL™ single wall carbon nanotubes were registered under the number 01-2120130006-75-0000 (ECn° 943-098-9). It allows OCSiAl to commercialize up to 10 tons in Europe annually, with a new goal of upgraded tonnage band up to 100 tons annually in 2019.

In December 2017, OCSiAl received a signed consent form from the EPA that allows selling up to 25 tons a year of TUBALL™ nanotubes in the US.

4.2 Integrated Management System Certification

In December 2017, OCSiAl obtained certificates that confirm the compliance of TUBALL™ nanotubes production process with requirements of the ISO 9001:2015 (Quality Management System), ISO 14001:2015 (Environmental Management System), and ISO 45001:2018 (Occupational Health and Safety Management System) standards. The certificates obtained confirm that OCSiAl determines and controls manufacturing risks, ensures product quality, takes care of personnel safety, and controls the environmental impacts in compliance with the country of manufacture.

4.3 Associated Partners

OCSiAl has joined several boards, groups, and associations committed to the health and safety in the use of nanomaterials.

The company was admitted as a business member to the European Chemical Industry Council (Cefic), which helps provide institutes and the scientific and business community with in-depth knowledge of chemicals and their management. Joint efforts in improving the transparency of nanotube use will lead to sustainable production and a wider application field for SWCNTs.

In 2016, OCSiAl joined EC4SafeNano as one of several associated partners, working to provide the market and communities with a thorough understanding of nanomaterials. The goal is to establish principles for the safe management of nanomaterials and nanotechnologies.

The company has attended the Nanosafety Conference as one of the only industry representatives, alongside representatives from research and development firms, regulatory agencies, and universities from all over the world. In collaboration with leading independent research and technology organizations, the company constantly initiates tests of its TUBALL™ nanotubes and shares its broad-based experience with industry players and policymakers.

5. Case Studies

Health, safety and environmental concerns are important to OCSiAl, as the manufacturer of TUBALL™ SWCNTs used in multiple products across a wide range of industries. Some examples and case studies show the company's focus on these concerns and dedication to research and development as the substance begins to be used in commercial applications.

5.1 Emissions from TUBALL™

How deeply can TUBALL™ enter the respiratory system? Medium-sized entangled TUBALL™ nanotubes were observed. But because of the low dustiness of TUBALL™ nanotubes, almost no nanotubes at all can be inhaled deep into the lung in actual circumstances. No other CNT material is less dusty.

At CEA-PNS Grenoble France, the dustiness test was performed by using a vortex shaker (VS) method in collaboration with INRS. The measurement of dustiness in terms of respirable mass fraction was performed and a mass-based dustiness index was calculated: DIRM = 1.66×10^3 mg/kg (Fig. 3). The results obtained with the VS method are quite reproducible.

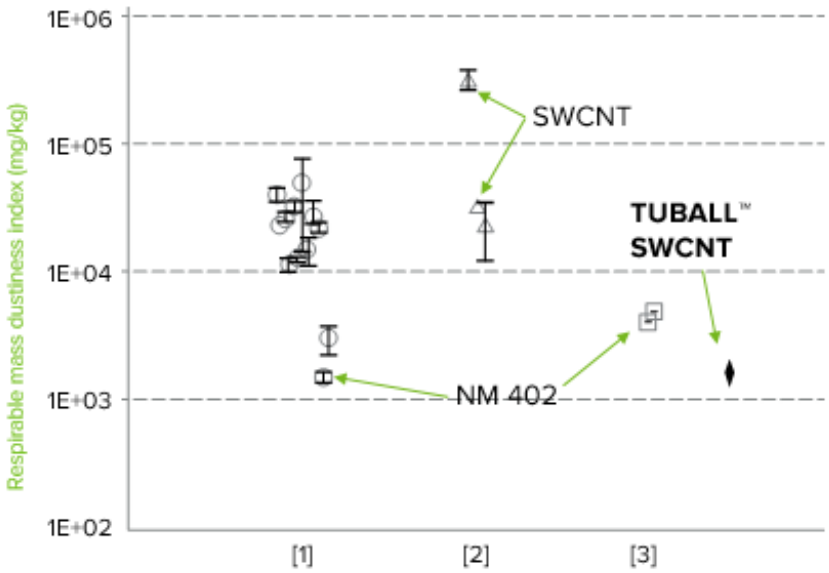

Fig. 3 Comparison of respirable mass-based dustiness indices (in mg/kg) obtained with available published indices from Refs. [1-3].

5.2 Measurement of Exposure to Inhalable Nanoparticles in the Workplace

During the case studies OCSiAl performed exposure monitoring on handling of TUBALL™ and TUBALL-containing products and monitored the exposure to nanotubes while handling TUBALL™ SWCNTs. The CNT release was observed during field test sampling; however, CNT amounts collected were well below the NIOSH REL of 1 μg/m³ 8 h TWA (< 5% NIOSH REL).

Additional testing was done with a TUBALL™ MATRIX product (a super-concentrate of TUBALL™ nanotubes), including exposure monitoring while handling and processing the product. In this study, no CNT release was observed. In general, TUBALL™ MATRIX products have an extremely low or no exposure in an industrial environment.

The low dustiness is the cause of the low concentration during exposure monitoring.

6. Conclusions

All conclusions made in this paper can be applicable exclusively to TUBALL™ SWCNTs produced by OCSiAl. The characteristics of various CNTs directly depend on their synthesis method. OCSiAl's patented scalable technology guarantees permanence and stability of each batch of nanotubes.

Numerous tests conducted allow the following conclusions regarding TUBALL™ single wall carbon nanotubes' nature and the use of materials containing them:

- TUBALL™ SWCNTs are non-rigid fibers—as a result, they do not behave as asbestos-like fibers. The flexible nanotubes appear to have lower health risks in inhalation scenarios.
- TUBALL™ SWCNTs are currently not classified as carcinogenic to humans, as a result of inadequate evidence in experimental animals.
- Nanoparticles do not become air borne when TUBALL™ containing products are being utilized. Different exposure monitoring case studies were executed in 2018 on a large research and development scale.
- SWCNT release was observed during the handling of TUBALL™, however nanotubes amounts collected were well below the NIOSH REL of 1 μg/m^3 8 h TWA (< 5% NIOSH REL).

• No relevant SWCNT release was observed during case studies of processing different TUBALL™ MATRIX products.

At the moment, the range of compliance and authorization procedures for single wall carbon nanotubes are finalized for some applications. Executed work leads to responsible approach of all nanotubes manufacturers and gives an opportunity to expand application fields widely by materials producers.

In the 2019-2020 HSE program, OCSiAl will continue to initiate different studies with leading research organizations, including VITO in Belgium, INERIS in France, CEA in France, BASF Ludwigshafen in Germany and participate in the R&D program of the German BAuA.

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