AGENZIA NAZIONALE
PER LE NUOVE TECNOLOGIE, L'ENERGIA
E LO SVILUPPO ECONOMICO SOSTENIBILE

NanoInnovation 2016

Occupational Exposure Scenario in a Value Chain Case Study

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REACH Regulation

REACH is the Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18/12/2006 concerning the **R**egistration,**E**valuation, **A**uthorization and Restriction of **Ch**emicals.

It came into force on 1 June 2007.

REACH applies to substances manufactured or imported into the EU in quantities of 1t per year or more. It covers substances on their own, in a preparation or in an article manufactured, imported, placed on the market or used

REACH Regulation

REACH requires European Union manufacturers and importers to register their chemical substances with the European Chemicals Agency (ECHA).

Each registration must include a full toxicological assessment of the hazards that the substance presents to man and the environment and for hazardous substances an assessment of risk to man and the environment.

Exposure Scenario

If the substance is determined to be hazardous then an Exposure Scenario (ES) for all of the substance uses will be required if the substance is produced and/or imported at 10 MT or greater.

The exposure scenario describes the process step, identifying the degree to which humans or the environment are exposed to the substance and how that exposure can be controlled by applying appropriate Operational Conditions and Risk Management Measures.

Exposure Scenario

Characteristics of a SE

For each phase of the life cycle of the substance an ES has to be created. The SE suitable for communication to ECHA has to contain at least the following four sections:

Section 1

Title: (short title, use descriptors, contributing scenarios separated for the environmental, workers, consumers)

Section 2

Conditions of use that influence the exposure :(operational conditions and risk management measures);

Section 3

Exposure estimation and characterization of risk divided by route of exposure and exposed (workers, consumers, environment); Information on the model used,

Section 4

A guide for downstream users to assess whether their operations fit within the scenario (Scaling)

Exposure scenario

1. TITLE SECTION

The title section gives the use name and an overview of all the tasks/activities covered by the ES.

2. CONDITIONS OF USE AFFECTING EXPOSURE

This section is the core of the ES as it includes the Operational Conditions (OCs) and Risk Management Measures (RMMs) for each contributing scenario. It is usually structured into sub-headings for each activity/contributing scenario.

2.1 ENVIRONMENT CONTRIBUTING SCENARIO:

The block below is repeated for each CS, generally starting with the CS title.

3.2 WORKER CONTRIBUTING SCENARIO

The block below is repeated for each CS, generally starting with the CS title.

Worker exposure

The following information is given for each exposure route (inhalation, dermal, combined routes…).

Example

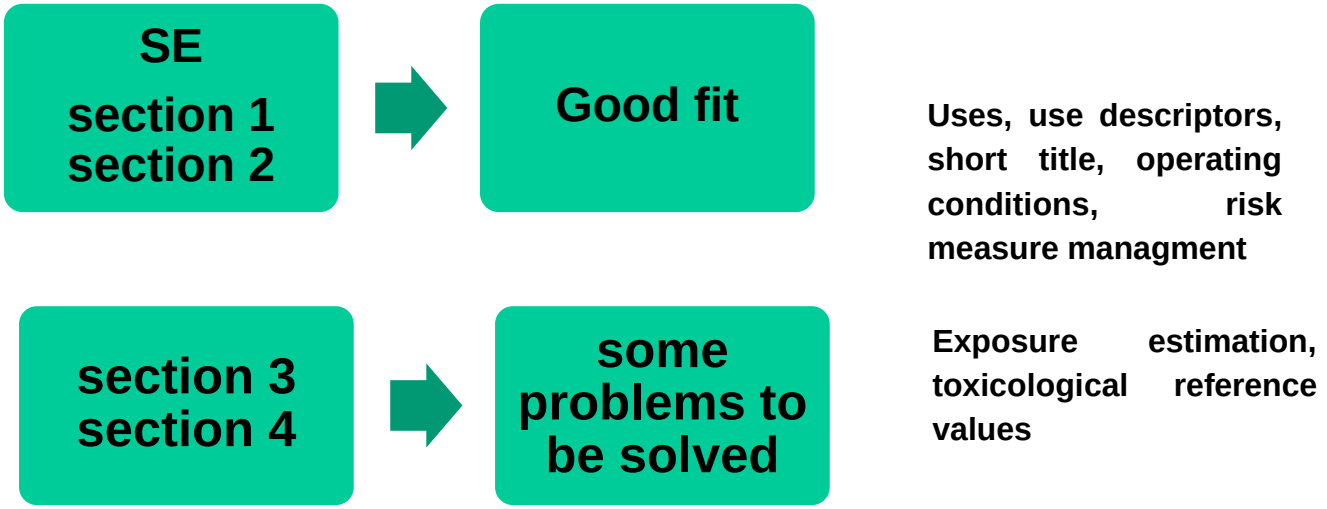
ROUTE OF EXPOSURE AND TYPE OF EFFECTS	EXPOSURE ESTIMATE	RCR
Inhalation, systemic, long-term	*2.5 mg/m³ (ECETOC TRA Worker v3)*	*0.10*
Dermal, systemic, long-term	*2.7 mg/kg bw/day (ECETOC TRA Worker v3)*	*0.39*
Combined routes, systemic, long-term (sum of the above)		*0.49*

4. GUIDANCE TO DU TO EVALUATE WHETHER HE WORKS INSIDE THE BOUNDARIES SET BY THE ES

This section includes advice to the downstream users on how they can verify that their use is covered by the ES, if their conditions of use don't exactly match the ES (termed "Scaling"). This information must include:

Nanoforms Exposure Scenarios

DO THE REACH EXPOSURE SCENARIOS FIT THE NANOFORMS ?



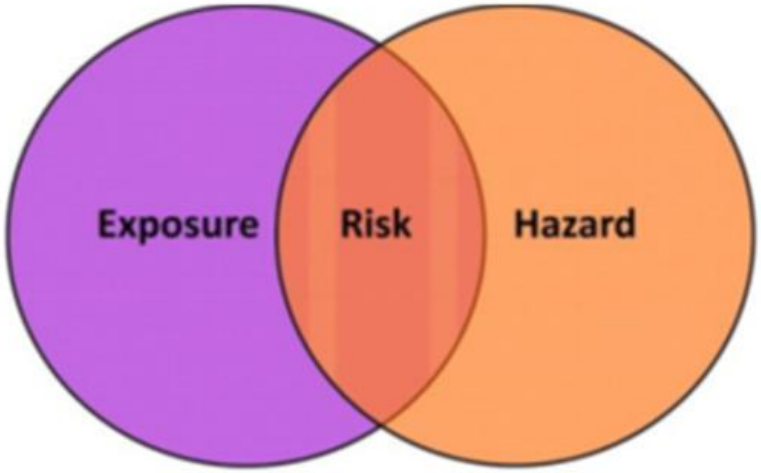
Main issues are:

1. determination of a limit value DNEL/DMEL (or at least a limit value (OEL)) for the workers and a PNEC for the environment

2. standardization of appropriate methods for the quantitative determination of nanometric particles in the air and in environmental matrices

Exposure Risk Hazard

Risk = Exposure x Hazard



Hazard: intrinsic property of the substance

$$Exposure = \sum_{i=1}^{n} t_i c_i$$

sum of the products of the exposure time and the concentration of the substance in the unit time

Risk Characterization Ratio

THE EXPOSURE SCENARIO (SE), AS DEFINED IN REACH, IS THE ELECTIVE TOOL FOR THE CONTROL OF RISK
IT PROVIDES A QUANTITATIVE BASIS (ESTIMATION) OF THE RISK EXPOSURE
IT IS DIMENSIONLESS

$$RCR = \frac{estimated\ /\ real\ Exposure}{safe\ Exposure}$$

IF RCR ≥1 THEN THE USE OF THE SUBSTANCE IS NOT ALLOWED, IF THE RISK IS <1 THEN THE SUBSTANCE MAY BE USED FOR THE GIVEN INTENDED USE IN SE

SPECIFIC HAZARD OF NANOMATERIALS

Some synthetic nanomaterials seem to pose a higher risk to health and the environment with respect to the corresponding bulk form.

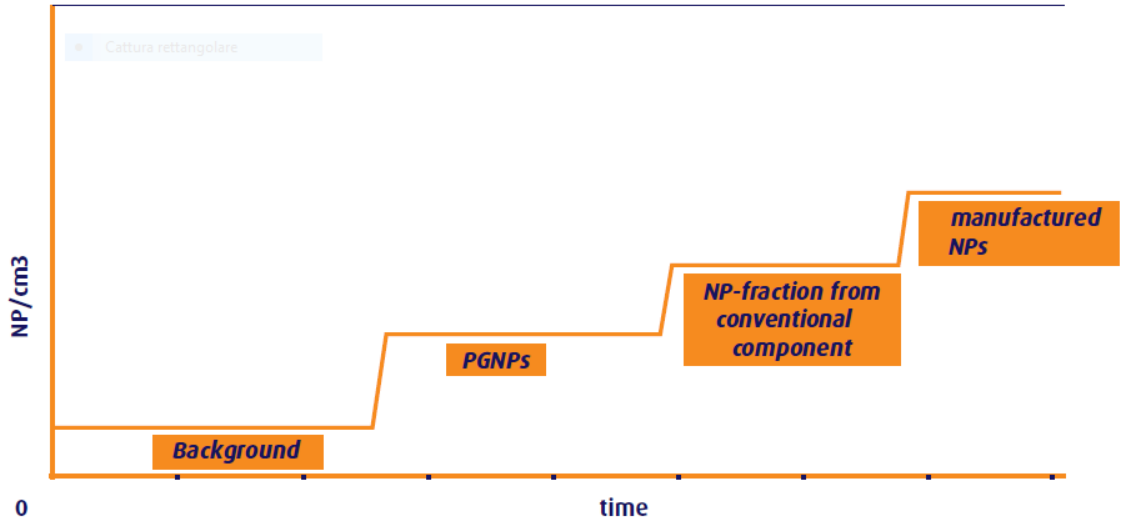
The approach recommended is for the case-by-case

«Natural background»

Check of the background

The presence of a "natural background" of ultrafine particles due to natural processes and human activities in all confined environments and ambient air is a parameter that varies in a relatively wide range and makes more difficult the determination of the contribution of emission of particles nanometric that comes from those working processes under study

Diagram showing potential concentration of airborne nanoparticles in the workplace.

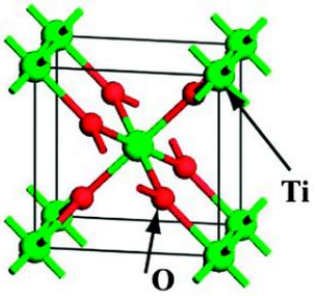


PGNPs:
process-generated nanoparticles (electrical equipment/engine-generated);
NP-fraction:
NP come from conventional component of bulk product that contains a subtantial fraction of nanoparticles

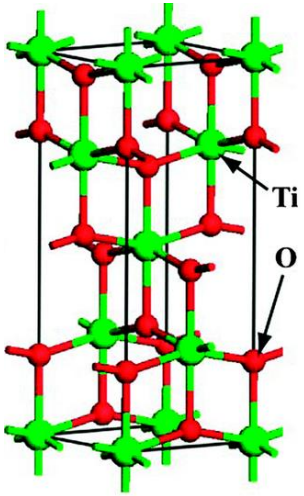
Titanium Dioxide

There exist two TiO_2 nanoforms

Rutile



Anatase



Anatase shows photocatalitic and antimicrobic properties

Toxicological endpoints

NIOSH: 0,3 mg/m3 (average value TWA 10 hours/day, 40 hours/week)
NEDO: 1,2 mg/m3 (average value TWA 8 hours/day, 5days/week)
P. Van Broekhuizen: 40,000 particles/m3

Reference

NIOSH: Occupational Exposure to Titanium Dioxide, Current Intelligence Bulletin 63: Occupational Exposure to Titanium Dioxide, National Institute for Occupational Safety and Health 2011. Available at http://www.cdc.gov/niosh/docs/2011-160/; further literature see also:

(NEDO-1. (2009) Sozuke Hanai, et all, NEDO project – research and development of nanoparticle characterization methods, risk assessment of manufactured nanomaterials – titanium dioxide. Interim Report 2009. Accessed 15 April 2012.

Exposure Limits for Nanoparticles: "Report of an International Workshop on Nano Reference Values" PIETER VAN BROEKHUIZEN et all, Annals of Occupational Hygiene (2012), 56(5):515–524

NanoReg Project

ENEA in WP1

Task 1.1: Refinement of problem identification and formulation of questions and requirements, including interaction with stakeholders

Task 1.2: Gap analysis

Task 1.3: Interaction with WP 2-6 on the scientific answers to the issues/questions related to regulatory needs for nanomaterials safety assessment and management

Task 1.4: Framework development

Task 1.5: Data platform and data management

Task 1.6: Working Groups (addressing Value Chain Case Studies and other R&D related activities)

Task 1.7: NANoREG Instruments Toolbox for regulators and legislators

ROLE of Colorobbia in Nanoreg

- (nano)material supply
- Participation to NICC
- Active collaboration with ENEA for developing case studies aimed to evaluate exposure scenarios (occupational)

ENEA- COLOROBBIA collaboration in NANOREG

Task 1.6: Value Chain Case Studies

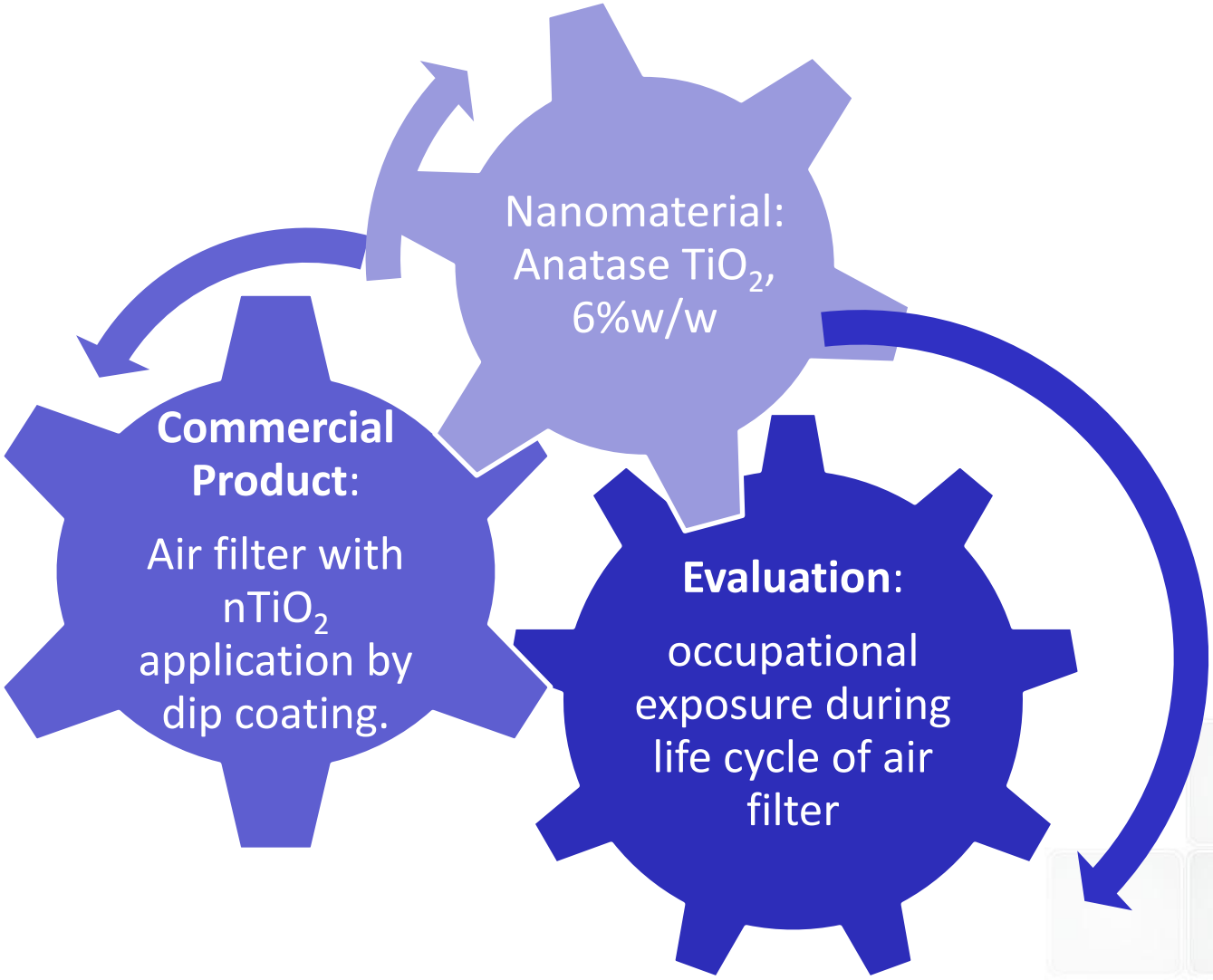
This task requires the collaboration with industrial partner

ENEA has activated a **collaboration with Colorobbia** SpA (including meeting, visits at plant, sharing of information and documentation) finalized to the development of workplace exposure scenarios during the production of NMs, using primary and real data.

Furthermore simulation of the entire value chain (in a Life Cycle prospective) has been planned.

Vccs: main aims

Evaluation of potential exposure in the case study of air filter with $nTiO_2$



Value Chain steps

PRODUCTION

- Mixture of TiO_2 precursor and additives
- Distillation and separation of main product and byproducts

FLOW-COATING

- Application on air filters using experimental set up

Thermal treatment

USE AND MAINTAINANCE

- Use of final product (experimental release tests)

END-OF-LIFE

- EoL, by simulating a disposal process

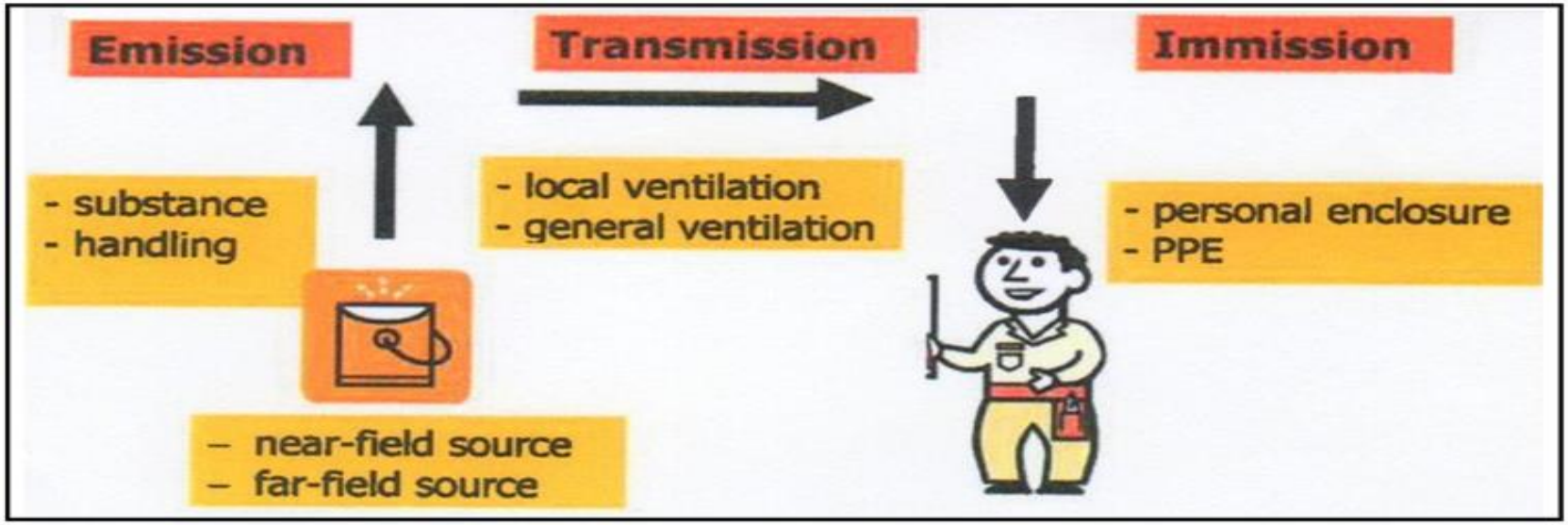
Contributing scenarios

According to REACH terminology each stage of the life cycle is named Contributing Scenario (CS).

- **CS 1**: Production (preparation of nano-based material suspension)
- **CS 2**: Application for spraying (application of nano material containing TiO2 suspension to the supports of ceramic Honeycombs)
- **CS 3**: Cooking (Cooking in the oven at 500 ° C)
- **CS 4**: Working (Putting into service of the filter)
- **CS 5**: Maintenance (simulation for filter maintenance by disassembling and washing of components)
- **CS 6**: End of Life (simulation of the end of life through the characterization of the waste)

StoffenNano 1.0

Qualitative approach because of the large uncertainties



Methodology

1. Stoffenmanager Nano

Step for Risk Management	Steps detail	Type of characteristics
Step 1: General	Source domain	Handling of bulk aggregated/agglomerated nanopowders
		Release of primary particles during actual synthesis
		Spraying or dispersion of a ready-to-use nanoproducts
		Fracturing and abrasion of Nanoproducts-embedded end products
Step 2: Product characteristics	Date PIS (Product Information Sheets)	
	Date MSDS (Material Safety Data Sheets)	
	Dustiness	(mg/kg)
	Moisture content	(%)
	Concentration of nanocomponent in the product	
	Inhalation hazard	• unknown, • mutagenic, • carcinogenic, • toxic corrosive and/or respiratory allergens, • harmful and/or irritating, • non-hazardous
Step 3: Handling process	Characterize task	handling of products, where due to high pressure, speed or force large quantities of dust are generated and dispersed
		handling of products with a relatively high speed/force which leads to dispersion of dust
		handling of products with low speed or little force or in medium quantities (several kilograms)
		handling of products in small amounts (up to 100 grams) or in situations where only low quantities of products are likely to be released
		handling of products in closed containers
		handling of products with medium speed/force which leads to some dispersion of dust
		handling of products with low speed or little force which leads to some dispersion of dust
	Duration task	from 30 min/day to 8 h/day
	Frequency task	from 5days a week to 1day a year
	Is this task being carried out in the breathing zone of an employee (distance head-product <1meter)?	
	Is there more than one employee carrying out the same task simultaneously?	
Step 4: working area	Is the working room being cleaned daily?	
	Are inspections and maintenance/ancillary equipment being done at least monthly to ensure good condition and proper functioning and performance?	
	Volume of working area	100-1000m^3; work performed outside
	Ventilation of working room	• No general ventilation; • mechanical and/or natural ventilation; • spraying booth
Step 5: Local control measures and personal protective equipment	Local control measures	• No control measures at the source; • use of a product that limits the emission; • local exhaust ventilation; • containment of the source
	Is personal protective equipment applied?	• filter mask P2 or P3; • half mask respirator with filter (type P2L o P3L); • full face respirator with filter (type P2L o P3L); • half/full face powered air respirator (type TMP1 o 2 o 3); • hood or helmet with supplied air system (type TH1 o 2 o 3)

StoffenNano 1.0

Control Banding approach

Exposure band \ Hazard band	A	B	C	D	E
1	3	3	3	2	1
2	3	3	2	2	1
3	3	2	2	1	1
4	2	1	1	1	1

Hazard: A minimum hazard, E maximum
Exposure: 1 minimum, 4 maximum
Risk: 1 maximum, 3 minimum

Quantitative approach

Precaution Characterization Ratio (PCR)

Nano Reference Value (NRV)

Nanoparticles concentration [NP]

PCR = [NP]/NRV

USEFUL for:

- comparative Risk analyses
- Risk Management Measures for risk reducing

(*) SER (2009) Advies Veilig omgaan met nanodeeltjes op de werkplek, publ.no. 2009/01.

Contributing scenarios

EXPOSURE SCENARIO: USE OF NANO SUBSTANCE IN WORKING AREA CS1			
TITLE	*Production of nano TiO_2*	*DATE*	*22/09/2016*
SUBSTANCE	*TiO_2 (Anatase)*	*UNDERTAKEN BY*	*ENEA*

LIST OF USE DESCRIPTORS RELATED TO THE STAGE OF LIFE CYCLE AND THE USES

LCS : Formulation; **ERC**: 2; **SU**: 9; **PC**: 15;
PROC: 3; AC: n/a ; TF: photochemicals

CONTRIBUTING SCENARIOS

production of TiO_2 from synthesis

DESCRIPTION OF THE PROCESS

The synthesis is carried out by placing the substance in a vacuum container (stirrer in an oil bath) of volume 150 liters together with the reagent substance (tetraetanolamina). the total time of processs is 24 hours, with a maximum temperature of 110 degrees. the reactor is placed in an environment equipped with general ventilation. In reaction time, the reactor is closed and not subject to emission. The possible phases of exposure is loading

PRODUCT CHARACTERISTICS

liquid substances precursors of TiO_2

SUBSTANCE CONCENTRATION

6%

QUANTITY USED (ABSOLUTE OR BY UNIT OF TIME)

9 KG (absolute)

OPERATING CONDITIONS

Working time (h)	01:30
Working frequency (day/week)	1

RISK MEASURES MANAGEMENT

Volume (m^3)	585
ventilation	natural
PPE	gloves, half mask with filter P3)

ESPOSURE ESTIMATION

Worker: absent n.r. (<0,001 mg/l)
Risk estimation (RCR)
RCR= 0

CS 1: Production (preparation of nano-based material suspension

Contributing scenarios

EXPOSURE SCENARIO: USE OF NANO SUBSTANCE IN WORKING AREA CS2			
TITLE	*Production of nano TiO_2*	***DATE***	22/09/2016
SUBSTANCE	*TiO_2 (Anatase)*	***UNDERTAKEN BY***	ENEA

LIST OF USE DESCRIPTORS RELATED TO THE STAGE OF LIFE CYCLE AND THE USES

LCS : Manufacturing **ERC**: *1*; **SU**: 13; **PC**: 15;
PROC: 13; **AC:** AC4g ; **TF:** photochemicals

CONTRIBUTING SCENARIOS 2

Application of TiO2 on a ceramic support by spraying

DESCRIPTION OF THE PROCESS

product application is carried out by means of a spray system manual, carried out by an operator who operates with a spraying lance on a row of ceramic supports (weight about 300 g) placed inside, a chamber closed in every part and open only in the side facing the operator, the camera is connected to an aspiration hood

PRODUCT CHARACTERISTICS

TiO2 is in diluted form in triethanolamine substance

SUBSTANCE CONCENTRATION

5,5 - 6%

QUANTITY USED (ABSOLUTE OR BY UNIT OF TIME

10 KG

OPERATING CONDITIONS

Working time (h)	2
Working frequency (day/week)	5

RISK MEASURES MANAGEMENT

Volume (m^3)	585
ventilation	LEV 614 m^3/h
PPE	gloves, half mask with filter P3)

ESPOSURE ESTIMATION

worker	0,093 mg/m3
environmental	n.r. (<0,001 mg/l)
Risk(worker) :	RCR= 0,3 (risk mass based)

CS 2 :
Application for spraying (application of nano material containing TiO2 suspension to ceramic substrates of Honeycombs.

Contributing scenarios

EXPOSURE SCENARIO: USE OF NANO SUBSTANCE IN WORKING AREA CS3			
TITLE	Production of nano TiO_2	***DATE***	22/09/2016
SUBSTANCE	TiO_2 (Anatase)	***UNDERTAKEN BY***	ENEA

LIST OF USE DESCRIPTORS RELATED TO THE STAGE OF LIFE CYCLE AND THE USES

LCS : Manufacturing **ERC**: *1*; **SU**: 13; **PC**: 15;
PROC: 3; **AC:** AC4g; **TF:** photochemicals

CONTRIBUTING SCENARIOS 3

Cooking in the oven

DESCRIPTION OF THE PROCESS

The ceramic supports, where the product film is deposited on their surfaces, are placed in an oven by an operator, then the oven is turned on and powered by three 15 KW resistors each one that operates in a pulsed mode. The thermal gradient is 5.5 ° C per hour. Once the temperature 550 C° is reached , the oven is turned off and reported in a natural way at room temperature

PRODUCT CHARACTERISTICS

the substance in the mixture is such a film on the ceramic support

SUBSTANCE CONCENTRATION

2% (on the article weight)

QUANTITY USED (ABSOLUTE OR BY UNIT OF TIME

n/a

OPERATING CONDITIONS

Working time (h)	1h 15'
Working frequency (day/week)	5

RISK MEASURES MANAGEMENT

Volume (m^3)	2414
ventilation	natural
PPE	gloves, half mask with filter P3)

ESPOSURE ESTIMATION

worker	n.r. (<0,01 mg/l)
environmental	0,01 mg/m3
environmental Risk:	RCR= 0,0.3 (risk mass based)

CS 3:
Cooking (Cooking in the oven at 500 ° C)

Contributing scenarios

EXPOSURE SCENARIO: USE OF NANO SUBSTANCE IN WORKING AREA CS4			
TITLE	Production of nano TiO_2	***DATE***	22/09/2016
SUBSTANCE	TiO_2 (Anatase)	***UNDERTAKEN BY***	ENEA
LIST OF USE DESCRIPTORS RELATED TO THE STAGE OF LIFE CYCLE AND THE USES			
LCS : Service Life ERC: *10A*; **SU:** 13; **PC:** 30; **PROC:** n/a; **AC:** AC4g ; **TF:** photochemicals			
CONTRIBUTING SCENARIOS 4			
Depurazione dell'aria.			
DESCRIPTION OF THE PROCESS			
the purifier is composed of a metal casing in which are placed 8 ceramic filters whose surface is covered with a layer of the substance a fan (with flow rate of 750 m3 / hour) conveys the air from the bottom upwards making it pass along the surfaces of the filters due to the geometry of the lower part of the casing			
PRODUCT CHARACTERISTICS			
the product is present in the article as a deposited film on the external surface			
SUBSTANCE CONCENTRATION			
2% (on the article weight)			
QUANTITY USED (ABSOLUTE OR BY UNIT OF TIME			
n/a			
OPERATING CONDITIONS			
Working time (h)	8		
Working frequency (day/week)	5		
RISK MEASURES MANAGEMENT			
Volume (m^3)	600 m^3		
ventilation	absent		
PPE	n/a		
ESPOSURE ESTIMATION			
consumer n.r (<0,001) mg/l RCR= 0			

CS 4: use (Commissioning of the filter operation)

Contributing scenarios

EXPOSURE SCENARIO: USE OF NANO SUBSTANCE IN WORKING AREA CS5			
TITLE	Production of nano TiO_2	***DATE***	22/09/2016
SUBSTANCE	TiO_2 (Anatase)	***UNDERTAKEN BY***	ENEA
LIST OF USE DESCRIPTORS RELATED TO THE STAGE OF LIFE CYCLE AND THE USES			
LCS : Service Life ERC: *10A*; **SU:** 13; **PC:** 30; **PROC:** n/a; **AC:** AC4g ; **TF:** photochemicals			
CONTRIBUTING SCENARIOS 5			
Washing of ceramic filters			
DESCRIPTION OF THE PROCESS			
the filters are removed from the purifier and soaked one by one in a container with 5 liters of distilled water. The filter after being agitated in water is sprayed with a jet of distilled water and put to dry. each operation has a duration of 30 seconds.			
PRODUCT CHARACTERISTICS			
the product is present in the article as a deposited film on the external surface			
SUBSTANCE CONCENTRATION			
2% (on the article weight)			
QUANTITY USED (ABSOLUTE OR BY UNIT OF TIME			
n/a			
OPERATING CONDITIONS			
Working time (h)	4'		
Working frequency (day/week)	2 times/week		
RISK MEASURES MANAGEMENT			
Volume (m^3)	600 m^3		
ventilation	natural		
DPI	gloves		
ESPOSURE ESTIMATION			
Worker : n.r. (<0,001 mg/l) RCR=0			

CS 5: Maintenance (simulation for filter maintenance by disassembling and washing of components)

Contributing scenarios

EXPOSURE SCENARIO: USE OF NANO SUBSTANCE IN WORKING AREA CS6			
TITLE	Production of nano TiO_2	***DATE***	22/09/2016
SUBSTANCE	TiO_2 (Anatase)	***UNDERTAKEN BY***	ENEA
LIST OF USE DESCRIPTORS RELATED TO THE STAGE OF LIFE CYCLE AND THE USES			
LCS : Service Life **ERC:** *10A*; **SU:** 13; **PC:** 30; **PROC:** n/a; **AC:** AC4g ; **TF:** photochemicals			
CONTRIBUTING SCENARIOS			
Disposal of ceramic filters			
DESCRIPTION OF THE PROCESS			
The disposal follows the current legislation: code CER 10.12.08/15.02.02/15.02.03 ceramic substrates are broken into several pieces to simulate a traumatic end of life the control procedure provides for a flow of water on ceramic pieces (Leaching) and sampling on the remaining water			
PRODUCT CHARACTERISTICS			
the product is present in the article as a deposited film on the external surface			
SUBSTANCE CONCENTRATION			
2% (on the article weight)			
QUANTITY USED (ABSOLUTE OR BY UNIT OF TIME			
n/a			
OPERATING CONDITIONS			
Working time (h)	1		
Working frequency (day/week)	infrequent event (1/10 years)		
RISK MEASURES MANAGEMENT			
Volume (m^3)	600 m^3		
ventilation	absent		
DPI	gloves		
ESPOSURE ESTIMATION			
worker	n.r. (<0,001 mg/l)		
environmental	n.r. (<0,001 mg/l)		
RCR=0			

CS 6:
End of Life (simulation of the end of life through the characterization of the waste)