



Innovative strategies, methods and tools for occupational risks management of manufactured nanomaterials (MNMs) in the construction industry

# **BEST PRACTICE GUIDE FOR RISK PROTECTION IN RELATION WITH MANUFACTURED NANOMATERIALS (MNMs) IN THE CONSTRUCTION SECTOR**

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## Disclaimer

This document was prepared following extensive consultation with a range of stakeholders (via workshops, meetings, surveys, interviews and document reviews):

- Representatives of the construction sector, including:
  - o European Construction Industry Federation (FIEC);
  - o European Federation of Building and Wood Workers (EFBWW);
  - o OHS Managers from several construction companies.
- Manufacturers of construction products;
- European and Spanish agencies for occupational safety;
- Manufacturers of personal protection equipment;
- Experts in nanosafety;
- Policy makers at European and national (Spain) levels.

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The views expressed herein are solely those of the authors.

## Presentation

The Best Practice Guide aims to help Occupational Health and Safety managers protect employees that work in the construction sector against the nano risk when they manipulated nano-objects, aggregates and agglomerates NOAAs (ISO 12901-2) [1]. It provides quick advice on methods, examples and good practices to perform the risk protection when NOAAs are incorporated in the products or the production processes in the sites.

This guide has been developed inside the SCAFFOLD project (Grant agreement Nº 280535, 2011-2015) which addresses five specific NOAAs that are the focus of this document: nano-TiO<sub>2</sub>, nano-SiO<sub>2</sub>, nano-clays, carbon nano-fibers and nano-cellulose. Apart from this guide, three other Best Practice Guides have been developed in the framework of SCAFFOLD, which would complete a set of documents whose main goal is to help the management of risks derived from the use of NOAAs in the construction sector. Additionally, the project has produced a Handbook where the topics of the quick guides are treated more extensively.

Knowledge in this area is emerging as research and experience grows. This quick guide is an initial step to assist the risk protection in the sector and its practical application jointly with future inputs from the science would lead to new improvements.

**Index**

Disclaimer ..... 2

Presentation ..... 3

Index ..... 4

List of figures ..... 5

List of tables ..... 5

Executive summary ..... 6

1. Mapping the construction sector & exposure scenarios to NOAAs ..... 8

2. Risk Protection..... 12

    2.1 Introduction: overview ..... 12

    2.2 Scenarios investigated..... 13

        2.2.1 Description of scenarios ..... 13

        2.2.2 Description of collective and personal protection systems ..... 14

3. Best Practice ..... 20

Annex 1: Definitions ..... 35

Annex 2: References..... 37

## List of figures

Figure 1 Life cycle steps of nano-enabled products and applications. ....	9
Figure 2 Decision tree in the case of NPs manipulation.....	22
Figure 3 Decision tree in the case of MNMs manipulation.....	23

## List of tables

Table 1. NOAAs and applications selected in the SCAFFOLD project.....	8
Table 2: Scope of the scenarios investigated in Scaffold project.....	10
Table 3: Summary of the investigated scenarios. ....	13
Table 4: Pictures (examples) of elements of ventilation systems used in nine investigated rooms – control categories (CB) according ISO/PDTS 12901-2:2014 [6] .....	15
Table 5: Description of the different type of respiratory devices investigated .....	17
Table 6: Description of the different personal dermal protection equipment’s investigated.....	18
Table 7: Description of typical working clothes investigated.....	19

## Executive summary

In the construction industry, nanotechnology creates the possibility to produce materials with novel functionalities and improved characteristics. Products containing nanomaterials, so called nanoproducts (NPs), have been developed for the construction sector (cement, wet mortar and concrete, paints, coatings, insulation materials, glass, and infra-structural materials) because of their improved functionalities such as higher durability, fire resistance, thermal stability, transfer, self-cleaning, and photocatalytic properties.

The presence of nanomaterials in construction products is increasing. Workers may come into contact with nanomaterials when using objects containing nanomaterials. There are three main routes of exposure to nanomaterials at the workplace.

**Inhalation** is the most common route of exposure. In the construction industry, exposure through inhalation can especially occur in activities generating dust (cutting, sanding, drilling or machining), or in applications involving spraying, which can result in aerosol formation.

**Dermal penetration** is still being investigated. The skin is generally considered a good barrier against particles, including NPs: intact skin is most likely an efficient barrier. However, the penetration of NPs through damaged or diseased skin, which end up in the systemic circulation, may be possible.

**Ingestion** of NPs primarily results from hand-to-mouth transfer from contaminated surfaces. Ingestion may also accompany inhalation exposure if a portion of the inhaled particles are transported from the airways to the mouth and swallowed.

As we don't know the health effects of nanomaterials because of gaps in toxicological data of nanomaterial, the worker's exposure should be reduced as low as possible. They have to be protected with efficient collective and personal protection systems. The efficiency of these systems is directly linked to the performed works. In the Scaffold project, the efficiency of collective and personal protection equipment was characterized in order to give clear conclusions and recommendations for the construction sector. This document gathers all this information and provides guidance on what constitutes good practice for risk protection for the construction sector.

The first recommendation is to obtain the maximum information on the composition of the NMs, even if relative data are not public. Based on these information, potential exposure sources must be identified and risk assessment must be conducted. For workers, a medical surveillance must be applied and a nanoexposure register must be established. Training sessions must be done to all workers that manipulate NMs because they have to be informed on NMs, on hazards coming from these materials, on collective and personal protections at workstations but also on waste management, storage and transport of such materials. If risks cannot be eliminated, engineering control has to be considered at first. Multistage filters F7+H14 are the most effective filters and working in glove box is the safer way but not realistic in the construction sector. If collective protection is not sufficient, we recommend the using of personal protection equipment. Respiratory devices as masks should be chosen in function of the work to do (chemical products, dust) and they must well fit to the face of each workers. Gloves must be also chosen in function of their use (chemical product, wear resistance, dust) and each workers should wear gloves that have size adapted to their hands. Concerning protective clothes, we recommend woven ones when working with hydrosols and non-

woven ones when working with aerosols. Wearing safety glasses is recommended for all workers because they prevent from liquid splash and from dust.

# 1. Mapping the construction sector & exposure scenarios to NOAAs

NOAA and nano-enabled products are being considered for various uses in the construction industry and related infrastructure industries, not only for enhancing material properties and functions but also in the context of energy conservation.

So far, only a limited number of nano-products make it to today's construction sites, the main ones are based on silicon and titanium oxides. The key areas of application are in: cement based materials, insulation materials, infrastructure coatings and coatings and paints for wood, glass and other materials as well as for self-cleaning purposes.

In Scaffold project we have selected five nano-objects: clay nanoparticles, carbon nanofibers, cellulose nanofibers, nano-SiO<sub>2</sub> and nano-TiO<sub>2</sub>; each of the above mentioned NOAAs are being studied in one particular application, due to the properties that they give to the matrix in which they are added (see table 1).

**Table 1. NOAAs and applications selected in the SCAFFOLD project.**

<b>NOAA</b>	<b>Application/matrix</b>	<b>Expected benefit</b>
<b>n-SiO<sub>2</sub></b>	Concrete	Improvement of rheology and mechanical properties
<b>n-TiO<sub>2</sub></b>	Mortar	Self-cleaning and decontamination
<b>n-TiO<sub>2</sub></b>	Self-cleaning coating	Self-cleaning and decontamination
<b>Nano-clay</b>	Fire resistance panels	Improvement of creep resistance and thermal stability
<b>Cellulose NFs</b>	Insulations	Improvement of mechanical and thermal properties
<b>Carbon NFs</b>	Coating/paint	Improvement of mechanical, thermal and electrical properties

Cementitious materials such as concrete experience changes in their properties by the incorporation of nano-SiO<sub>2</sub>; nano-particles of SiO<sub>2</sub> can fill the spaces between particles of gel of C-S-H, acting as a nano-filler and basically improving the strength and durability of the materials. In contrast to the bulk TiO<sub>2</sub> (>100 nm) that is considered chemically inert, nano-scale TiO<sub>2</sub> can act as a photo-catalyst, and can generate reactive oxygen species upon illumination. A wide range of applications exist, exploiting the various properties of TiO<sub>2</sub> nanomaterials. For instance, in coating paints nano-sized TiO<sub>2</sub> is used as a photocatalyst producing reactive oxygen that may degrade other organics. The addition of TiO<sub>2</sub> to the common mortar implies the improvement of barrier properties of the material. These NOAAs add to the mortar the capacity to maintain the surface of the product clean more time than the common mortar, therefore the maintenance tasks of the product will be reduced during the use of the product. Nanoclays are usually incorporated into polymeric matrixes in order to improve or modify one or more characteristics of the material: improve their mechanical properties, increase their resistance to thermo-oxidative processes, modify their surface properties, increase their crystallinity, improve their creep behavior, reduce the gas permeability, give antibacterial properties,

etc. This nano-filler is industrially used in the automotive and packaging sectors as well as in the construction for the preparation of materials and elements with improved fire resistance, since the clay layers reduce the gas permeation and act as protection to the polymeric matrix. Cellulose fibers are extensively used in paper production, cotton textiles, and as insulation and structural strengtheners in construction products. Finally, carbon nanofibers (CNF) are used in construction, for example, in composite materials to improve strength, stiffness, electrical conductivity, or heat resistance.

Although the use of NOAAs in the construction sector is growing, they have found some barriers; the main ones have been identified:

- the expensiveness of NOAAs compared to traditional solutions,
- the conservative profile of the sector and the lack of awareness about emerging technologies,
- the general uncertainty with respect to health and safety risks and how to properly manage them in order to protect the workers and be in compliance with the existing OHS legislation.

Workers exposure to NOAA may occur over the life cycle of nano-enabled products: during the nano-objects manufacturing process, in the manufacturing of products containing NOAAs, their application and installation, during their use (e.g. maintenance tasks) and finally in the products end of the life including demolition/disposal and recycling processes. In all these steps, many enterprises from the sector with different profiles are implied.

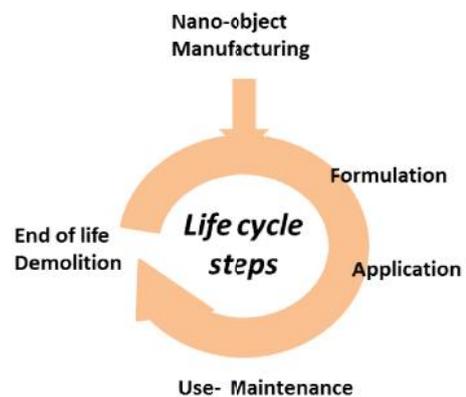


Figure 1: Life cycle steps of nano-enabled products and applications.

Exposure predominantly can occur via inhalation, dermal, oral and ocular routes. The major possible portals of NOAAs entry are lung, skin, gastrointestinal tract, nasal cavity and eyes. Exposure through inhalation of dust is the scenarios most likely to pose health risks. Skin penetration may in theory play a role as well, but most studies have shown little to no transdermal absorption through healthy skin. However, the uptake via damaged skin cannot be ruled out. Oral exposure can occur from intentional ingestion and from unintentional hand-to-mouth transfer. Swallowing inhaled particles that are cleared via the mucociliary escalator, and of drainage from the eye socket via the nasal cavity following ocular exposure are less important ways of exposure.

Critical factors affecting exposure to NOAAs include the amount of material being used, the ability of the material to be dispersed (in the case of a powder) or form airborne sprays or droplets (in the case of suspensions), the degree of containment, and duration of use.

Jobs and operations that may increase the likelihood of exposure to nanoparticles include for example:

- Generating nanoparticles in the gas phase in non-enclosed systems.
- Handling nanostructured powders.
- Working with nanomaterials in liquid media without adequate protection (e.g., gloves).
- Working with nanomaterials in liquid during pouring or mixing operations or where a high degree of agitation is involved.
- Machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles (e.g. during the installation of materials, in demolition/recycling processes).
- Conducting maintenance on equipment and processes used to produce or fabricate nanomaterials, or the clean-up of spills or waste material.
- Cleaning of dust collection systems used to capture nanoparticles.

In Scaffold the occupational exposure to the five selected NOAAs has been measured in scenarios covering the life cycle of the six applications; see next matrix summarizing the scope of the scenarios investigated in the project (table 2).

Life cycle step	Nano-object and application					
	nano-TiO2 depollutant mortar	nano-TiO2 self-cleaning coating	nano-SiO2 self-compacting concrete	nano-Clay(fire retardant panels	carbon nano-fibers coating laminates	nano-cellulose insulations
Nano-object manufacturing	X	X	○			
Manufacturing nano-enabled products and application	X	○	○	○	X	X
Use/maintenance: Machining	X	X	X	○	X	X
Demolition	X	X	X	○	X	X
Accidental fires	X	X	X	X	X	X

Table 2: Scope of the scenarios investigated in Scaffold project.

Note: cells marked with X have been investigated at lab/pilot scale; cells marked with the red circle have been investigated in the case studies.

The results found are encouraging and in general workers performing the tasks measured were not overexposed to NOAAs in the scenarios investigated. Data of occupational exposure were below the limits proposed for the NOAAs by Scaffold (Stockmann-Juvala H. et al, 2014), NIOSH (NIOSH 2011) and the nano-reference values proposed by IFA (IFA, 2014, SER 2012); the limits used are showed

later in this document. For that reason, the scenarios in the matrix are showed in green color although some remarks have been marked for some of them.

- 1) Considering the metric of mass concentration ( $\text{mg}/\text{m}^3$ ), the occupational exposure measured in all scenarios was below proposed limits by NIOSH and SCAFFOLD. As expected, the highest mass concentration measured was found in tasks where nano-objects were handled directly and in significant quantities as for example, during cleaning operations in the nano-TiO<sub>2</sub> manufacturing process or during the spraying of a self-cleaning coating in a wall (marked with (1) in table 2).
- 2) Considering the metric of particles concentration ( $\text{particles}/\text{cm}^3$ ), the occupational exposure measured in all scenarios was also below the recommended nano-reference value of 40 000  $\text{particles}/\text{cm}^3$  (IFA, 2014). As expected, common activities in this sector produced a high release of particles. For instance, the highest values measured were during the machining of quite hard materials such as the self-compacting concrete and the laminates filled with CNF marked with (2) in table 2. However two issues should be underlined here. On the one hand, the release of particles is intrinsic to the machining process and in fact, no sticking differences have been found for processes performed with control materials (without NOAAs) and materials filled with NOAAs. On the other hand, the machining processes were performed during short times and, consequently, the concentrations averaged to the 8 h-day did not exceed the OELs; however, other working conditions with longer processes may lead to higher exposures.
- 3) Fire tests performed with the materials from the six applications did not observe the release of the NOAAs added to the materials with the exception of the fire retardant panels where there may be indications of possible release of nano-clays during the combustion of the materials.

Nowadays there are still very few data available on workers exposure to NOAAs in the construction sector. The data achieved in Scaffold contributes to clarify if the use of new nano-enabled products may increase the risk of workers handling these materials. It should be noted that most of the measurements have been taken at pilot scale, so short times and small quantities have been handled. More data from real scenario would help to incorporate in a safe way these new materials in the sector. Finally, it should be underlined that construction work environments are rather complicated, typically handling different activities and chemicals, and where other hygienic risks may be more relevant than exposure to NOAAs.

## 2. Risk Protection

### 2.1 Introduction: overview

Risks should be avoided wherever possible. Risk assessment is the key element in the prevention process. For nanomaterials and nanoparticles the employer must take into account the available knowledge based on the products and its use.

From its assessment, the employer must establish preventive measures including the **RISK PROTECTION**. Currently, the inhalation and dermal penetration of nanomaterials is possible and control measures have to be taken to avoid or minimize personnel exposure. The employer must take action both for the engineering control and for the personal protection in order to reduce the risk to a minimum when it is impossible to reduce it. The risk protection starts with a knowledge of the material composition and of the process in which the MNMs is involved. The performance of current protective measures for nanoparticles must be assessed to determine the best collective and personal protection systems for each case study. Moreover, ventilation systems and engineering control equipment suitable for the risks must be regularly checked and maintained in operating condition. Appropriate personal protective equipment (PPE) will be provided, in addition to engineering control equipment. This PPE must be changed regularly in function of their use.

Generally speaking, employers must give appropriate instructions to workers by providing information and training for the exposed employees.

Several collective and personal protecting equipment have been studied during the project in order to know their efficiency according to their use and are listed in this quick best guide. With all of the results obtained, two general decision trees have been made; one for the manipulation of NPs and one for the manipulation of MNMs. Based on them, some recommendations for the construction sector are given for each real scenarios investigated during the project.

## 2.2 Scenarios investigated

In this part, all the investigated scenarios are summarized and a description of the engineering control and personal protection systems investigated in the project is made.

### 2.2.1 Description of scenarios

Scenarios investigated are listed in Table 3.

STEPS OF LIFE CYCLE	N°	SCENARIOS
Synthesis	1	Production of NPs (TiO <sub>2</sub> , SiO <sub>2</sub> , nanoclay) in powder form
Handling/Formulation	2	Collection, transferring NPs (TiO <sub>2</sub> , SiO <sub>2</sub> , nanoclay) and NFs (carbon NFs, cellulose NFs) in powder form
	2bis	Weighing and bagging NPs (TiO <sub>2</sub> , SiO <sub>2</sub> , nanoclay) and NFs (carbon NFs, cellulose NFs) in powder form
	3	Dissolution of NPs in water (TiO <sub>2</sub> , SiO <sub>2</sub> , nanoclay) Powder form to liquid state
Manufacturing NanoMaterials (MNMs)	4	Manufacturing insulating and fire resistant panels with nanoclay in solid form.
	5	Manufacturing and formulation of self-cleaning external coatings with nano TiO <sub>2</sub> in liquid state.
	5bis	Manufacturing and formulation of self-cleaning external coatings with cellulose NFs in liquid state.
	6	Manufacturing and formulation of mortar with nanoTiO <sub>2</sub> in solid state
	7	Manufacturing and formulation of concrete with nanoSiO <sub>2</sub> in solid state
Using MNMs	8	Manufacturing bituminous road-surface pavements with carbon NFs in solid state
	9	Drilling holes, machining, sanding, cutting materials containing NPs. Generation of aerosolized and solid NPs
	9bis	Drilling holes, machining, sanding, cutting materials containing NFs. Generation of aerosolized and solid NPs
	10	Applying a mortar containing TiO <sub>2</sub> on a wall in a solid state
Cleaning and Maintenance	11	Spraying sol-gel mortar containing TiO <sub>2</sub> on a wall in a liquid state
	12	Of filters and equipment used to produce NPs and MNMs by a wet procedure
End of Life of NPs and NFs	13	Demolishing a work-cabin containing NPs. Generation of dust and aerosolized NPs
	13bis	Demolishing a work-cabin containing NFs. Generation of dust and aerosolized NPs
	14	Accidental fire of panels containing NPs. Generation of aerosolized NPs

**Table 3: Summary of the investigated scenarios.**

## 2.2.2 Description of collective and personal protection systems

In the presented scenarios, different collective and personal protection systems were investigated:

- current alternative protection of different enclosure/containments existing among the partners
- different types of the most commonly used current respiratory protective devices intended for use in any construction industry
- various types of protective clothing and dermal protective equipment (gloves and chemical protective clothing) used in the construction sector.

### 2.2.2.1 Engineering control systems

Engineering controls against nano-objects can be assured by the application of effective ventilation systems equipped with appropriate air filters.

#### Investigated collection protection systems operated in real conditions

In ISO/PDTS 12901-2:2014 [6] are proposed five control categories:

- CB 1: Natural or mechanical general ventilation;
- CB 2: Local ventilation: extractor hood, slot hood, arm hood, table hood, etc.;
- CB 3: Enclosed ventilation: ventilated booth, fume hood, closed reactor with regular opening;
- CB 4: Full containment: glove box / bags, continuously closed systems;
- CB 5: Full containment and review by a specialist: seek expert advice.

During experimental campaigns, investigations were carried out in nine rooms with different ventilation systems with control categories: CB 1, CB 2, CB 3 and CB 4.

Pictures of elements of ventilation systems (with control categories: CB 1, CB 2, CB 3 and CB 4) used in the nine investigated rooms are shown in Table 4.

Type of ventilation systems	Pictures (examples)		
Natural ventilation (CB 1): – opened door – opened window – hole in the wall			
Mechanical general ventilation (CB 1): – openings of supply system			

<ul style="list-style-type: none"> <li>– openings of exhaust system</li> </ul>	
<p>Local ventilation (CB 2):</p> <ul style="list-style-type: none"> <li>– elements of extractor hoods system</li> </ul>	
<p>Local ventilation (CB 2):</p> <ul style="list-style-type: none"> <li>– arm hood</li> <li>– side hood</li> </ul>	
<p>Enclosed ventilation (CB 3):</p> <ul style="list-style-type: none"> <li>– fume hoods</li> </ul>	
<p>Enclosed ventilation (CB 3):</p> <ul style="list-style-type: none"> <li>– elements of closed reactor with regular opening</li> </ul>	
<p>Full containment (CB 4):</p> <ul style="list-style-type: none"> <li>– glove box</li> </ul>	

**Table 4: Pictures (examples) of elements of ventilation systems used in nine investigated rooms – control categories (CB) according ISO/PDTS 12901-2:2014 [6]**

### 2.2.2.2 Personal respiratory protection systems

The protection efficiency of different types of commercially available Respiratory Protective Devices (RPDs) intended for use in the construction industry was investigated in order to classify them and select appropriate devices for different workplaces and hazards. All the different types of respiratory devices selected and investigated are listed in Table 5.

Type of respiratory device	Pictures
<p><b>FFP2 and FFP3 filtering half masks</b></p> <ul style="list-style-type: none"> <li>-used to protect the respiratory system against aerosols containing solid and liquid aerosols.</li> <li>- the examined half masks differed in terms of the protection</li> <li>- not to be used if oxygen content in the air is lower than 19% v/v, as well as in inadequately ventilated or very compact spaces, such as tunnels, wells, or tanks.</li> </ul>	
<p><b>Half masks</b></p> <ul style="list-style-type: none"> <li>- the second most widespread type of respiratory protective devices, used with a variety of filtering elements (particle filters, gas filters, or a combined filters), depending on the type of pollutants present, to ensure protection against aerosols and/or vapors and gasses.</li> <li>- connected with filtering elements it should not be used if oxygen content in the air is lower than 19% v/v, as well as in inadequately ventilated or very compact spaces, such as tunnels, wells, or tanks.</li> <li>- half masks can be used also with a breathing apparatus to give protection against all air pollutants and oxygen deficiency.</li> <li>- tested half masks were equipped with particle filters class P2 and P3</li> </ul>	
<p><b>FFA1P2 and FFA2P3 filtering half masks against organic vapours and/or gases and particles</b></p> <ul style="list-style-type: none"> <li>- are classified as filtering equipment.</li> <li>- used when workplace hazards include solid and/or liquid aerosols as well as gasses and/or vapors of organic substances.</li> <li>- not to be used if oxygen content in the air is lower than 19% v/v, as well as in inadequately ventilated or very compact spaces, such as tunnels, wells, or tanks.</li> <li>- the examined half masks differed in terms of the protection class of the combined filters.</li> </ul>	
<p><b>Full face masks</b></p> <ul style="list-style-type: none"> <li>-the most typical and effective RPDs, they cover the whole face of the user, giving protection not only to the respiratory system, but also to the eyes and face.</li> <li>- can be used with air-purifying elements, compressed air line breathing apparatuses and closed and open circuit self-contained breathing apparatuses (SCBAs).</li> <li>- tested full face mask is intended to be connected with to two filtering elements by means of bayonet connectors and they were tested with P3 particle filters.</li> </ul>	

**Powered filtering device with hood,**

- the most commonly used powered (equipped with a fan) RPDs that are used in the construction industry.
- the hood covers the entire head of the user, and it can ensure protection not only to the respiratory system, but also to other parts of the face and head.
- hoods may contain eye and face protecting elements, a helmet protecting the head against mechanical impacts, and earmuffs.
- the powered filtering device is one of the most comfortable RPD types.
- slight overpressure in the breathing zone does not increase breathing resistance during use and prevents the intrusion of contaminants.
- tested device was TH2 protection class.



**Table 5: Description of the different type of respiratory devices investigated**

Respiratory protective devices were assessed using the following methods:

- testing the penetration of nanoparticles that are commonly found in the construction industry, such as  $\text{TiO}_2$ ,  $\text{SiO}_2$ , nanoclays, cellulose nanofibers and also nanoNaCl aerosol.
- testing the total inward leakage (TIL) of test NaCl aerosol in experiments involving human subjects and testing the TIL of  $\text{TiO}_2$ ,  $\text{SiO}_2$ , nanoclays, cellulose nanofibers and test nanoNaCl aerosol with a computerized dummy head and torso.

Particles of the generated aerosols were tested and analyzed in the size range from 7 nm to 270 nm using Condensation Particle Counters (CPC) with electrostatic classifiers.

A robotic head and torso manikin was developed, built and deployed. It was used for testing the TIL of selected RPDs in the presence of nanoaerosols containing toxic nanoparticles.

The five subjects and the manikin walked on the treadmill at a speed of 6 km/h and performed the following exercises:

- 10 min walking without head movement or talking,
- 10 min head movement from left to right, as if inspecting the walls of a tunnel,
- 10 min head movement up and down, as if inspecting the ceiling and the floor,
- 10 min uttering the letters of the alphabet or a set text, as if talking to a colleague,
- 10 min walking without head movement or talking.

### 2.2.2.3 Personal dermal protection systems: gloves and clothing

Different gloves and clothes were used by workers in construction sites at different steps of the NPs life cycle (synthesis, handling, using, cleaning and end of life). They are listed in Table 6 and 7.

Type of gloves for dermal protection	Pictures
<p><b>Gloves A</b> Bi-colour rubber gloves are ideal for <b>chemical handling</b>, heavy duty industrial applications, on assembly lines, for use with pesticides, within the construction industry, within laboratories, industrial cleaning, and manufacturing. The gloves are manufactured from natural rubber latex with a polychloroprene coating, complete with a soft cotton lining which absorbs perspiration and provides excellent grip and durability. They offer protection against a wide range of detergents, alcohols, alkalis, acids, caustics and salts. They comply the requirements for chemical protection glove (EN 374).</p>	
<p><b>Gloves B</b> Nitrile coated gloves protecting against <b>mechanical risks</b>. The inner liner is a 100% jersey, with a cotton knitted safety cuff. Ideal for handling abrasive materials such as castings, wrought iron and bricks. Not required for chemical protection.</p>	
<p><b>Gloves C</b> 100% nitrile high quality gloves providing resistance to a wide range of <b>chemicals</b>. Resistant to a broad range of chemicals particularly petroleum based solvents, oils and grease. Good protection against <b>abrasion</b> and snags due to their thickness.</p>	
<p><b>Gloves D</b> 100% nitrile gloves very sensitive. The finger tips have a textured pattern that helps with dexterity. They provide superior protection from most <b>chemicals</b>.</p>	

Table 6: Description of the different personal dermal protection equipment's investigated.

Type of cloth	Pictures
<p><b>Fleece jacket composed of 100% polyester</b>            Non-woven material            Density: 300-340g/m<sup>2</sup>            Thickness: 3.8 mm            Porosity: 90-95%</p>	
<p><b>Jacket composed of 65% polyester and 35% of cotton</b>            Woven material            Density: 245-350g/m<sup>2</sup>            Thickness: 500 microns            Porosity: 50-60%</p>	
<p><b>Rain jacket composed of polyamide coated with polyurethane</b>            Coated material            Woven material            Density: n.a.            Thickness: 340 microns            Porosity: 20-30%</p>	
<p><b>Chemical protective clothing category 3, type 5 and 6</b>            High protection against particles, splashing aqueous liquid chemicals (up to 0.13 bar pressure) and inorganic liquids. Durability because resistant to tearing, puncture and abrasion.</p>	

**Table 7: Description of typical working clothes investigated.**

The aim was to determine if NPs can diffuse through PPEs and clothes when they are in contact with NPs and MNMs in different states (liquid, powder, solid and aerosolized NPs) during different steps of their life cycle (synthesis, handling, manufacturing, using and end of life).

### 3. Best Practice

At first, two decision trees (Figure 2 and 3) have been made allowing us to classify 9 levels of hazards present in the construction sector. The first decision tree is more dedicated to the manipulation of NPs in liquid state and in powder state and the second one, to the manipulation of MNM (NPs embedded in a matrix).

Exposure to NMs may happen by ingestion, inhalation and dermal contact. These both decision trees have been organized according to different parameters listed below:

- If the environment is confined (as in glove box), no personal protection equipment against NPs and no engineering control systems against NPs are required. But in the construction sector, the use of a glove box is rare due to the large quantity of NPs and MNMs used.
- We distinguished fibers from others NPs because of their morphology (length-diameter aspect ratio larger than 3) which is in relation with their toxicity as asbestos fibers.
- If the environment is open, we can distinguish 2 cases: the outdoor and the indoor working.
- For the case of the outdoor working, no collective protection can protect workers but only PPEs (masks, gloves and clothes).
- For the case of indoor working, collective protections have to be implemented at first.
- If no collective protection OR collective protection is not sufficient, personal protections equipment have to be implemented.
- For ingestion and inhalation hazards, the best fitted respiratory masks have to be chosen in function of the workers.
- For the dermal hazard, appropriate gloves and clothes have to be chosen.
- For the indoor working, the quantity of NPs and MNMs manipulated is very important and impacts the level of hazard. In the construction sector, workers are always in the case where very large quantities of material are used. That's why for each cases, we distinguished small quantities for R&D and larger quantity for plants.
- The fact that NPs are embedded in a matrix or isolated is not separated because industrials can't observe NPs by SEM or TEM. For the recommendations, we assume that all the NPs are always isolated, even it is not the case in real life.

All levels of hazards are listed just below; Nano 9 is the highest hazard and Nano 0 is the lowest hazard. For each level, different requirements for protection measures are given.

#### **Nano 0**

- 1) No engineering control systems against nano hazards
- 2) No respiratory equipment against nano hazards
- 3) No dermal protection equipment against nano hazards

#### **Nano 1**

- 1) General mechanical ventilation system with F7+H14 air filters **OR** natural ventilation by windows, doors, holes in walls
- 2) FFP3 filtering half mask in all cases (indoor, outdoor)
- 3) Safety glasses, non-woven clothes like fleece jacket, 1 pair of nitrile gloves (B)

#### **Nano 2**

- 1) Natural ventilation by windows, doors, holes in walls if indoor
- 2) Full-face mask with a P3 filter in all cases (indoor, outdoor)
- 3) Safety glasses, chemical protective clothing cat. 3, 1 pair of nitrile gloves (B)

#### **Nano 3**

- 1) General mechanical ventilation system with F7+H14 air filters **OR** natural ventilation by windows, doors, holes in walls
- 2) FFP3 filtering half mask if powder state
- 3) Safety glasses, lab coat, 1 pair of nitrile gloves (D)

#### **Nano 4**

- 1) General mechanical ventilation system with F7+H14 air filters **OR** natural ventilation by windows, doors, holes in walls
- 2) No mask if closed environment (reactor)  
FFP3 filtering half mask if open environment  
Best fitted mask with powered filtering device incorporating a TH2 hood / full face mask with particle filter P3 if no collective protection **AND** open environment
- 3) Safety glasses, lab coat, 1 pair of nitrile gloves (D).  
Safety glasses, chemical protecting clothing cat.3, 1 pair of nitrile gloves (B) if accidental fire.

#### **Nano 5**

- 1) General mechanical ventilation system with F7+H14 air filters **AND** fume cupboard
- 2) FFP3 filtering half mask if no collective protection
- 3) Safety glasses, lab coat, 2 pairs of nitrile gloves (C and D). Addition of safety sleeves if no collective protection.

#### **Nano 6**

- 1) General mechanical ventilation system with F7+H14 air filters **OR** natural ventilation by windows, doors, holes in walls
- 2) FFP3 filtering half mask in all cases
- 3) Safety glasses, lab coat, 1 pair of bi-colour rubber gloves (A).

### Nano7

- 1) General mechanical ventilation system with F7+H14 air filters **AND** local exhaust system **OR** natural ventilation by windows, doors, holes in walls
- 2) FFP3 filtering half mask if collective protection.  
Best fitted mask with powered filtering device incorporating a TH2 hood / full face mask with particle filter P3 if no collective protection
- 3) Safety glasses, lab coat, 2 pairs of adapted nitrile gloves (C and D). Addition of a chemical protective clothing cat.3 if no collective protection.

### Nano 8

- 1) General mechanical ventilation system with F7+H14 air filters **AND** fume cupboard
- 2) FFP3 filtering half mask if collective protection. Best fitted mask with powered filtering device incorporating a TH2 hood / full face mask with particle filter P3 if no collective protection
- 3) Safety glasses, lab-coat, 2 pairs of adapted nitrile gloves (C and D).

### Nano 9

- 1) General mechanical ventilation system with F7+H14 air filters **AND** local exhaust ventilation
- 2) FFP3 filtering half mask if collective protection. Best fitted mask with powered filtering device incorporating a TH2 hood / full face mask with particle filter P3 if no collective protection
- 3) Safety glasses, 2 pairs of adapted nitrile gloves (C and D) and chemical protective clothing cat.3 in all cases.

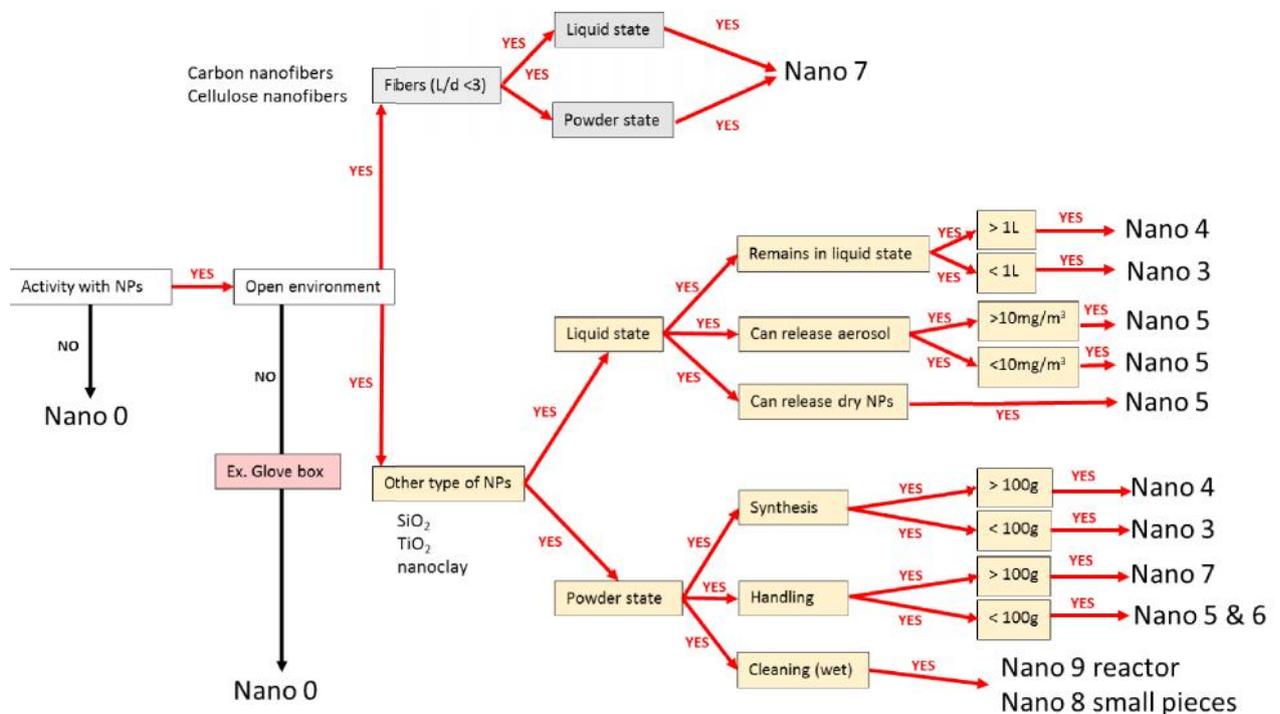


Figure 2: Decision tree in the case of NPs manipulation.

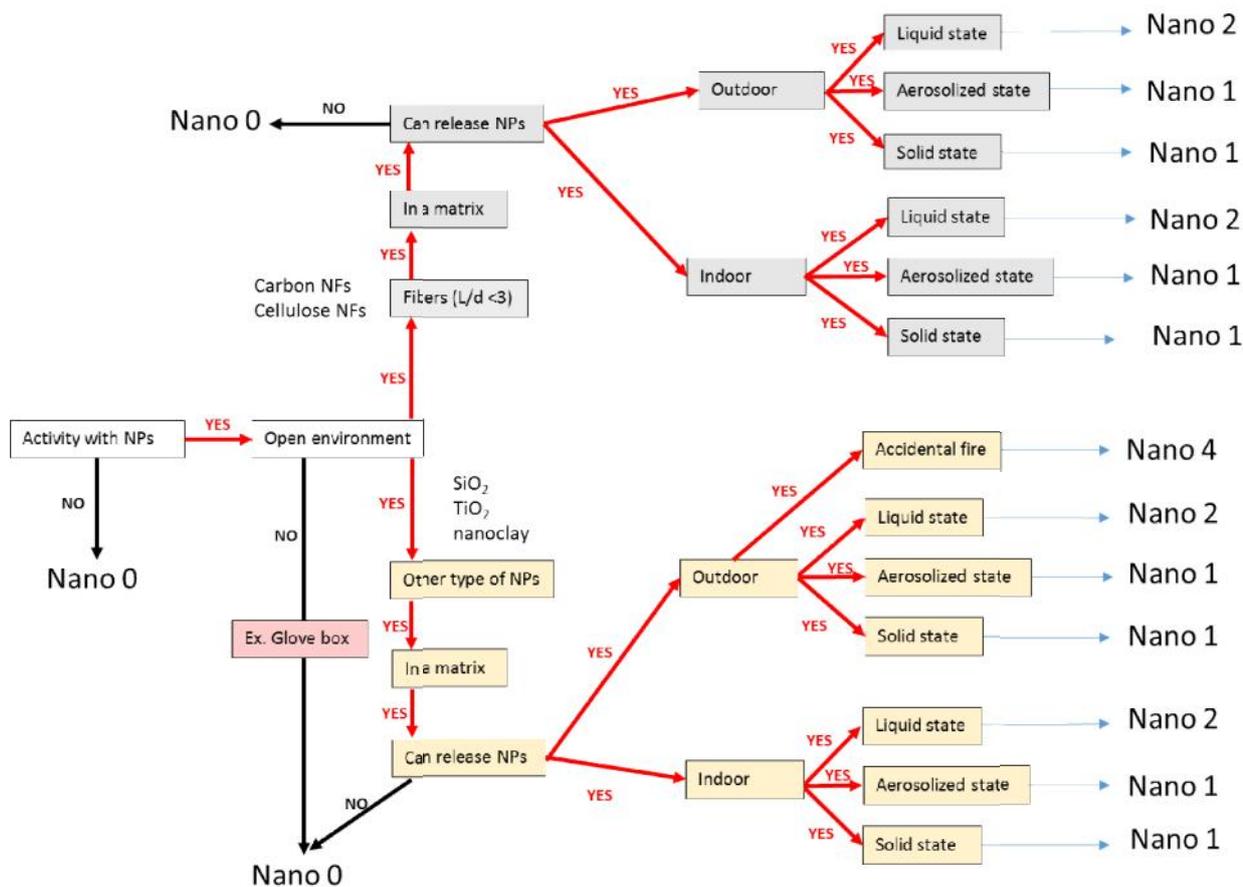


Figure 3: Decision tree in the case of MNMs manipulation.

According to these information, we analyzed each scenarios investigated in the project and we gave a series of requirements for collective and personal protections. See below:

**Scenario 1:**

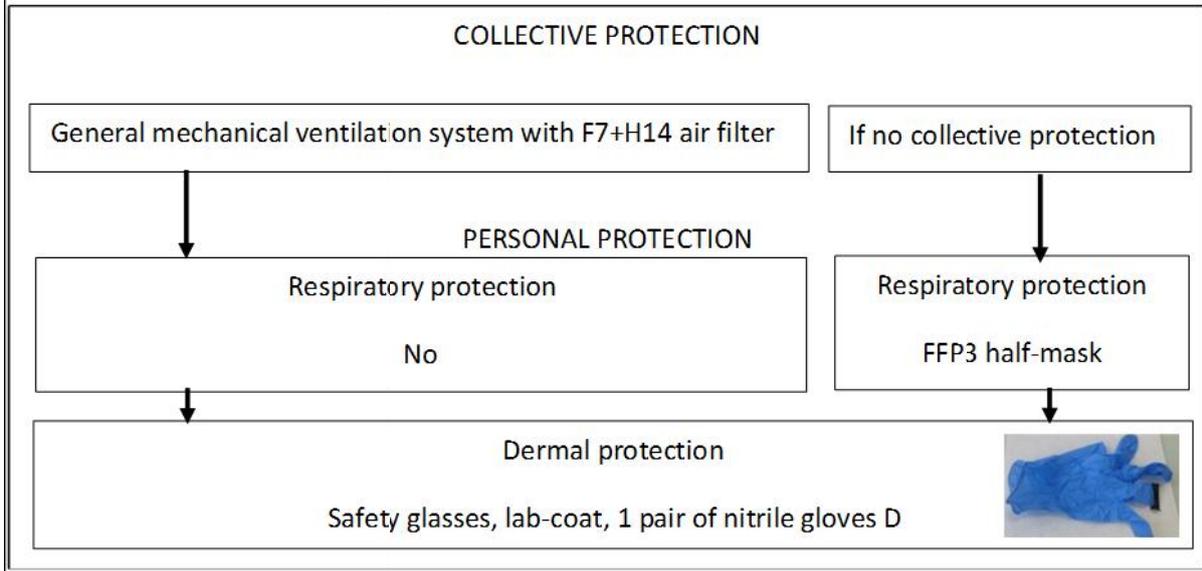
**Exposure scenario:** Synthesis in a closed reactor of a large amount of TiO<sub>2</sub> NPs (> 1kg/h).

**Localization:** in a very large room (hangar).

**State:** powder.

**Nano 4**

Decision tree 1.



**Scenario 2:**

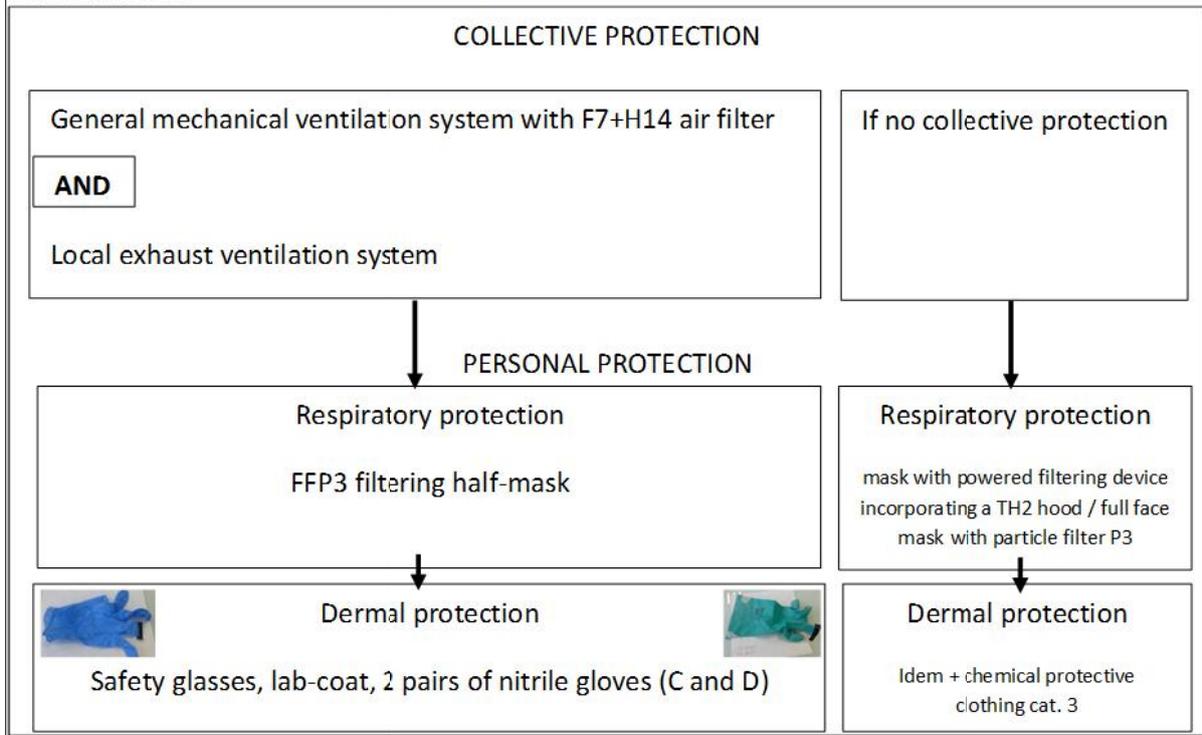
**Exposure scenario:** Handling a large amount of TiO<sub>2</sub> NPs (> 100g): collecting, transferring, weighing, bagging.

**Localization:** in a very large room (hangar).

**State:** powder.

**Nano 7**

Decision tree 1.



**Scenario 2 bis:**

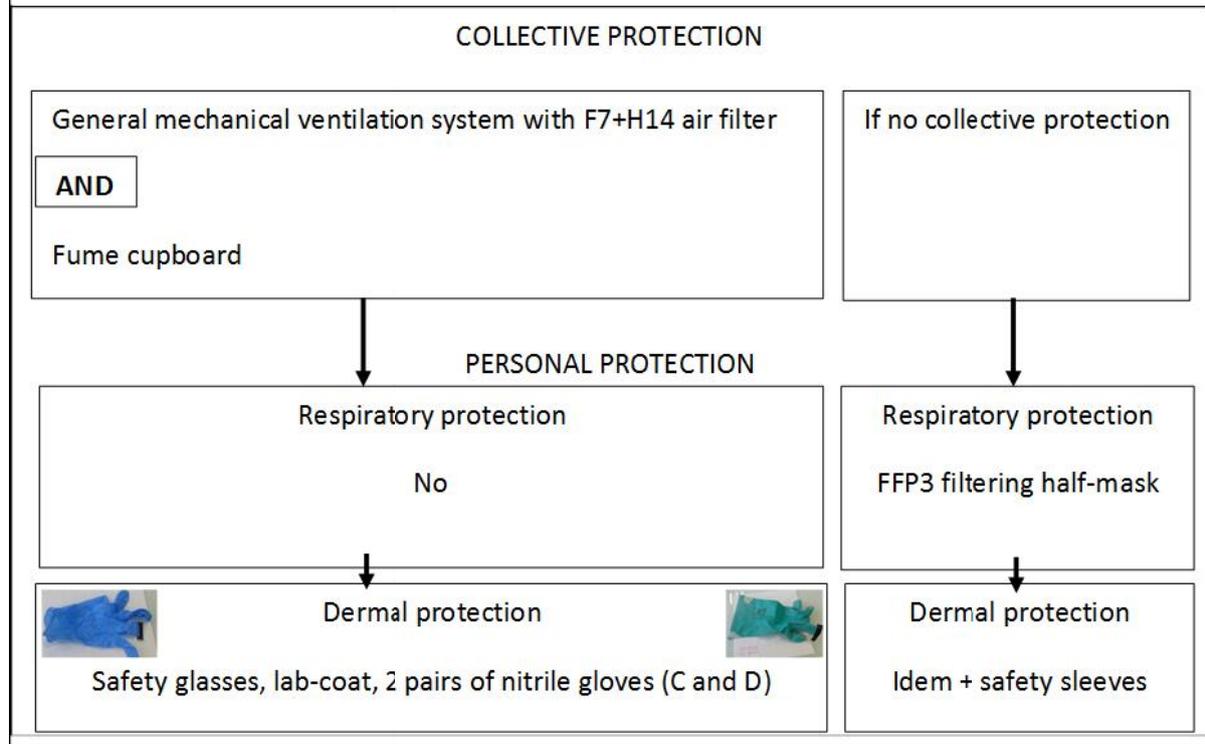
**Exposure scenario:** Handling a small amount of  $\text{TiO}_2$  NPs : weighting, bagging.

**Localization:** in a large room.

**State:** powder.

**Nano 5**

Decision tree 1.



**Scenario 3:**

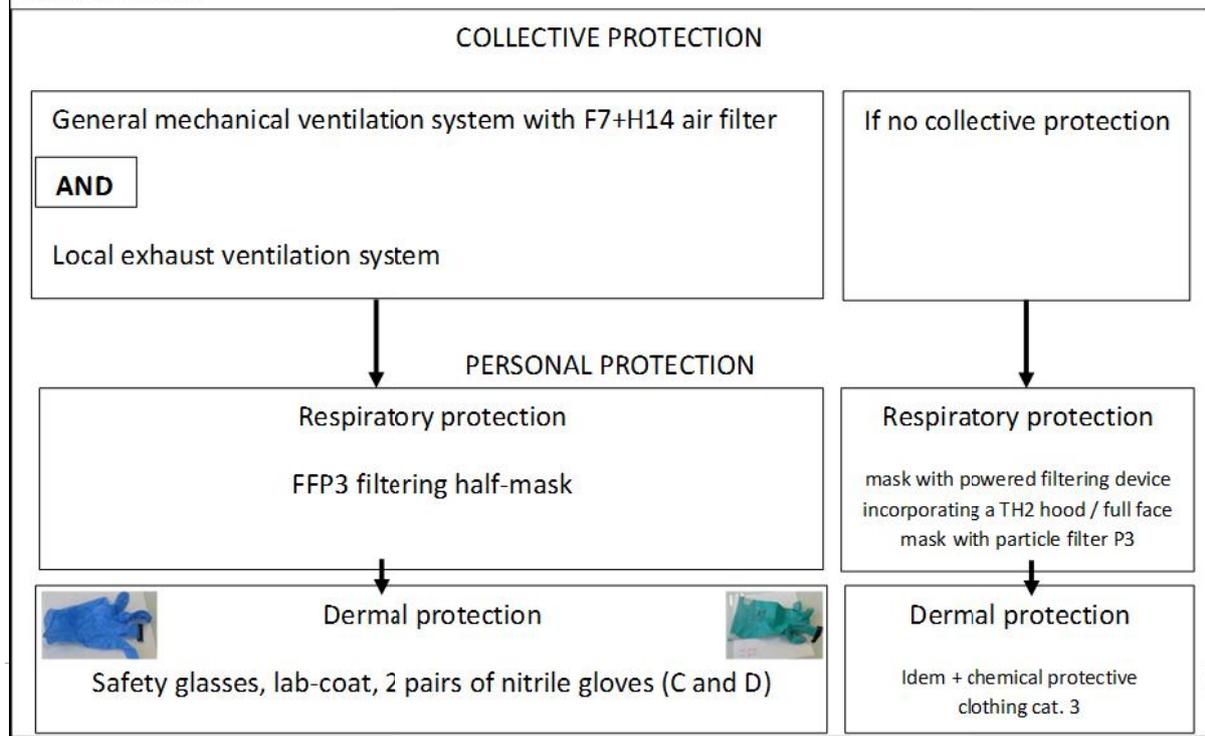
**Exposure scenario:** Dissolution of a large amount of nano $\text{TiO}_2$  (> 100g) in water (>1L).

**Localization:** in a large room.

**State:** powder.

**Nano 7**

Decision tree 1.



**Scenario 4:**

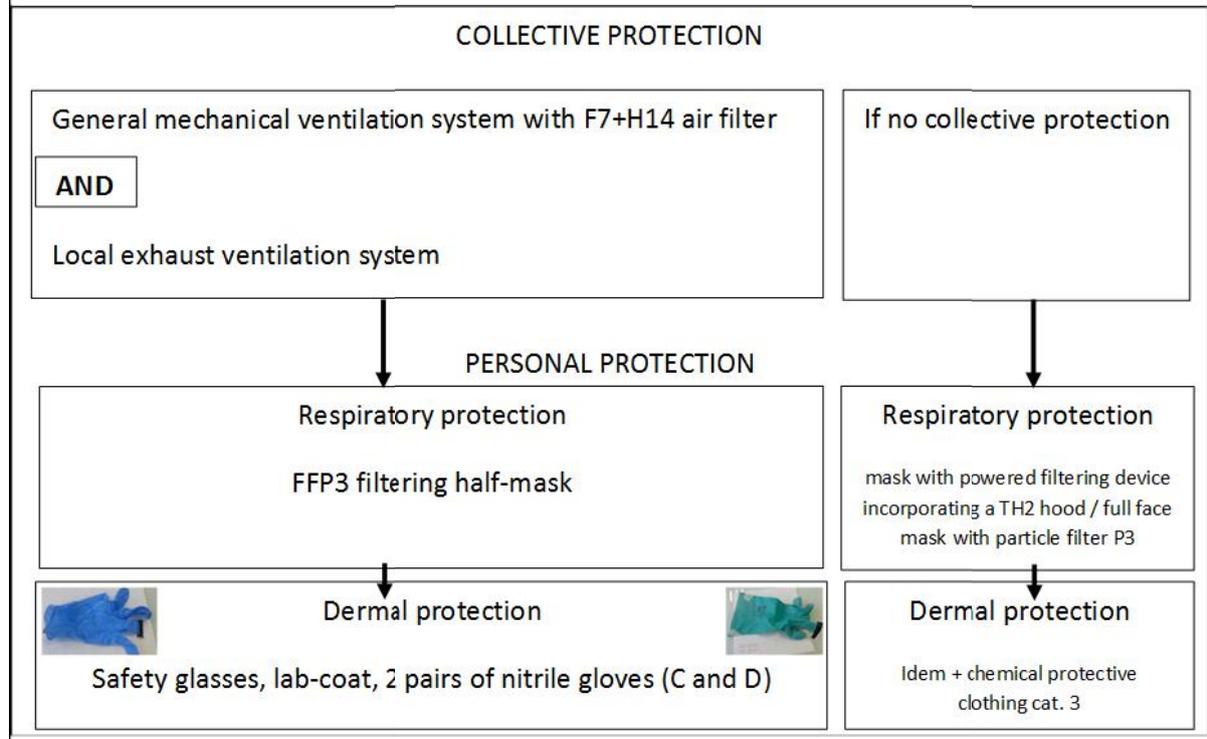
**Exposure scenario:** Manufacturing of a big quantity of insulating and fire resistant panels with nanoclay

**Localization:** indoor.

**State:** powder

**Nano 7**

Decision tree 1.



**Scenario 5:**

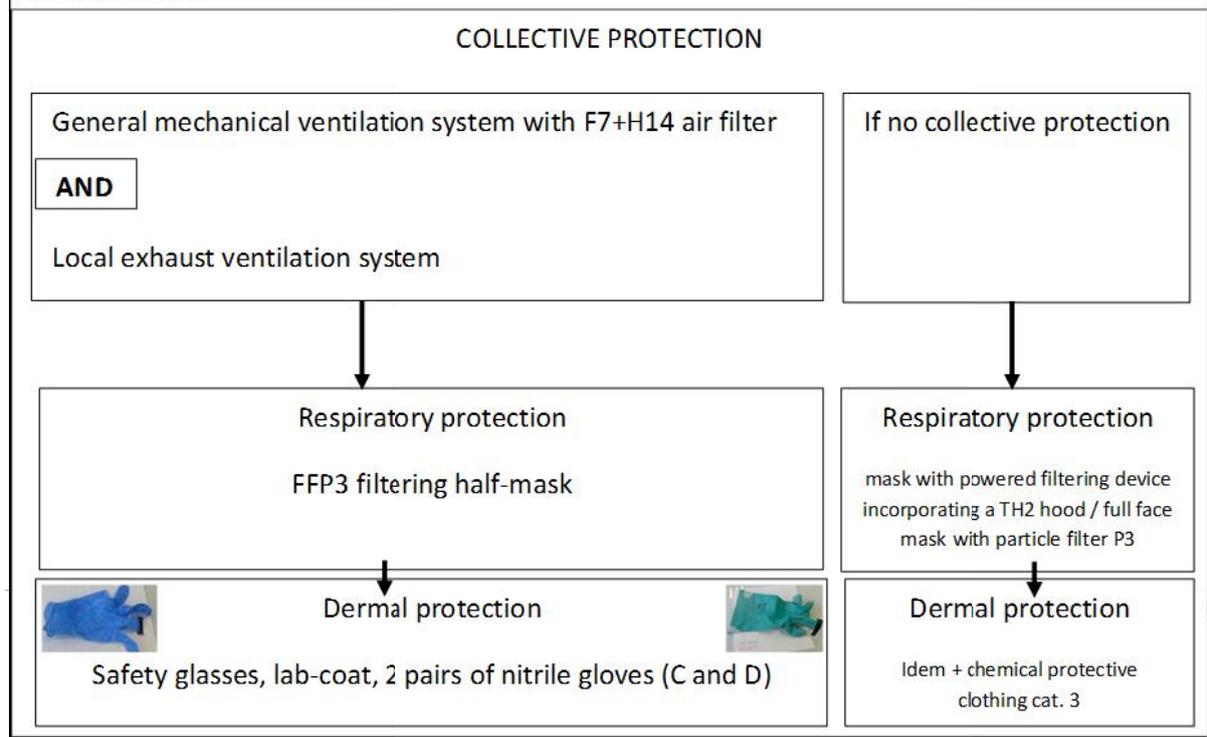
**Exposure scenario:** Manufacturing and formulation of self-cleaning external coatings with nanoTiO<sub>2</sub>.

**Localization:** indoor.

**State:** powder.

**Nano 7**

Decision tree 1.



**Scenario 5 bis:**

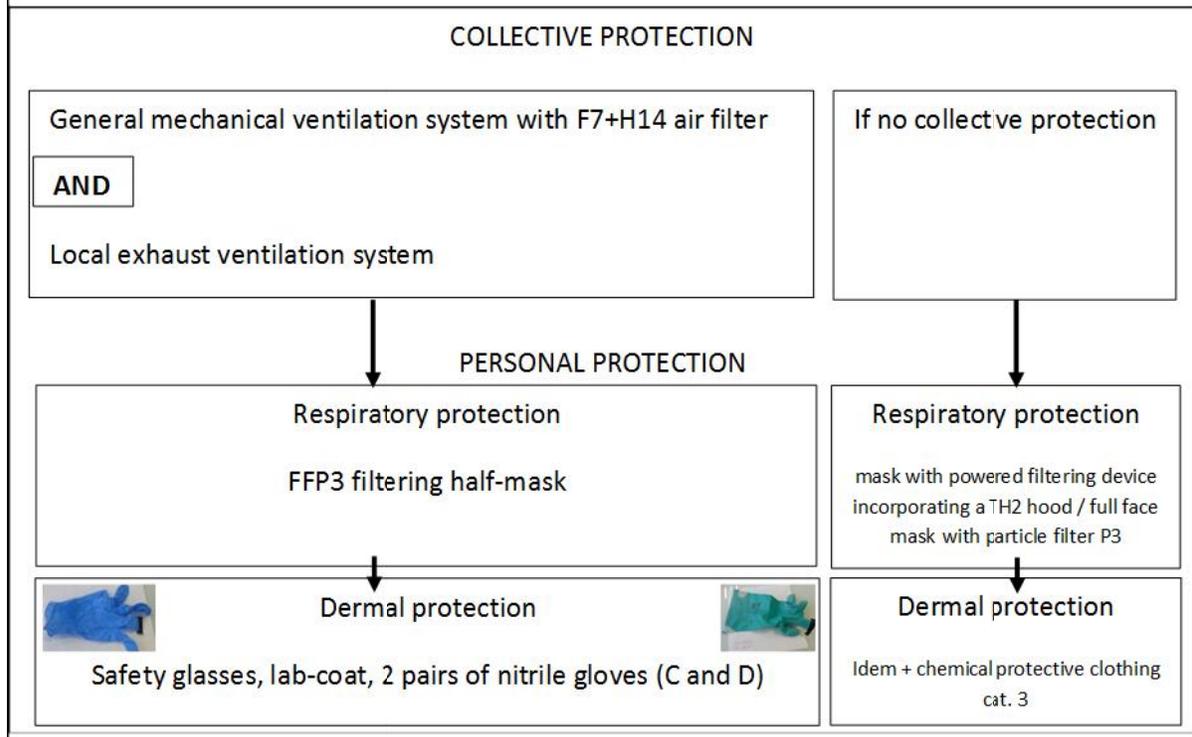
**Exposure scenario:** Manufacturing and formulation of self-cleaning external coatings with cellulose NFs.

**Localization:** indoor.

**State:** powder.

**Nano 7**

Decision tree 1.



**Scenario 6:**

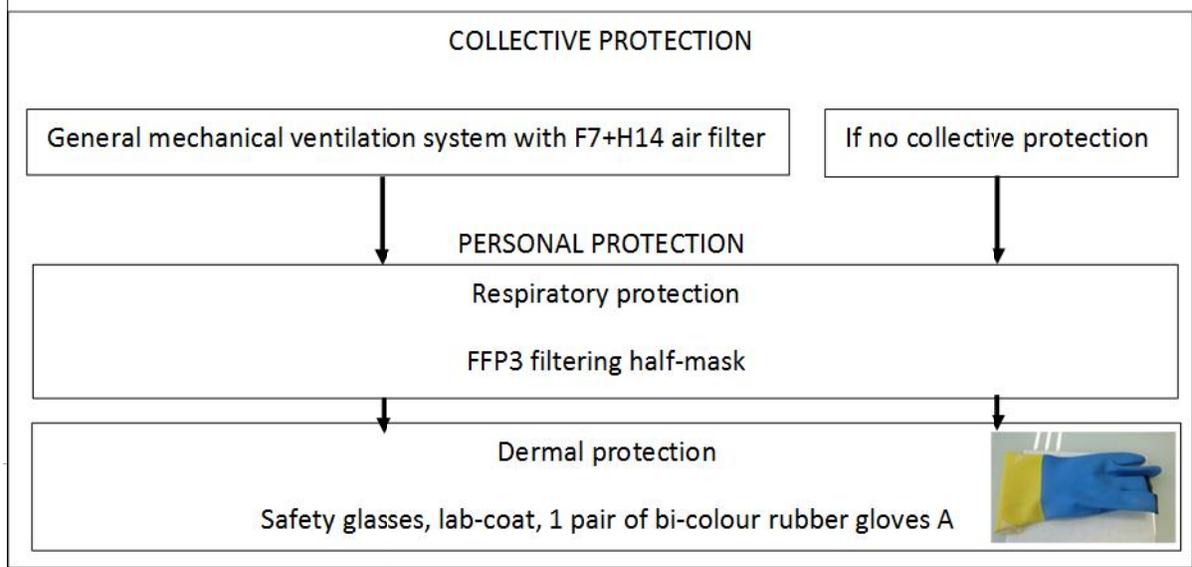
**Exposure scenario:** Manufacturing and formulation of mortar containing <1% of nanoTiO<sub>2</sub>.

**Localization:** large room.

**State:** powder.

**Nano 6**

Decision tree 1.



**Scenario 7:**

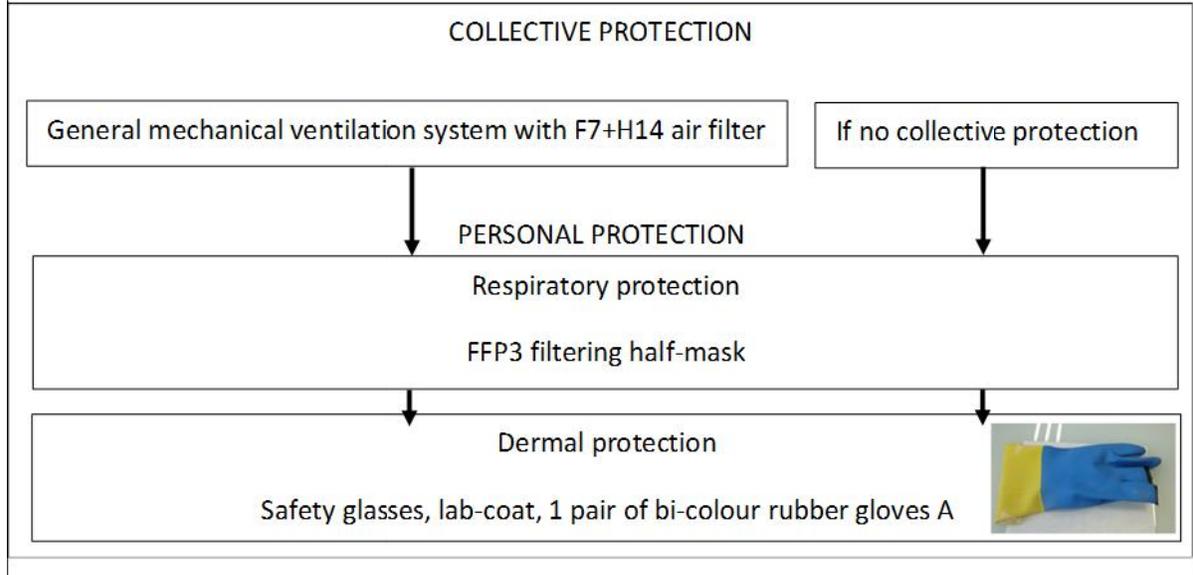
**Exposure scenario:** Manufacturing and formulation of concrete containing <1% of nanoSiO<sub>2</sub>.

**Localization:** large room.

**State:** powder.

**Nano 6**

Decision tree 1.



**Scenario 8:**

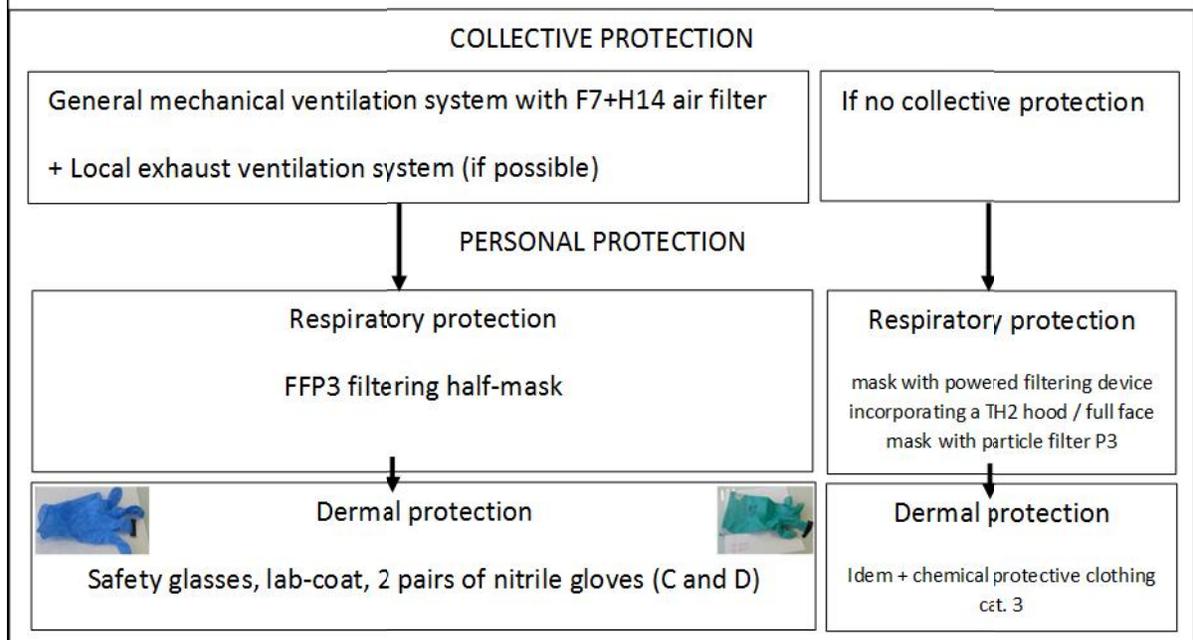
**Exposure scenario:** Manufacturing bituminous road surface pavements containing carbon NFs.

**Localization:** large room.

**State:** powder.

**Nano 7**

Decision tree 1.



**Scenario 9:**

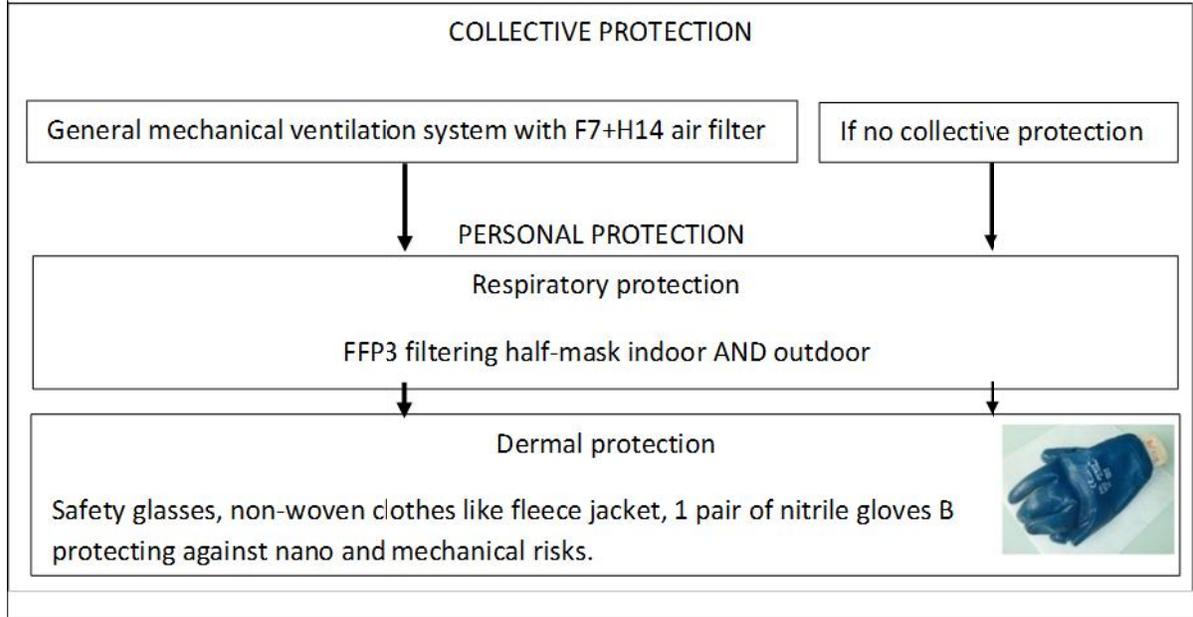
**Exposure scenario:** Drilling holes in panels containing nanoclay.

**Localization:** indoor.

**State:** generates solid and aerosolized NPs.

Nano 1

Decision tree 2.



**Scenario 9 bis:**

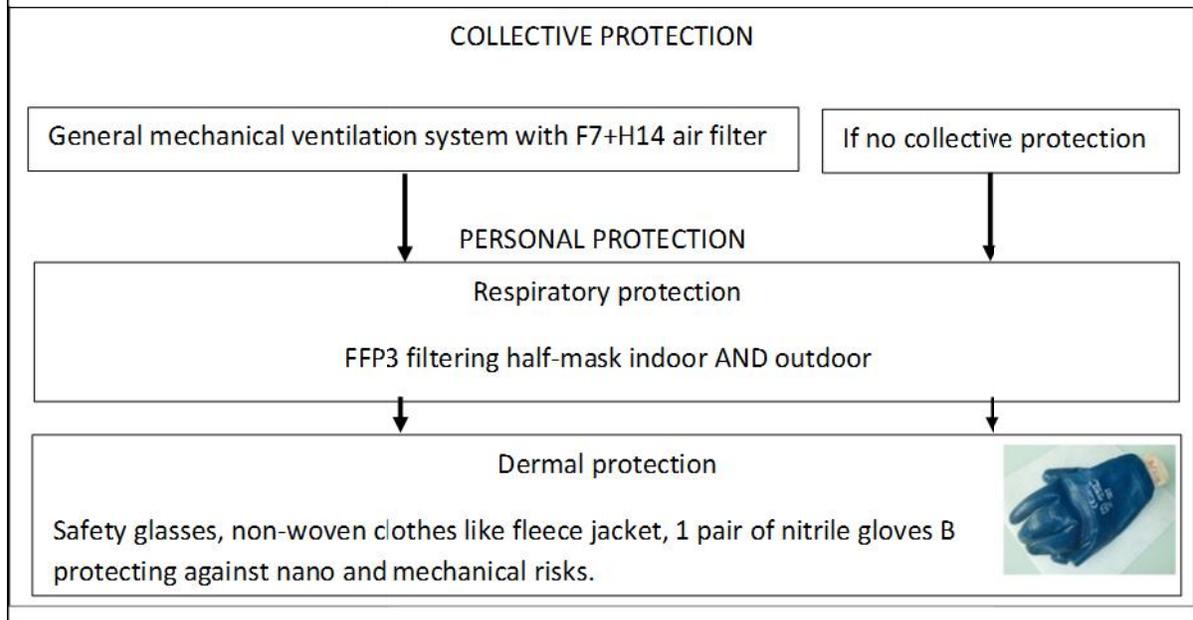
**Exposure scenario:** Drilling holes in panels containing carbon NFs.

**Localization:** indoor.

**State:** solid, aerosolization of NPs.

Nano 1

Decision tree 2.



**Scenario 10:**

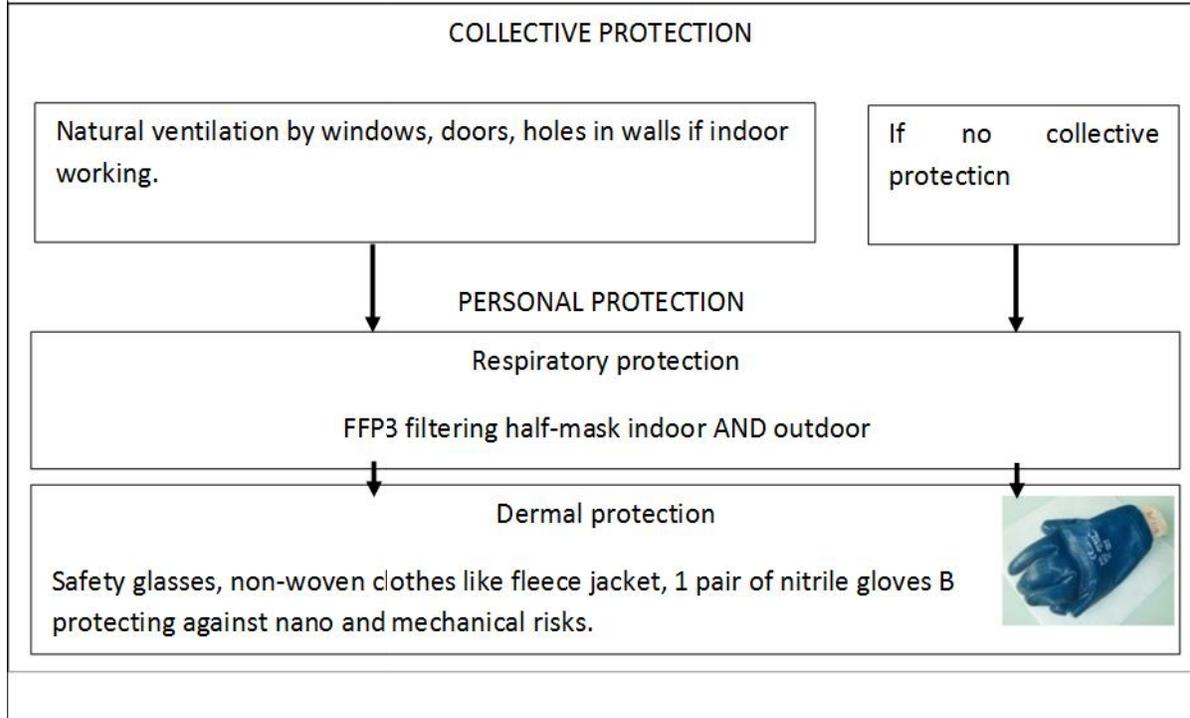
**Exposure scenario:** Applying a mortar containing  $\text{TiO}_2$  NPs on a wall.

**Localization:** outdoor.

**State:** solid.

Nano 1

Decision tree 2.



**Scenario 11:**

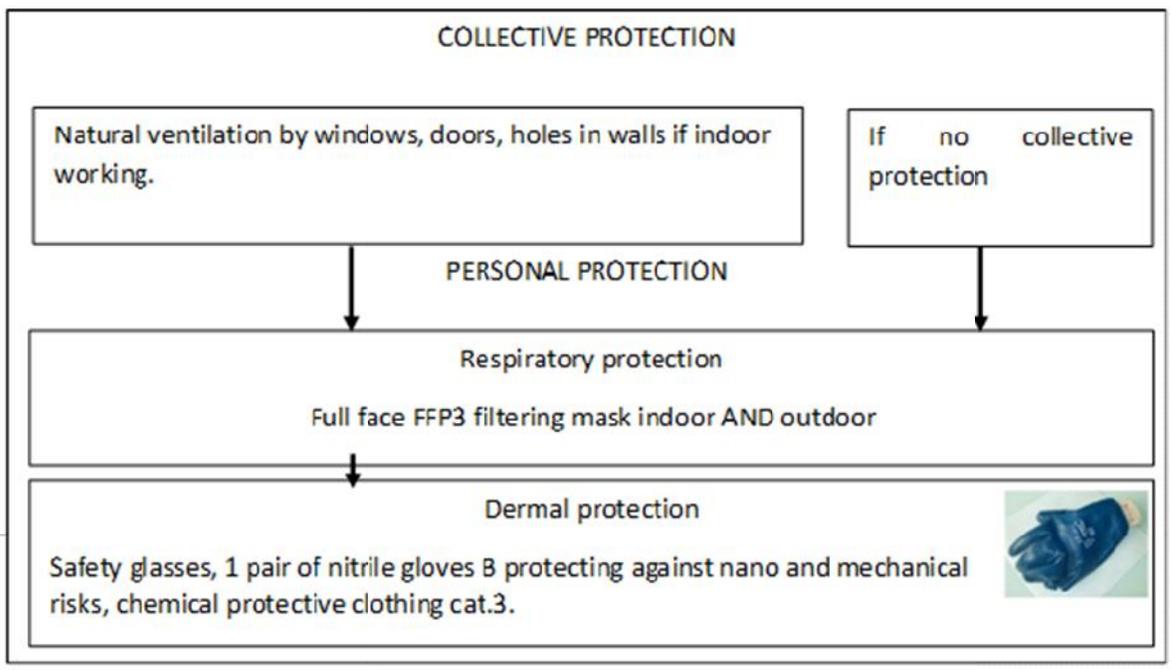
**Exposure scenario:** Spraying sol-gel mortar containing  $\text{TiO}_2$  NPs on a wall.

**Localization:** outdoor.

**State:** liquid.

Nano 2

Decision tree: 2.



**Scenario 12:**

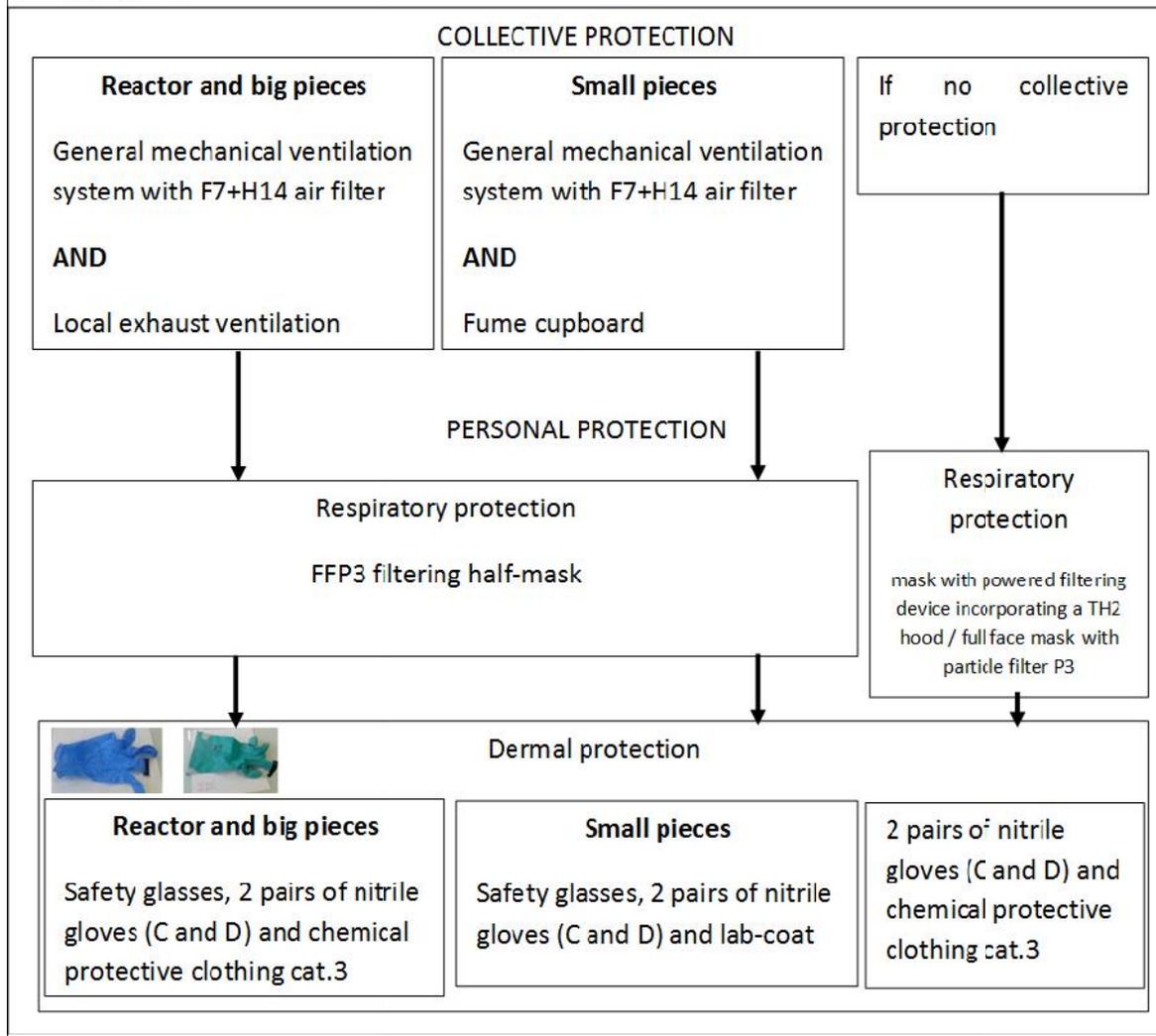
**Exposure scenario:** Cleaning of a reactor after synthesis of  $\text{TiO}_2$  nanopowders.

**Localization:** in a large room.

**State:** liquid.

**Nano 9**

Decision tree 1.



**Scenario 13:**

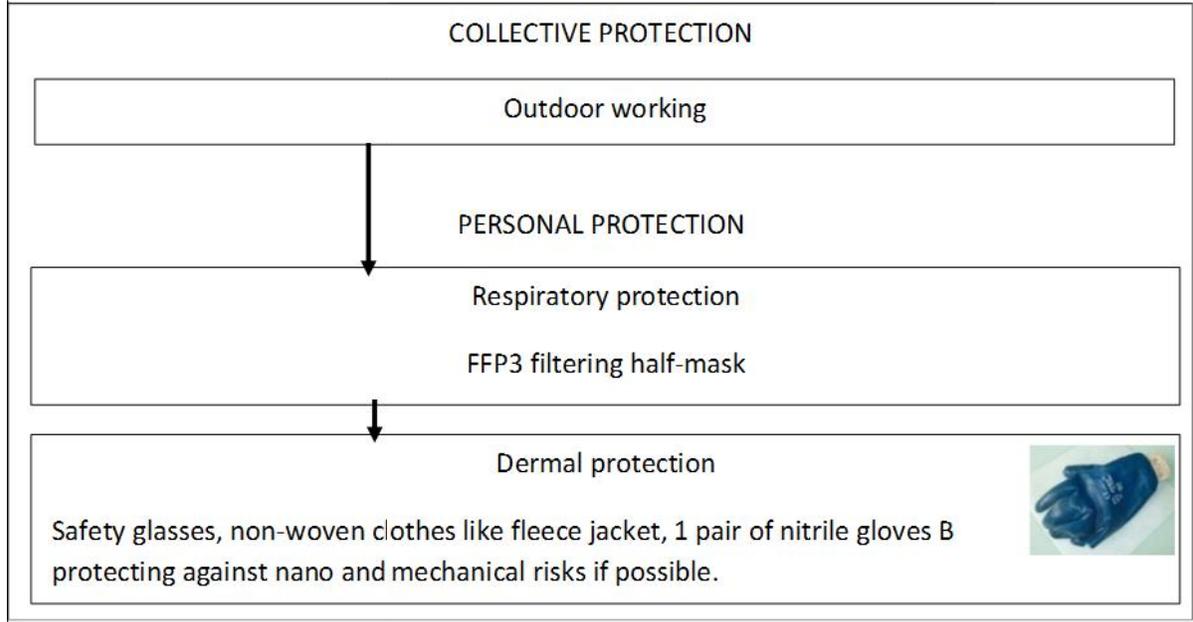
**Exposure scenario:** Demolishing a work cabin containing  $\text{TiO}_2$  NPs.

**Localization:** outdoor.

**State:** Generation of dust and aerosolized NPs.

Nano 1

Decision tree 2.



**Scenario 13b:**

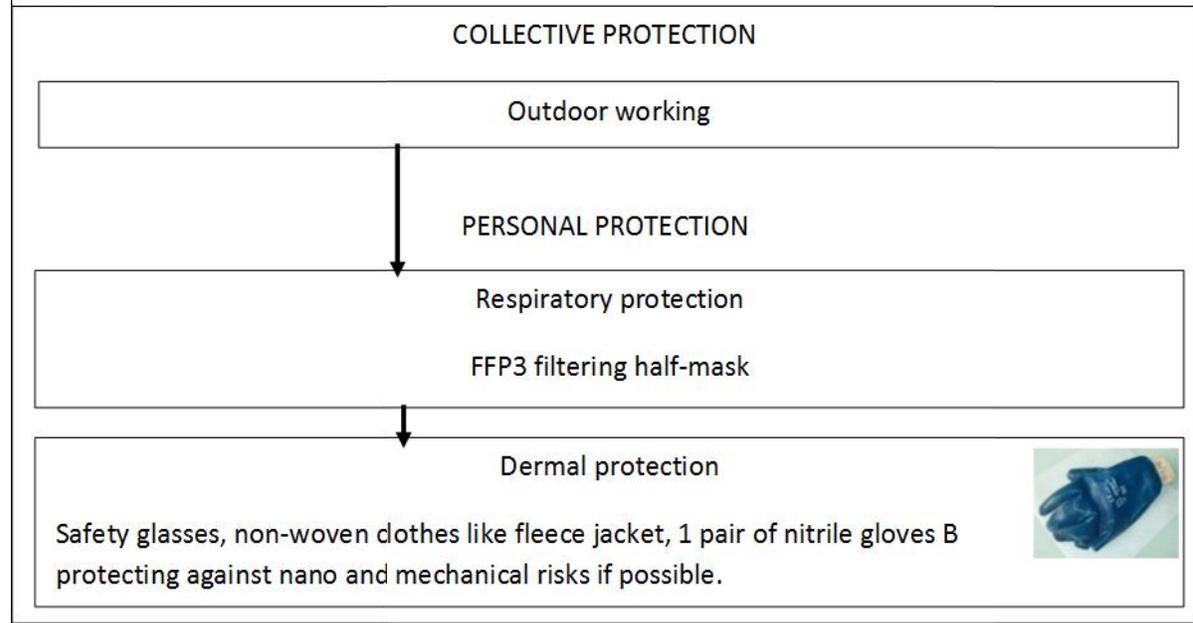
**Exposure scenario:** Demolishing a work-cabin containing carbon NFs.

**Localization:** outdoor.

**State:** Generation of dust and aerosolized NPs.

Nano 1

Decision tree 2.



**Scenario 14:**

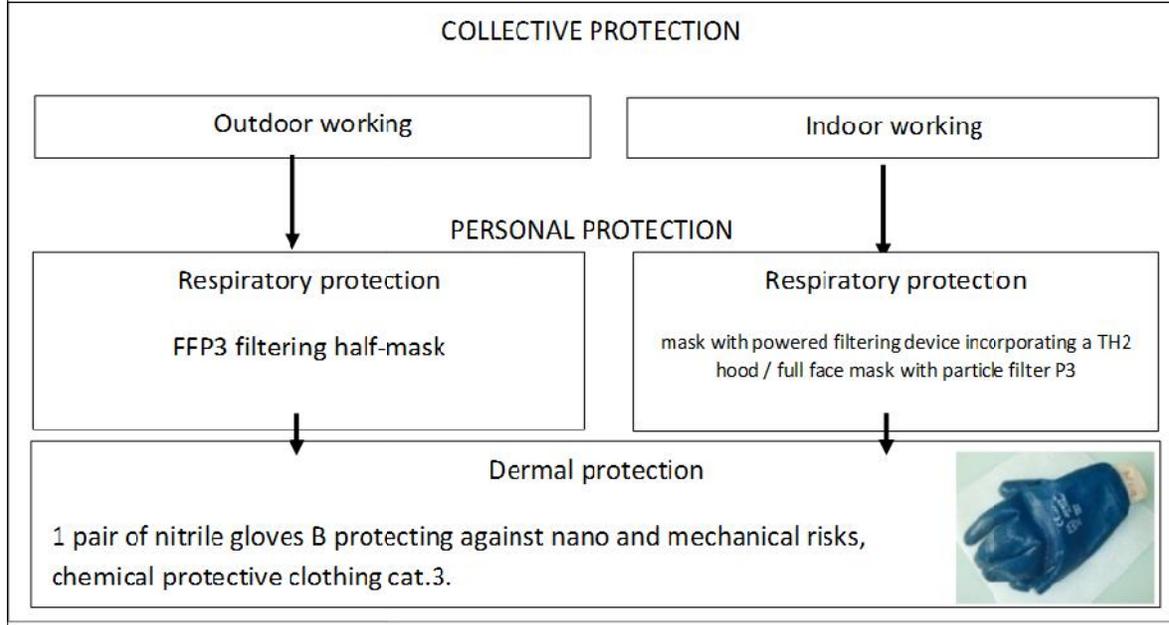
**Exposure scenario:** Cleaning a room after an accidental fire of panels containing nanoclay.

**Localization:** indoor.

**State:** Generation of aerosolized NPs.

**Nano 1**

Decision tree 2.



With all of these particular recommendations, general ones have to be mentioned too:

**First general steps:**

- Identify the used product
- Seek the relative data to evaluate hazards
- If these information are not public, try to obtain them with the competent person
- Identify the potential exposure sources and take technical measures to control exposure
- Conduct risk assessment. In the absence of relevant toxicological data to set up occupational exposure limits, a Control Banding method can be employed for qualitative assessment and management of occupational risks. The method can be used for:
  - providing hazard control guidance to small and medium size enterprises;
  - prioritizing hazards and for hazard communication in larger enterprises.
- Implement required engineering controls and other required risk management measures
- For workers probably exposed to nanomaterials, establish a nanoexposure registry to enable the assessment of the level of exposure
- Continue applying established medical surveillance approaches to construction workers (periodic health examination from 1 to 5 years)
- Training sessions adapted to the construction sector must be done for all workers. Objectives are the following:
  - Specificity of nanomaterials
  - Nanomaterials as a potential source of danger
  - Differentiation between concepts of danger and of risk (principle of prevention)
  - Other risks associated with nanomaterials
  - Rules or standards applicable to nanomaterials
  - Collective and individual protections at the workstation
  - Waste management
  - Security of storage and transport

## **Annex 1: Definitions**

### **Agglomerate**

Collection of weakly bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components [ISO/TS 27687:2008, 3.2]

### **Aggregate**

Particle comprising strongly bonded or fused particles where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components. [ISO/TS 27687:2008, 3.3]

### **Bulk material**

Material of the same chemical nature as the NOAA, at a non-nano scale (ISO/TS 12901-2).

### **Exposure**

Contact with a chemical, physical or biological agent by swallowing, breathing, or touching the skin or eyes. (ISO 12901-1:2011).

### **Health hazard**

Potential source of harm to health [ISO 10993-17:2002, 3.7]

### **Health risk**

Combination of the likelihood of occurrence of harm to health and the severity of that harm [ISO 10993-17:2002, 3.8]

### **Nanomaterial**

Material with any external dimension in the nanoscale (2.1) or having internal or surface structure in the nanoscale (ISO/TS 80004-1)

### **Nano-object**

Material with one, two or three external dimensions in the nano-scale [ISO/TS 27687:2008]

### **NOAA**

Nano-objects, and their aggregates and agglomerates greater than 100 nm (ISO/TS 12901-2)

**Nanoscale**

Size range from approximately 1 nm to 100 nm [ISO/TS 27687:2008]

**Particle**

Minute piece of matter with defined physical boundaries [ISO/TS 27687:2008, 3.1]

## Annex 2: References

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NIOSH (2009) Approaches to Safe Nanotechnology

Asbach et al (2012). NanoGEM Tiered approach for the assessment of exposure to airborne nanoobjects in work-places.

NIOSH (2013). Bulletin 65. Occupational Exposure to Carbon Nanotubes and Nanofibers)

NIOSH 0500 Particulates not otherwise regulated, total

NIOSH 0600. Particulates not otherwise regulated, respirable

NIOSH 5040. Elemental Carbon

NIOSH 7300 Elements by ICP

NIOSH 7402 Asbestos by TEM

NIOSH 7501. Silica, amorphous

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