



Risk management of occupational exposure to nanoparticles during a development project: A case study

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Abstract

The production of nanotechnology based products is increasing, along with the conscience of the possible harmful effects of some nanomaterials. Along with technological advances, there is the need to improve knowledge of safety and health and apply that knowledge to the workplace. The “safety-by-design” approaches are attracting attention as helpful tools to develop safer products and production processes. The Systematic Design Analysis Approach could help to identify the solutions to control workplace risks by defining the emission and exposure scenarios and the possible barriers to interrupt them. When managing risks during a photocatalytic ceramic tiles development project, it was possible to identify relevant nanoparticles emission scenarios and related barriers. Possible ways to reduce them could then be defined, which would in turn, lead to an inherently safer production process.

Keywords: photocatalytic ceramic tiles; risk assessment; systematic design analysis; inherently safer process.

Gestión de riesgos de exposición ocupacional a las nanopartículas en un proyecto en desarrollo: Estudio de caso

Resumen

La producción de productos basados en la nanotecnología va en aumento, junto con la conciencia de los posibles efectos nocivos de algunos nanomateriales. Junto con los avances tecnológicos, existe la necesidad de mejorar el conocimiento de la seguridad y salud y aplicar ese conocimiento en los entornos laborales. Los enfoques "Safety-by-design" están atrayendo la atención como herramientas útiles para desarrollar productos y procesos de producción más seguros. El enfoque de Análisis Sistemática de Diseño podría ayudar a identificar las soluciones para el control de los riesgos laborales mediante la definición de los escenarios de emisiones y de exposición y los posibles obstáculos a interrumpirlos. Cuando la gestión de riesgos durante un proyecto de desarrollo de las azulejos cerámicos fotocatalíticos, fue posible identificar escenarios de emisiones de las nanopartículas relevantes y las barreras relacionadas. Así, las posibles formas de reducirlos podrían ser definidas, lo que, a su vez, pueden dar lugar a un proceso de producción inherentemente más seguro.

Palabras clave: azulejos cerámicos fotocatalíticos; evaluación de riesgos; análisis sistemática de diseño; proceso inherentemente más seguro.

1. Introduction

Photocatalytic ceramic tiles containing nano-sized titanium dioxide (TiO₂) have self-cleaning characteristics and are also able to transform some air pollutants like nitrogen oxides, contribute to a cleaner ambient air, and

reveal anti-bacterial properties [1].

In general, the in-vitro and in-vivo tests done with both fine (particles with nominal diameter > 100 nm) and ultrafine TiO₂ particles (with nominal diameter <100 nm, also called nanoparticles or nano-sized particles), have potentially harmful health effects in humans. TiO₂ nanoparticles induce

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inflammatory responses in the lung tissue, particularly in high doses [2]. The International Agency for Research on Cancer (IARC) classified TiO₂ as “possibly carcinogenic to humans”: a carcinogenic Group 2B substance [3]. In a review on the animal and human data relevant to assessing the carcinogenicity of TiO₂, published in 2011, the National Institute for Safety and Health (NIOSH), concluded that exposure to ultrafine (or nano) TiO₂ should be considered a potential occupational carcinogenic agent, and recommended an airborne exposure limit of 2.4 mg/m³ for fine TiO₂ and 0.3 mg/m³ for ultrafine (including engineered nanoscale) TiO₂ [4].

Some authors have been defending the need for methodologies that address the risks related to nanotechnologies, based on the processes or product design [5-7]. One approach cited in the literature is the “Design for Safer Nanotechnology” proposed by Morose [8] in which the author suggests an intervention during the design stage for nano-objects and products that incorporate them. Schulte et al. [5] also mention the Prevention through Design (PtD) initiative as a valuable methodology to manage occupational risks. Swuste and Zalk [9] also propose the use of design analysis to achieve safer production processes in the nanotechnology field.

The aim of this paper is to present the work that is carried out to establish a safer production process resulting from a development project. The underlying research questions are:

- Does a design approach to the production line of photocatalytic ceramic tiles generate relevant emission scenarios and related barriers?
- What are the possibilities of the Systematic Design Analysis Approach (SYDAPP) reducing emission scenarios during the production of photocatalytic ceramic tiles?
- Could managing risks during the development phase of a new production process help to define safer processes?

2. Methodology

2.1. Framework

The work presented in this paper was performed during a photocatalytic ceramic tiles development project, using TiO₂ (anatase) and employing a common ceramics production processes. It was part of a SELFCLEAN funded research project.

The project lasted for approximately two years, from the first exploratory tests to the final product prototype. The OSH intervention, including the work described in this paper, lasted six-months, plus another two months to produce the OSH issues report.

The project team included several materials science researchers and engineers from a university, a technological institute and a ceramic tile company, and one occupational safety and hygiene (OSH) practitioner.

Discussions on the health and safety aspects for the project were held on an interdisciplinary knowledge basis. These discussions were complemented by observation and information collection during laboratory sessions and semi-industrial tests that were performed during the project.

OSH issues were included in the agenda of three of the project’s plenary meetings. For approximately 45 minutes in each of the meetings, the SYDAPP was presented and the team members had the opportunity to contribute their inputs to the process design analysis and related emission and exposure scenarios. The group discussions gathered contributions, particularly from the design analysis, the identification of emission and exposure scenarios and the possible barriers. The experts proposed alternative production principles and forms, including their feasibility evaluation, which helped to identify their impact on the possible scenarios. In parallel, several face-to-face informal meetings were held by the OSH practitioner with the other members of the group, including the ceramic company engineer and the university researchers, in order to refine knowledge on different options and confirm information collected during the meetings and project tests. Finally, the OSH practitioner, based on the collected information, produced a report for the project manager.

2.2. Systematic design analysis approach

Although occupational safety and hygiene research pays more attention to risk analysis [10], several authors in this domain have undertaken research in the safety by design field, especially the Safety Science Group from Delft University of Technology [11–13]. Swuste [10], for example, proposed a systematic approach towards solutions based on three complementary elements:

- A hazard process model;
- Design analysis;
- A problem-solving cycle.

The two first elements are the basis for the SYDAPP. Combining the process design analysis with the emission and exposure scenarios, it is possible to acquire a clear vision of how the different process operations will affect a worker’s exposure.

2.3. Hazard process model - Bow-tie

The bow-tie model is used in the safety science field as a tool to prevent the occurrence of accidents [14]. Its adaptation to the occupational hygiene field (see Fig. 1) helps to establish the necessary barriers to control risks arising from different workplace exposure scenarios [15]. The use of the bow-tie model as a support tool to risk management is also referred to by Fleury et al. [7]. An example of the use of this model, defining exposure scenarios and evaluating the risks during the production of carbon nanotubes polymer composites is presented in another article [16].

The bow-tie model also stresses the importance of management as the entity responsible for implementing the barriers [17].

When the bow-tie model and the design analysis are performed together, it is possible to have a detailed vision of the production process and the occupational risks related with the production process. Emissions and, consequently, exposure are identified on a production form level. Thus, the options to reduce emissions and exposure are usually limited to LEV and personal protective equipment. As these controls

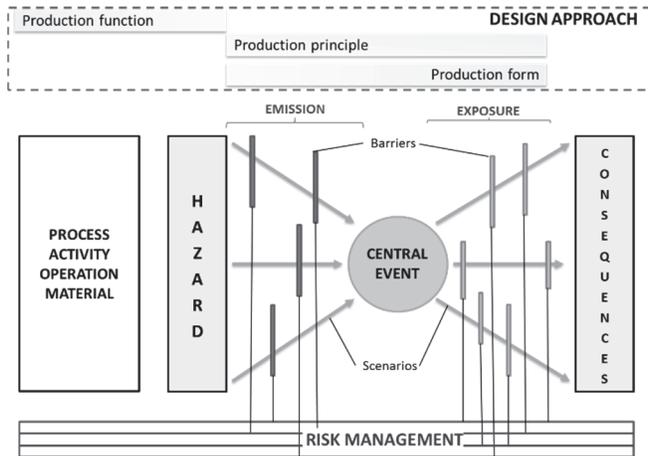


Figure 1. Bow-tie model with arrows representing different exposure scenarios.
Source: The authors

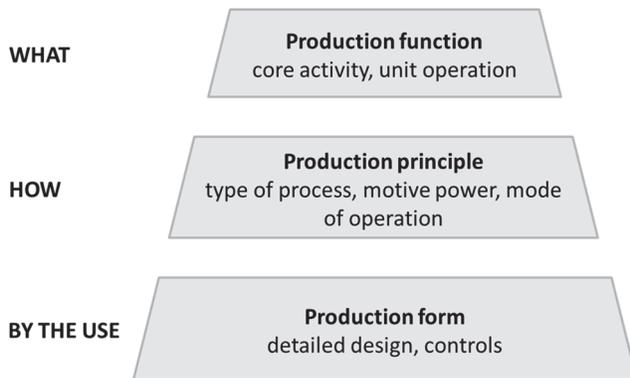


Figure 2. Design analysis hierarchy [10].
Source: The authors

could become ineffective due to the high level of exposure, or their own characteristics, it is useful to act with production principles or production functions, which provide more operative controls.

2.4. Design analysis

The design analysis methodology allows workplace conditions to be understood and studied. In design analysis, the production process is split into three decision levels (see Fig. 2), described below [10]:

- **Production function:** is the highest level and divides the production process into its core activities, similar to unit operations;
- **Production principle:** identifies the general process, motives, power, and operational control methods by which the production function can be achieved;
- **Production form:** is the lowest level and specifies the detailed design by which the production principle will be accomplished.

If there are a large number of production processes, the type of functions (or unit operations in rigor) in which each process can be broke down is relatively small. The main unit

operations categories are: material reception, material storage, transport and feed, processing, packaging, and waste disposal. The processing operations can be subdivided in subcategories that vary from one industry sector to other. When they are enumerated, they will allow the more effective and reasonable control measure or set of control measures to be applied in each particular situation to be studied. Some examples of processing production functions or unit operations in the ceramic tiles industry are milling, conformation, drying, glazing, firing and sorting, etc.

At the production principle level, it is possible to choose the type of process to achieve the function (eg., different shaping processes), the motive power (ex. electricity or fossil combustible), and the mode of operation (eg., manual operation, mechanical or automatic). There are hundreds of different production principles to undertake unit operations.

At the production form level the machine, the equipment, or set of equipment that will be used in the process is defined (e.g., the hydraulic press type, if shaping by press is the principle used to achieve the unit operation “conformation”). It is also at this level that the exposure controls are defined (e.g., a local exhaust ventilation (LEV) or a closed cabin).

From an occupational safety & health point of view, the focus on the production functions and principles will allow the less hazardous way to achieve the same production result to be found, the best available techniques to control the hazard can be chosen.

2.5. Risk and exposure assessment

In order to undertake risk assessment, a control banding based method was used: the CB Nanotool, which is a four by four matrix that relates severity parameters on one-axis and probability parameters on the other. The severity parameters consider physicochemical and toxicological properties of both nanomaterial and parent material, including, surface reactivity, particle shape and diameter, solubility, carcinogenicity and mutagenicity. The probability band scores are based on factors affecting the potential exposure to the nanomaterial, namely, the estimated amount of chemical used in one day, dustiness, number of employees with similar exposure, frequency of operation and operation duration. The obtained control bands by risk level can be classified in RL1 – general ventilation, to RL4 – seek specialist advice [18].

For exposure assessment, the usual occupational hygiene method was used, namely the NIOSH 0500 for total dust [19]. This consists of collecting the airborne particles in one filter through filtering workplace air. The samples were personal, thus the filter support was placed in the worker’s breathing area.

3. Results and discussion

3.1. Production process and the design analysis

After the preliminary tests, the planned photocatalytic ceramic tiles production process was defined and the use of already existing equipment in the ceramic production plant was proposed. Then, the first step was to detail the production

process, dividing its functions, principles and forms (see Table 1). This work was performed during the project meetings, by getting contributions from all the project's team members.

The production process is similar to the usual ceramic tiles production process. The most relevant unit operations in the process are those related to the processing of raw materials and surface coating.

During a project meeting when contributions from team members were obtained, it was possible to define alternative production principles and forms for the production process. The possible options were the automation of the sack emptying operation, ultrasound agitation for raw materials mixing, and a few non-spraying techniques to apply the TiO₂ aqueous suspension in the ceramic tiles (ex. roll printing, serigraphy or ink-jet). This information is presented in Table 2.

Beside the possible changes in the process itself, other possible action that has a positive impact in the emission and exposure scenarios, contemplated during the design analysis group discussions, was the acquisition of pre-prepared slurry. This would eliminate several unit operations, as the product would arrive at the facilities in liquid form. In particular, pouring raw materials (sack emptying) will be eliminated, which is a dusty operation in the production process.

Considering the bow-tie model together with the design analysis, it was possible to identify the emission scenarios and the barriers for each production function, and related principles and forms. The scenarios and barriers are defined for the normal functioning situations, process disturbances, facilities cleaning and equipment maintenance (Table 2). The identification of the possible emission scenarios and emission barriers was based on the knowledge of the processes and related engineering risk control measures.

It is possible to see that changing the production principle in the pouring raw materials function from the manual operation to the automatic operation will make it possible to introduce a barrier, a closed cabinet with LEV, in the emission scenario. Moreover, considering the acquisition of pre-prepared slurry, the emission scenario is eliminated.

Comparing the possible production principles for the surface coating, once again it is possible to eliminate the dust release emission scenario by choosing a non-spraying technique instead of the air-less spraying (or another spraying technique) to apply the TiO₂ on the ceramic tile surface.

3.2. Pilot-test

During the project, a pilot-test was performed, allowing part of the production process operations and tasks to be simulated. Previous to pouring raw materials, one additional operation was considered, weighing TiO₂. To undertake a risk assessment, 4 different tasks were considered: Task 1- Titanium dioxide weighing; Task 2- Pouring titanium dioxide; Task 3- Mixing slurry; Task 4- Surface coating.

Another relevant question was the use of fine TiO₂, instead of nano-sized form, which resulted from the fact that the photocatalytic properties were optimized with that material.

The risk assessment of the unit operations was performed with the CB Nanotool, which considered the possible use of nano-sized TiO₂. The severity factors are presented in Table 3.

Table 1. Production functions, production principles and production forms for the photocatalytic ceramic tiles production process

Production Function	Production Principle	Production Form	Description
Reception of raw materials	Mechanical, discontinuous transport	Palletized bags, forklift	The nano-TiO ₂ is received in paper bags, which are packed in wood pallets. The pallets are handled with a forklift and/or an electric pallet-truck.
Storage of raw materials	Mechanical, discontinuous transport	Palletized bags, forklift	
Transport of raw materials	Mechanical, discontinuous transport	Palletized bags, forklift	
Pouring raw materials (sack emptying)	Manual operation	Emptying bags to a container	The TiO ₂ powder is poured into water and is dispersed in the liquid with a column stirrer to obtain homogenized slurry. When the suspension is homogeneous it is milled in a micro-balls mill in order to de-aggregate. Finally, the slurry is sieved.
Mixing raw materials	Mechanical stirring	Column stirrer and micro-ball mill, container	
Surface coating	Spraying, automatic	Air-less spraying, booth disk glazing, booth spray-gun, booth	The slurry is applied in the already fired ceramic pieces by spray technic.
Transport of materials	Mechanical, automatic	Parallel belt line, ceramic tiles loading and unloading machines, storage boxes	The coated tiles are transported over two parallel trapezoidal belts on the glazing line. At the end of the line the tiles are loaded on a "ceramic tiles box" for storage before firing. At the kiln, the tiles are unloaded from the box and transported to the kiln entrance over parallel trapezoidal belts and/or roller conveyor.
Processing - firing	Thermal, automatic	Roll kiln	After the coating, the pieces are fired (2nd fire) at a temperature of around 950 °C in a continuous roll kiln.
Sorting	Manual, mechanical automatic transport	Ceramic tiles sorting line	The fired pieces are sorted (defects on the surface and body of the pieces are checked for) and packed in cardboard boxes.
Packaging	Mechanical, automatic	Ceramic tiles packaging line	

Source: The authors

In Table 4 presents the exposure factors considered for the different tasks assessed.

Table 5 presents the CB Nanotool assessment results are.

Table 2.

Emission scenarios and related barriers related to possible options for the production principle

Production function	Production principle	Normally functioning		Process disturbances		Cleaning		Maintenance	
		Emission scenario	Emission barrier	Emission scenario	Emission barrier	Emission scenario	Emission barrier	Emission scenario	Emission barrier
Raw materials reception, storing and transport	Mechanical, discontinuous transport			Damaged bags, powder spills	Metal containers	Cleaning powder spills	Vacuum-cleaner		
	Manual operation	Dust release		Powder spills		Cleaning powder spills		Intervention for dirty equipment	
Pouring raw materials	Automatic process	Dust release	Closed cabinet	Powder spills	Closed cabinet	Cleaning powder spills	Vacuum-cleaner	Intervention for dirty equipment	
	Pre-prepared slurry			Slurry spills	Closed containers	Cleaning dried slurry spills			
Mixing raw materials	Mechanical stirring			Slurry spills		Cleaning dried slurry spills		Intervention for dirty equipment	
	Ultrasound agitation			Slurry spills		Cleaning dried slurry spills		Intervention for dirty equipment	
Surface coating	Spraying, automatic	Spraying (aerosol release)	Closed cabin with LEV	Slurry spills, spray gun clog		Cleaning dried spills		Intervention for dirty equipment	
	All non-spraying technics, automatic			Slurry spills		Cleaning dried spills		Intervention for dirty equipment	
Material transport	Mechanical, automatic			Tiles jam in line or loading/unloading machines		Removing jammed material			

Source: The authors

Table 3.

CB Nanotool Severity band factors

Hazard Factor	Answer
Parent material hazard	
OEL (µg/m³)	2400
carcinogen?	yes
reproductive hazard?	no
mutagen?	no
dermal hazard?	no
asthmagen?	no
Nanoscale material hazard	
Surface reactivity	unknown
Particle shape	spherical
Particle diameter (nm)	>40
Solubility	insoluble
carcinogen?	yes
reproductive hazard?	unknown
mutagen?	unknown
dermal hazard?	unknown
asthmagen?	no

Source: The authors

During the pilot-test, the airborne particles concentration was measured using the NIOSH 0500 method in order to have a perception of the worker's exposure to TiO₂ particles during operations. Considering task durations and the workers present in the workplace, it was decided to sample

during the TiO₂ aqueous suspension, including weighing raw materials, pouring raw materials and mixing, and performing two personal samplings on both the workers operating the glazing line (surface coating and transport of materials). Table 6 presents the results of airborne sampling.

The sampling time corresponds to the whole working time. In the first attempt to produce the ceramic tiles, several disturbances occurred and the results should be considered to only represent the conditions of the test. They could not be considered as representing future exposure during industrial

Table 4.

CB Nanotool probability band factors

Probability factor	Answer			
	Task 1	Task 2	Task 3	Task 4
Estimated amount of chemical used in one day (mg)	10 ⁶	10 ⁶	10 ⁶	10 ⁶
Dustiness	Medium	High	Low	High
Number of Employees with Similar Exposure	1 - 5	1 - 5	1 - 5	1 - 5
Frequency of Operation (annual)	Monthly	Monthly	Monthly	Monthly
Operation Duration (hours per shift)	< 30 min	< 30 min	< 30 min	1 - 4 h

Source: The authors

Table 5.
Pilot-test risk assessment using CB Nanotool

Task	Severity band	Probability band	Overall risk band	Control required
1- Titanium dioxide weighing	Medium	Less Likely	RL1	General ventilation
2- Pouring titanium dioxide	Medium	Likely	RL2	Fume hood or local exhaust ventilation
3- Mixing slurry	Medium	Less Likely	RL1	General ventilation
4- Surface coating	Medium	Likely	RL2	Fume hood or local exhaust ventilation

Source: The authors

Table 6.
Airborne particles concentration during pilot-test tasks

Tasks	Sampling time (min)	Concentration (mg/m ³)
Worker during raw material weighing and slurry preparation	33	1.1 ¹
Surface coating in glazing line – Worker 1	160	0.9
Surface coating in glazing line – Worker 2	150	1.5

Source: The authors

production of this type of ceramic tiles, but they could give a rough estimation.

3.3. Discussion

The SYDAPP creates a cooperative environment between process engineers, safety practitioners and other people involved in the development of the process, and facilitating the communication and understanding inside the multidisciplinary team. With this approach it is possible to truly involve the designers and engineers in the occupational risk management.

The production functions and production principles are crucial to design solutions since emissions are directly related to the production functions applied. These functions will limit the number of possible principles, and consequently the number of forms. The actual emission that results in exposure always becomes visible in the production form. Conventional occupational hygiene control measures, such as LEV, enclosure, etc. will act on the production form level.

However, when the emission (and the related exposure) is too excessive, or the contaminants are too dangerous, (re)design approaches will be the only option left to reduce or eliminate emissions (apart from cancelling the whole production). (Re) design consists of changing production-principles under an unchanged production function, or changing or eliminating production functions. This last option is very effective, because the corresponding principles and forms will also be eliminated. Using pre-mixed slurries instead of mixing powdered raw materials is an example in which all functions related to raw materials processing are

eliminated. When a company introduces these changes, it is substantially reducing the sources of emission and exposure at the initial phase of the production process. Obviously, other companies will need to perform these production-functions, but when volumes are big enough, these firms can also modify their production methods, for example, by changing their mode of operation from manual to automatic.

Accordingly, the use of the supply chain with OSH purposes is one question raised by the SYDAPP. The design analysis performed along the supply-chain helps to identify opportunities to transfer higher risk operations to facilities that are prepared to address it. This allows others to focus on the core process operations, which will ultimately result in safer workplaces, by implementing cost-effective solutions. This approach is only acceptable if the risks are transferred to adequate facilities, not to less controlled subcontractors.

Both the CB Nanotool risk assessment and the airborne particles sampling pointed to potential risk to workers during the pilot-test, considering the possible use of nano-sized TiO₂. It is clear that the pilot-test conditions do not exactly replicate the future production conditions but could help to better understand the main emission and exposure scenarios. By replacing nano-TiO₂ by fine-TiO₂ it is possible to reduce the risk for workers. Based on the existing knowledge of the TiO₂ toxicological properties, it is clear that its nano form is more hazardous than the fine-TiO₂ [4]. Furthermore, the toxicological assays performed with nano-TiO₂ reveal potential effects to health resulting from the possible translocation of the nanoparticles in the human body and also from the capability of cell internalization. Considering the bow-tie model, acting on the hazard itself is an advantageous strategy to deal with the workplace risks as this takes place prior to the emission and, of course, the worker's exposure. The results obtained from the airborne particles sampling during the pilot-test show that the exposure to TiO₂ airborne particles is below the proposed limit value of 2.4 mg/m³, even when considering that all the airborne particles were TiO₂.

In the tests performed during the Selfclean Project, the medium size TiO₂ particles was in the 150-200 nm range, while the nano-sized TiO₂ particles have diameters below 100 nm. According, to the International Commission on Radiological Protection's (ICRP) respiratory tract deposition model for particles, quoted by the International Organization for Standardization, it is evident that the probability of the particles with sizes from 150 nm to 200 nm depositing in all respiratory tracts is lower than particles smaller than 100 nm [20].

Considering the lack of knowledge and the potential for harm of the different types of nano-objects, and the uncertainties related to risk and exposure assessment [21], the safety-by-design approaches become relevant. What has previously been learnt from the safety science field could help by defining ways to deal with potentially high-risk production processes. The inherently safer process concept developed in the late 1970's, which focuses on the avoidance or reduction of the hazard at source [22,23] is adaptable to the nanotechnologies field. The SYDAPP allows the project team to identify the unit operations with a lower emission potential.

¹ Result below quantification limit. The uncertainty is higher compared with the other results.

4. Conclusions

The use of the SYDAPP helps to find solutions to reduce the workers' exposure during their work with engineered nano-objects. As shown in the case presented in this model, it seems that there is an advantage to be had in applying it in a development project, or in other words, during the project phase and before the final process design is set.

With this approach, it was possible to generate emission scenarios resulting from the photocatalytic ceramic tiles production process operations. The bow-tie was a helpful concept model to achieve this.

Following identification of the emission scenarios, it was also possible to define emission reduction barriers. In the particular case of the production of photocatalytic ceramic tiles, it was possible to identify opportunities to reduce nanoparticle emission.

Risk management during the project phase allows safer production processes, changing materials, methods or equipment to be developed, the result being an inherently safer production process.

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