



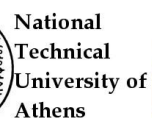
Task 01/A2

REPORT ON THE MAIN RISK SITUATIONS IN PRODUCTION AND USE OF NANOMATERIALS IN STONE SECTOR



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INTRODUCTION

The use of nanomaterials is representing a revolution in improving the performance of products made from natural stone. The mechanical characteristics of stone materials have increased their properties thanks to the use of coatings and surface treatments based on the application of nanoparticles and nanocomposites. But at the same rate as the quality of the material has increased with the application of these nanocomposites, the safety of workers is being greatly compromised. Nanomaterials are an invisible threat to workers' health.

Despite the advantages they offer, many workers are not aware that they are working with them and their harmful effects are not yet clear. Numerous studies establish that there are proven health risks linked to various manufactured nanomaterials, which, given their size, can interact at the cellular level.

In this report included in the task O1/A2 "*Report on the main risk situations in the production and use of nanomaterials in the Stone Sector*" corresponding to Intellectual Output 1 "*Guide to risks and health and environmental prevention measures in the safe production and use of nanomaterials in the Stone Sector*" the main objective has been to know what are the main risk situations in the stone sector for companies that use nanotechnology in their industry and have workers that apply nanomaterials to their products in each participating country.

This is absolutely necessary because it serves as a basis for developing the key situations and makes the target group identify with the risk situations they experience in their own workplaces.



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1. MAIN RISK SITUATIONS

1.1. GERMAN LIST

Situation of type, application or use of nanomaterials	Risks inherent	Health and Safety equipment (collective or individual)
Cutting stones to size (production)	<p>a) Inhalation of dust → respiratory problems, secondary diseases (alveolar, stomach and intestinal reaction, immune system?)</p> <p>b) Skin and eye contact → Skin irritation, mucous membrane irritation, possible after-effects</p> <p>c) Known risks of injury when handling sawing and grinding machines</p>	<p>Technical Extraction equipment with filter effect, wet cutting</p> <p>c) Known safeguarding measures (stationary, mobile),</p>
Grinding, profiling and polishing stone surfaces (production)	<p>a) Inhalation of dust → respiratory problems, secondary diseases (alveolar, stomach and intestinal reaction, immune system?)</p> <p>b) Skin and eye contact → Skin irritation, mucous membrane irritation, possible after-effects</p> <p>c) Known risks of injury when handling sawing and grinding machines</p>	<p>Technical Extraction equipment with filter effect, wet cutting</p> <p>c) Known safeguarding measures (stationary, mobile),</p>



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<p>Cutting, grinding, profiling and polishing stone surfaces (construction site)</p>	<p>a) Inhalation of dust → respiratory problems, secondary diseases (alveolar, stomach and intestinal reaction, immune system?)</p> <p>b) Skin and eye contact → Skin irritation, mucous membrane irritation, possible after-effects</p> <p>c) Known risks of injury when handling sawing and grinding machines</p>	<p>Mobile extraction units with filtration;</p> <p>Personal protective equipment (hand protection, eye protection, respiratory protection)</p> <p>c) Known safeguarding measures</p>
<p>Manufacture of mortar mixtures</p>	<p>a) Inhalation of dust → respiratory problems, secondary diseases (alveolar?); Accidental ingestion</p> <p>b) Skin and eye contact → Skin irritation, mucous membrane irritation, possible after-effects</p>	<p>Personal protective equipment (hand protection, eye protection, respiratory protection)</p>
<p>Processing of the mortar, bricklaying, plastering</p>	<p>Skin and eye contact → Skin irritation, mucous membrane irritation, possible after-effects</p>	<p>Personal protective equipment (hand protection, eye protection, respiratory protection)</p>
<p>Filling, decanting and mixing of coating materials (e.g. multi-component)</p>	<p>Skin and eye contact → Skin irritation, mucous membrane irritation, possible after-effects; Accidental ingestion</p>	<p>Personal protective equipment (hand protection, eye protection, respiratory protection)</p>



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Applying coatings to masonry and facades	Skin and eye contact → Skin irritation, mucous membrane irritation, possible after-effects; Accidental ingestion	Personal protective equipment (hand protection, eye protection, respiratory protection)
General conditions on construction sites: Pollution, dust accumulation, waste disposal, contact with soiled clothing, etc.	Known hazards that arise from any construction site	Organisation and implementation of statutory occupational health and safety, cleanliness, regular cleaning, etc.
Fire and explosion (e.g. with dust-air mixtures)	Known hazards that arise from any construction site	Organisation and implementation of known measures against fire and explosion hazards (demarcations, zoning, avoidance of ignition sources, etc.).
Hardening and drying of the mortar and coatings	Possible environmental impacts during curing and drying of the nanomaterial	Enclosure of the construction site, extraction and filtering of contaminated air



1.2. SPANISH LIST

Situation of type, application or use of nanomaterials	Risks inherent	Health and Safety equipment (collective or individual)
Abrasion of stone material.	Disintegration of fine respirable airborne particles and direct contact of dust with the skin.	Collective equipment: -Screening of abrasion areas -Use of tools with vacuum systems -Use of tools with water supply systems. Individual equipment: -Full face mask -Half mask and dust-proof safety goggles -Gloves -Work coverall
Sweep.	Resuspension of respirable dust.	Collective equipment: -Use of tools with suction systems. Individual equipment: -Full face mask Half mask and dust-proof safety goggles -Work coverall
Use of cutting tools or drills.	Disintegration of fine respirable airborne particles and direct contact of dust with the skin.	Collective equipment: -Screening of work areas -Use of tools with suction systems -Use of tools with water supply systems. Individual equipment: -Full face mask Half mask and dust-proof safety goggles -Gloves



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		<ul style="list-style-type: none"> -Gloves -Work coverall
Application of nanoparticulated consolidants to stone material.	Volatilization of particles of the applicable mixture and direct contact with the skin.	<p>Collective equipment:</p> <ul style="list-style-type: none"> -Working in ventilated spaces <p>Individual equipment:</p> <ul style="list-style-type: none"> -Full face mask -Half mask and safety goggles -Gloves -Work coverall
Application of nanoparticulated dyes to the stone.	Volatilization of particles of the applicable mixture and direct contact with the skin.	<p>Collective equipment:</p> <ul style="list-style-type: none"> -Working in ventilated spaces <p>Individual equipment:</p> <ul style="list-style-type: none"> -Full face mask -Half mask and safety goggles -Gloves -Work coverall
Application of nanoparticulated water repellents to the stone material.	Volatilization of respirable particles of the applicable mixture and direct skin contact.	<p>Collective equipment:</p> <ul style="list-style-type: none"> -Working in ventilated spaces <p>Individual equipment:</p> <ul style="list-style-type: none"> -Full face mask -Half mask and safety goggles -Gloves -Work coverall
Application of titanium dioxide for photocatalytic and self-cleaning activity.	Volatilization of nanoparticles and the possibility of producing inflammatory and genotoxic effects via inhalation.	<p>Collective equipment:</p> <ul style="list-style-type: none"> -Application in areas with good ventilation <p>Individual equipment:</p> <ul style="list-style-type: none"> -Full face mask



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		<p>Half mask and dust-proof safety goggles</p> <p>-Gloves</p> <p>-Work coverall</p>
<p>Application of zinc oxide to provide resistance, photocatalytic activity, biocidal activity, self-cleaning and hydrophobicity.</p>	<p>Volatilization of nanoparticles causing inflammatory effects in the lung.</p>	<p>Collective equipment:</p> <p>-Application in areas with good ventilation</p> <p>Individual equipment:</p> <p>-Full face mask</p> <p>Half mask and dust-proof safety goggles</p> <p>-Gloves</p> <p>-Work coverall</p>
<p>Application of silicon dioxide for cooling, anti-reflective and fire resistance properties.</p>	<p>Possibility of crystalline silica volatilization causing progressive fibrosis.</p>	<p>Collective equipment:</p> <p>-Application in areas with good ventilation</p> <p>Individual equipment:</p> <p>-Full face mask</p> <p>Half mask and dust-proof safety goggles</p> <p>-Gloves</p> <p>-Work coverall</p>



1.3. ITALIAN LIST

Situation of type, application or use of nanomaterials	Risks inherent	Health and Safety equipment (collective or individual)
processing with nanomaterials in a liquid	SKIN ABSORPTION AND EYE EXPOSURE	Individual: Gloves (waterproof in nitrile or neoprene), full coverage glasses range of use 5 (goggles), disposable coverall (Type 4-5-6 non-woven fabric)
generation of gas-phase nanomaterials in open systems	INHALATION	Individual: Combined filter and full face mask FFP2 filter Collective: Work area segregation Use of class M vacuum cleaners
handling (for example, weighing, mixing, spraying) with powders of nanomaterials	INHALATION	Individual: Combined filter and full face mask FFP2 filter Collective: Work area segregation Use of class M vacuum cleaners



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Use of nanomaterials: waste cleaning or disposal;	INHALATION	Individual: Combined filter and full face mask FFP2 filter
cleaning of dust collection systems used to capture nanoparticles;	INHALATION	Individual: Combined filter and full face mask FFP2 filter Collective: Work area segregation Use of class M vacuum cleaners
sanding, perforation of nanomaterials, or other mechanical processes that can lead to the aerosolization of nanoparticles.	INHALATION	Individual: Combined filter and full face mask FFP2 filter Collective: Work area segregation Use of class M vacuum cleaners
Application of liquid / fluid products containing nanomaterials that can lead to the aerosolization of nanoparticles.	SKIN ABSORPTION AND EYE EXPOSURE INHALATION	Individual: Combined filter and full face mask FFP2 filter Collective: Work area segregation Use of class M vacuum cleaners



1.4. GREEK LIST

Situation of type, application or use of nanomaterials	Risks inherent	Health and Safety equipment (collective or individual)
<p>Pouring of nanomaterial (received in powder form) in a liquid matrix for creating an application mixture</p>	<ul style="list-style-type: none"> • Respiratory Hazard: Exposure via inhalation route/pathway • Dermal Hazard: Exposure via Dermal absorption (depends on the state of the skin) 	<p><u>Collective measures at the workplace:</u></p> <p>Local exhaust system, confinement</p> <p><u>PPE (Personal Protective Equipment):</u></p> <p>Gloves: Nitrile gloves type B, but latex is also used</p> <p>Coveralls: Nonwoven coverall: Tyvek type</p> <p>Chemical protective clothing type 5</p> <p>Respiratory protection: FF-P3 type disposable masks and FF –P2 type disposable masks have been recommended. FF P3-type mask are recommended for greater worker protection.</p> <p>Eye protection: Minimum: close-fitting safety glasses</p>
<p>Nanomaterial in suspension in a liquid matrix applied with a spray-gun on a stone material surface:</p> <p><i>For example, a worker is applying a self-cleaning coating on a stone surface. According to the technical data of the product, the active nano-components is TiO2 (anatase). For application, a paint spraying system is used</i></p>	<ul style="list-style-type: none"> • Respiratory Hazard (High): Exposure via inhalation route/pathway • Dermal Hazard (High): 	<p><u>Collective measures at the workplace:</u></p> <p>Use of localised extraction systems, suction systems (ventilation with HEPA filters)[10], confinement</p>



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<p>(i.e., Wagner W850F). The actual activities concerned applying the self-cleaning coating on a stone surface (approx. 75 m²). One worker applied the coating for 1 hour. The activities carried out were filling the spraying system with 1 L premixed coating dispersion, followed by the spraying activities. In total, ca 250–330 mL coating was used, with an estimated use of 17mg nano-TiO₂. The electric generator of the spraying system was placed at approximately 1.5 meter distance from the worker position. The weather conditions were dry with a mild wind (approximately 3 Beaufort). (adapted from [5])</p>	<p>Exposure via dermal contact</p> <ul style="list-style-type: none"> Exposure via ingestion 	<p><u>PPE (Personal Protective Equipment):</u></p> <p>Gloves: Nitrile gloves type B, but latex is also used</p> <p>Coveralls: Nonwoven coverall: Tyvek type</p> <p>Chemical protective clothing type 4</p> <p>Safety glasses</p> <p>Respiratory protection: FF-P3 type disposable masks and FF –P2 type disposable masks. FF P3-type mask are recommended for greater worker protection.</p>
<p>Nanomaterial in liquid matrix applied with paint roller</p>	<ul style="list-style-type: none"> Respiratory Hazard: Exposure via inhalation Dermal Hazard: Exposure via dermal contact Exposure via ingestion 	<p><u>Collective measures:</u></p> <p>Use of localised extraction systems, suction systems, confinement</p> <p><u>PPE (Personal Protective Equipment):</u></p> <p>Gloves: Nitrile gloves, but latex is also used</p> <p>Coveralls: Nonwoven coverall: Tyvek type</p> <p>Chemical protective clothing type 6</p> <p>Safety glasses</p> <p>Respiratory protection: FF-P3 type disposable masks and FF-P2 type disposable masks. FF P3-</p>



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		<p>type mask are recommended for greater worker protection.</p>
<p>Nanomaterial fixed in a solid matrix, e.g. coating already applied and mechanical activities occur, e.g. cutting, sanding, drilling, abrasion, grinding [13]</p>	<p><i>All these activities might produce dust that will contain nano-objects</i></p> <ul style="list-style-type: none"> • Respiratory Hazard Exposure via the inhalation route • Dermal Hazard: Exposure via dermal contact • Exposure via Ingestion 	<p><u>Collective measures:</u></p> <p>Use of localised extraction systems, suction systems, confinement</p> <p>Use of tools with systems for powder elimination/extraction</p> <p>Examination of wet working method applicability</p> <p><u>PPE (Personal Protective Equipment):</u></p> <p>Gloves: Nitrile gloves type B, but latex is also used</p> <p>Coveralls: Nonwoven coverall: Tyvek type</p> <p>Chemical protective clothing type</p> <p>Safety glasses</p> <p>Respiratory protection: FF-P3 type disposable masks and FF –P2 type disposable masks. FF P3-type mask are recommended for greater worker protection.</p>



2. ADDITIONAL MATERIAL RELATED TO LISTS

Factors affecting exposure severity

- **Dermal exposure**
 - ➔ Dermal dose (mg/kg/day)
 - ➔ Product ingredient (g/g)
 - ➔ Contact area (cm²)
 - ➔ Frequency of use (events/day)
 - ➔ Thickness of layer (cm) – for D and F
 - ➔ Amount per kg body weight
- **Inhalation exposure**
 - ➔ Concentration in room air (mg/m³) over a day
 - ➔ Inhalation exposure dose (amount per kg body weight)
 - ➔ Fugacity classes (low, medium, high based on the physical form, the melting point of the metal, the temperature of the process, the vapor pressure, and the selected process category.
 - ➔ Near field (NF) or Far field (FF) distinction.

Factors related to the nanosubstance

- ➔ Dispersion (free, bound, aggregates, agglomerates)
- ➔ Size of primary particles (1-500nm or higher)

Tables regarding PPE [9]

Chemical Protective Clothing



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leak tightness and efficacy increases	CPC type and purpose	Standard
	Type 1 gas-tight suit	EN 943-1
	Protection against hazardous gases, liquids, aerosols, and solid particles	EN 943-2
	Type 2 air-fed non-gas-tight suits	EN 943-1
	Protection against hazardous gases, liquids, aerosols, and solid particles	
	Type 3 liquid-tight suit	EN 14605
	Protection against pressurised liquids	
	Type 4 spray-tight suits	EN 14605
	Protection against sprayed liquids	
	Type 5 suits against solid particles	EN ISO
	Protection against dusts and solid particles	13982-1
	Type 6 suits offering limited protective performance against liquid chemicals	EN 13034
Protection against e.g. minor splashes of irritant chemical		

Protective gloves

Classification	Performance	Marking
Type A	Min 30 minutes break through time against at least 6 chemicals	EN ISO 374-1/Type A AJKLPS
Type B	Min 30 minutes break through time against at least 3 chemicals	EN ISO 374-1/Type B JKL
Type C	Min 10 minutes break through time against at least 1 chemical	EN ISO 374-1/Type C



3. CONCLUSIONS

According to literature, airborne nanomaterials release characteristics could be grouped by activity type. Process characteristics, such as energy input and system parameters influence release level and thus exposure. High - energy processes /activities such as synthesis, spraying and machining were associated with the release of large number of nanoparticles. Low - energy processes/activities, including laboratory handling, cleaning, and industrial bagging activities, usually resulted in slight or moderate releases of relatively large agglomerates. Considering the above statement, spraying and machining activities related to nanoparticle applications on stone are ranking high for inherent risks related to inhalation, dermal absorption and digestion (from hand to mouth exposure).

Collective control measures such as ventilation systems are rarely practical on temporary or outdoor sites. Control of airborne dust is usually through a combination of water suppression, maintaining distance and the use of personal protective equipment (PPE).

Good work practices are very important, related to both the environment (equipment and work processes): such as placing nonskid mats on the floor so that any material that falls on the mats can be easily cleaned by just removing it, or preventing people from moving around a worker handling nanoparticle products to avoid air turbulence and personal hygiene measures (do not store or consume food and drink in the workplace, avoid applying cosmetics, wash hands before eating or leaving the job, and avoid touching your face or other exposed parts of the body with contaminated fingers).

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