



Task 01/A4

COMMON GUIDELINE OF PREVENTION MEASURES IN SAFE PRODUCTION AND USE OF NANOMATERIALS IN STONE SECTOR



This work is licensed under a [Creative Commons Attribution-ShareAlike 4.0 International License](https://creativecommons.org/licenses/by-sa/4.0/)

"The European Commission's support for the production of this publication does not constitute an endorsement of the contents, which reflect the views only of the authors, and the Commission cannot be held responsible for any use which may be made of the information contained therein".



Centro Tecnológico del mármol, piedra y materiales



National Technical University of Athens



COMMON GUIDELINE OF PREVENTION MEASURES IN SAFE PRODUCTION AND USE OF NANOMATERIALS IN STONE SECTOR.

This report is included in the task "O1-A4. *Common guideline of prevention measures in safe production and use of nanomaterials in Stone Sector*", corresponding to Intellectual Output 1 "Guideline of risks, health and environmental prevention measures in safe production and use of nanomaterials in Stone Sector" of the NanoSafe project.

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.

Therefore, there is a need for updated knowledge on the part of users about possible adverse health effects on workers and for the adoption of measures to control the risk.

Thanks to the research carried out in the previous studies, a methodological framework of preventive measures in the handling and application of nanomaterials in products for the stone sector has been implemented in the 3D training tool.

The development of the Guideline of risks, health and environmental prevention measures in safe production and use of nanomaterials in stone sector, which is available to all workers in the stone industry, has been the central task of this first Intellectual Output.

The Guideline and all the information about the project are available in the following url:

- NanoSafe project web: <https://www.nanosafeproject.eu/>



Contents

1. INTRODUCTION	5
2. BASIC CONCEPTS	6
2.1. Nanotechnology	6
2.2. Nanomaterial.....	6
2.3. Nanoproduct	7
3. NANOTECHNOLOGY IN THE CONSTRUCTION SECTOR.....	8
3.1. Most used nanomaterials in construction	9
4. NANOMATERIALS IN STONE SECTOR	15
4.1. Consolidants	15
4.2. Water repellents	17
4.3. Oil repellents	19
5. APPLICATION OF NANOPRODUCTS.....	20
5.1. Laboratory application	20
5.2. On site application	20
6. ASSOCIATED RISKS.....	22
6.1. toxicological proprieties.....	22
6.2. Toxicological effects.....	22
7. PREVENTION MEASURES.....	26
7.1. Organisational measures.....	26
7.2. Collective protective equipment:.....	27
7.3. Personal protective equipment:.....	29
8. BIBLIOGRAPHY.....	35



TASK 01/A4. COMMON GUIDELINE OF PREVENTION MEASURES IN SAFE PRODUCTION AND USE OF NANOMATERIALS IN STONE SECTOR.

Figure 1. Titanium dioxide. Source: www.nanomateriales.lineaprevencion.com	9
Figure 2. Zinc oxide. Source: www.nanomateriales.lineaprevencion.com	10
Figure 3. Silicon dioxide. Source: www.nanomateriales.lineaprevencion.com	11
Figure 4. Carbon nanotubes. Source: www.nanomateriales.lineaprevencion.com	12
Figure 5. Copper oxide. Source: www.nanomateriales.lineaprevencion.com	13
Figure 6. Silver. Source: www.nanomateriales.lineaprevencion.com	14
Figure 7. Natural stone treated with Ca(OH) ₂ /ZnO NPs under UV light. Source: Cultural Heritage—Science, Materials and Technologies	16
Figure 8. Natural stone treated with water repellent. Source: CSIRO	18
Figure 9. Localised extraction system. Source: ECL	28
Figure 10. Full mask. Source: ISEM	29
Figure 11. Half mask. Source: Grupo Casa Lima	30
Figure 12. Gloves I. Source: TG Medical	31
Figure 13. Gloves II. SW Safety Work	31
Figure 14. Protective clothing. Source: https://www.segutecnica.com/	32
Figure 15. Safety glasses. Source: www.walmart.com	33
Figure 16. Safety goggles with rubber. Source: https://www.freeimageslive.co.uk/	34
Figure 17. Face shield. Source: https://www.faceshield.com/	34



1. INTRODUCTION

Nanotechnology, in recent years, is dramatically revolutionizing the industrial development of new materials. The continuous advances in the field of nanotechnology, its rapid implementation throughout the industrial fabric and the high number of nanomaterials used in different industrial sectors, are coming up against a limited level of knowledge about the health and safety risks that nanomaterials generate for workers and the environment.

Now, the great revolution of nanotechnology, after great progress in other sectors, is reaching the construction sector, generating great changes in the traditional methodology of manufacturing construction materials. Therefore, it is necessary to reconsider the risk assessment and the effectiveness of preventive measures usually applied in workplaces with exposure to nano agents.



2. BASIC CONCEPTS

Before delving into measures to prevent exposure to nanomaterials, it is necessary to know a few terms:

2.1. Nanotechnology

In recent years, the most famous concept related to the great development in the world of science and technology is nanotechnology. The term "nanotechnology" was first used in 1974 by Professor Norio Taniguchi of the Tokyo University of Science to describe the basic concepts of manipulating matter at the nanometre level (Quintili, 2012). In July 1990, one of the first international symposia on Nanoscience and Nanotechnology was held in Baltimore (USA), where the study of nanomaterials and nanotechnology was formally defined as a sub-area of the basic sciences.

Nanotechnology makes it possible to produce new materials, structures and devices with extraordinary properties by exploiting the different characteristics of materials at the nanoscale (European Commission, 2012b).

2.2. Nanomaterial

In Europe, the most common definition of nanomaterials is that recommended by the European Commission, and definitions in ISO standards of a wide range of nano terminology.

According to Commission Recommendation 2011/696/EU1 a nanomaterial is: "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the numerical particle size, one or more external dimensions is in the size range 1 nm-100 nm.

Nanomaterials started to become popular in the 1980s, encompassing particles within a range of 1-100 nm, at least in one dimension. At these scales, due to an increase in specific surface area per unit volume, the usual laws of physics cease to apply, and quantum physics sets out its precepts, manifesting different optical, mechanical, magnetic, electrical, thermal and biological properties than usual.

Since 1990 there has been a rapid growth in the development of nanotechnology (Bystrzejewska et al., 2009) due to the development of synthesis techniques and equipment that allow the manipulation of nanoparticles (Nowack & Bucheli, 2007).



2.3. Nanoproduct

The advent of nanotechnology has led to the development of countless new applications and products, encouraging the incorporation of nanostructured materials into commercial products known as nanoproducts. The trend in the diversification and manufacture of nanoproducts will increase exponentially in the years to come, as they will be offered to consumers as affordable wonder products (Chih-cheng et al. 2012).

The variety of nanoproducts has grown by leaps and bounds and will continue to do so, including textiles, cosmetics, paints, food supplements, electronic devices, cleaning products and construction materials, among others (Wilson Center, 2015).



3. NANOTECHNOLOGY IN THE CONSTRUCTION SECTOR

The construction sector has also received many innovations so far in relation to the use of nanotechnology. The applications of nanotechnology in building materials today offer new opportunities in the sector, generating materials with specific and advanced properties such as higher mechanical strength, higher durability, corrosion resistance, fire resistance, superhydrophobic materials, self-cleaning, antibacterial, etc.

Despite this, nanotechnology in the construction industry, compared to other sectors, is at an early stage of development and expansion. This situation is justified by the traditional inertia of the sector to invest little in innovation and exploit ideas that have been contributed by other sciences and industries, and the high level of initial capital required for the provision of nano-instrumentation for research and technical development is also not motivating.

On the other hand, nanoproducts may not be competitive, compared to the acceptable performance and price of existing products, although the most important factor in the slow pace of use of nanomaterials in this sector is the lack of knowledge about nanotechnology in the industrial sector and the lack of connection between research and industrial development.

However, the potential of nanotechnology applications cannot be ignored, and the use of nanoproducts in construction is expected to increase as a result of the small quantity needed to achieve the properties in products and the expected decrease in the cost of nanomaterials when produced in large quantities.

Nanotechnology is capable of improving the properties of traditional materials or developing new ones (Hanus & Harris, 2013), some examples illustrating possible applications are given below.

- Firstly, in relation to cement derivatives, by adding carbon nanotubes and nanofibres, the strength of cement can be doubled (Nasibulina et al., 2010). Nano-silica also makes it possible to obtain high-strength concretes that can reach 500MPa (Schmidt et al., 2013).
- As for coatings, it is possible to provide antimicrobial properties with the addition of nanosilver, for use in hospital environments, for example (Kumar, Vemula, Ajayan, & John, 2008).
- Another solution to prevent potential road failures due to water penetration is to provide the soil with hydrophobic properties while improving its geotechnical properties (Ugwu, Arop, Nwoji, & Osadebe, 2013).

In the construction sector, nanomaterials are often used in the form of additives, coatings and treatments. Studies in Switzerland and Japan show that nanomaterials such as Ag, CeO₂, Fe₂O₃, SiO₂, TiO₂, ZnO and Al₂O₃ are already present in the construction sector. Despite their presence in various building materials, products containing nanoparticles in their composition and used

in the sector are still niche products in Europe and very little information is currently available on them, both in the health and environmental fields.

3.1. Most used nanomaterials in construction

TITANIUM DIOXIDE (TiO₂)

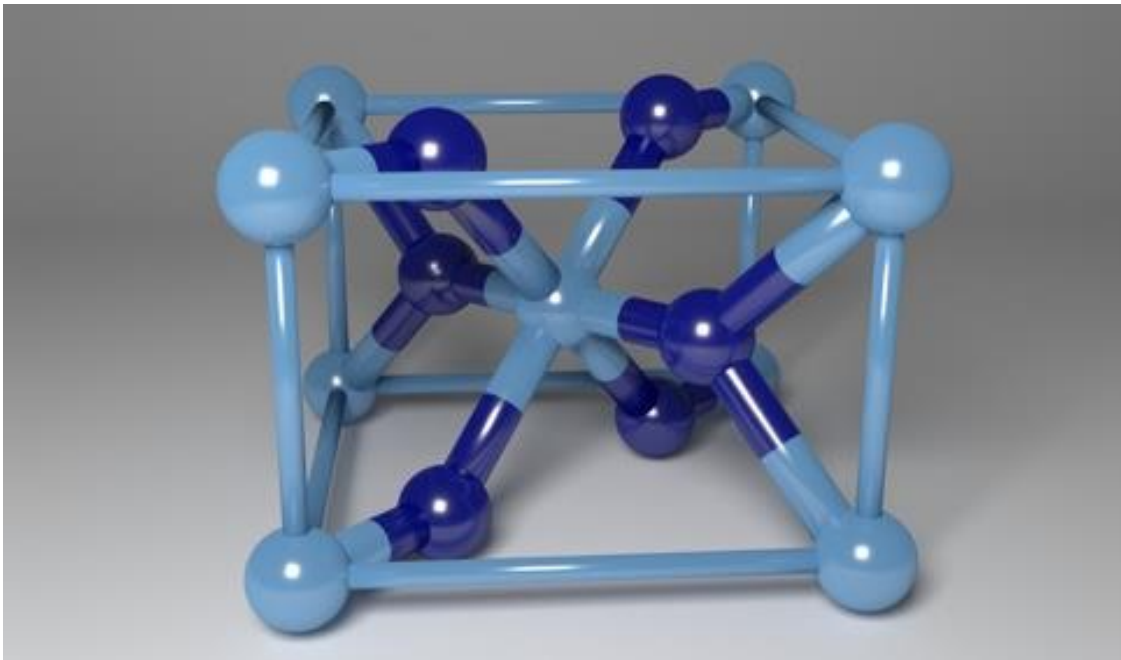


Figure 1. Titanium dioxide. Source: www.nanomateriales.lineaprevencion.com

Its main applications on site are as follows:

- **Structures:**
Concrete and Cement: in external coating for self-cleaning surfaces.
- **Finishes and coatings:**
 - Paints provides photocatalytic and self-cleaning functionalities.
 - Surface coatings on wood provides protection of wood against ultraviolet radiation.
 - Insulation/enclosures: in window glazing, it has anti-fogging, dirt resistance, self-cleaning and photocatalytic properties.
- **Insulation/enclosures:**
Windows/Glasses: in glazing, has anti-fogging, dirt resistance, self-cleaning and photocatalytic properties.

- **Installations:** in solar cells for energy generation.
- **Infrastructures:** in asphalt, road pavements, acoustic screens and tunnels: for durability, noise reduction, reduction of air pollutants. Photocatalytic activity in tunnel walls.

ZINC OXIDE (ZnO)

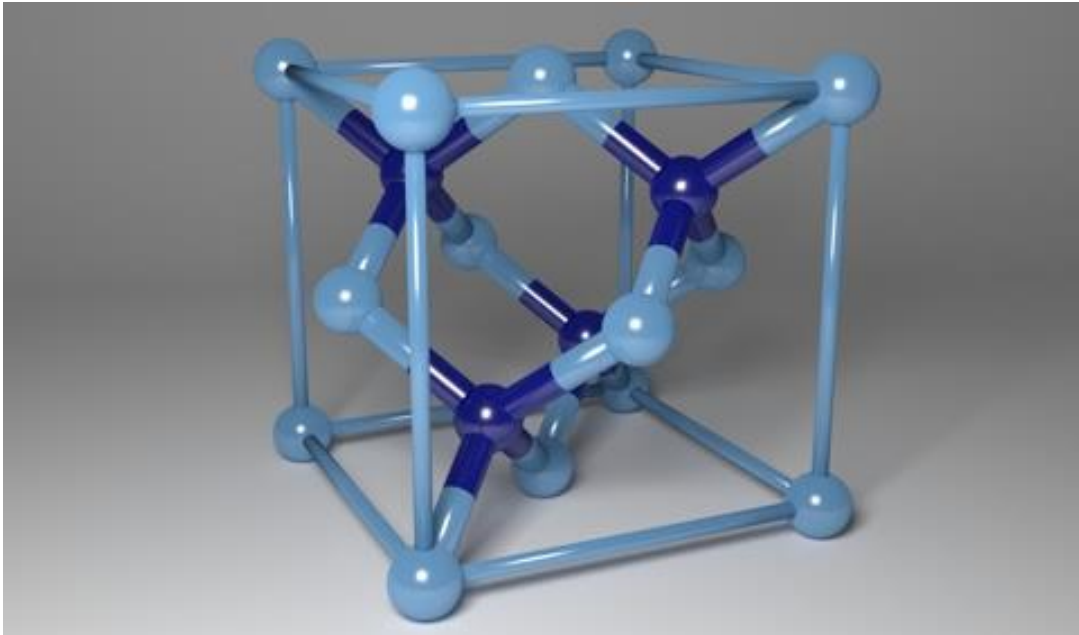


Figure 2. Zinc oxide. Source: www.nanomateriales.lineaprevencion.com

Its main applications on site are as follows:

- **Finishes and coatings:**
 - Paints: provides resistance, photocatalytic activity, biocidal activity, self-cleaning, maintain transparency, hydrophobic.
 - Surface coatings on wood: provides protection of wood against Ultraviolet (UV) radiation.

SILICON DIOXIDE (SiO₂)

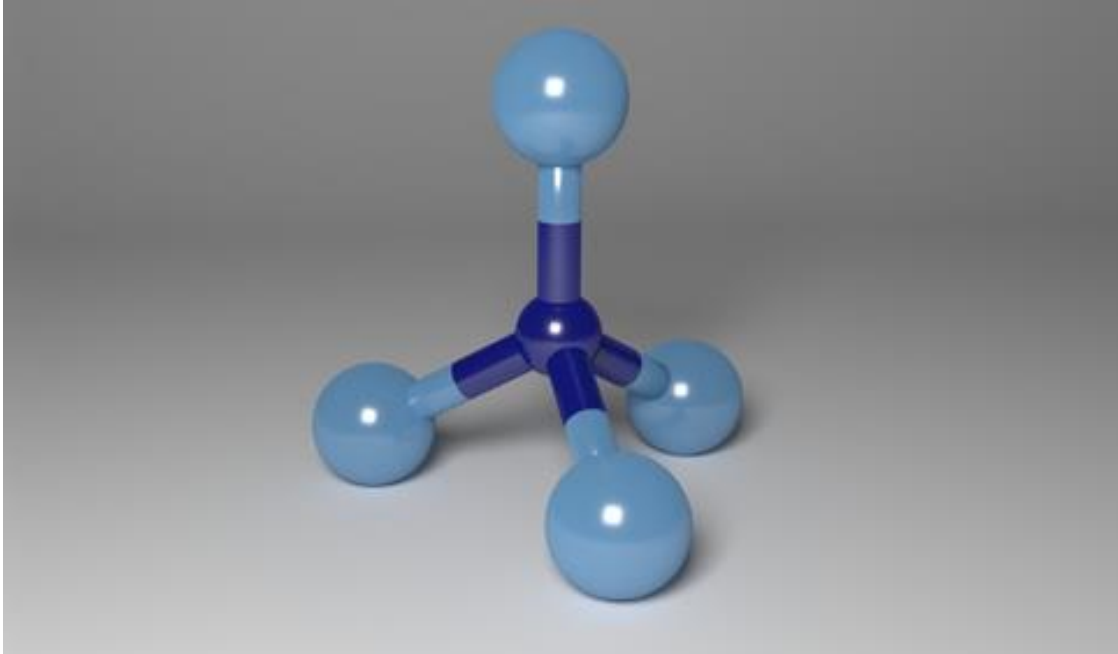


Figure 3. Silicon dioxide. Source: www.nanomateriales.lineaprevencion.com

Its main applications on site are as follows:

- **Concrete and Cement:** concrete and Cement: it produces ultra-strong concretes and cements, improving mechanical strength, protecting it from corrosion, increasing its durability and making it more permeable to water.
- **Finishes and coatings:**
 - Ceramic materials: applied in coatings, has cooling, anti-reflective and fire-resistant properties.
 - Paints: improves adhesion and durability.
 - Surface coatings on wood: applied on the surface, it protects wood by making it hydrophobic.
- **Insulation/enclosures:**
Windows/Glasses: in glass, this nanomaterial protects it from fire or heat sources and even has anti-reflective properties.

CARBON NANOTUBES (CNT)

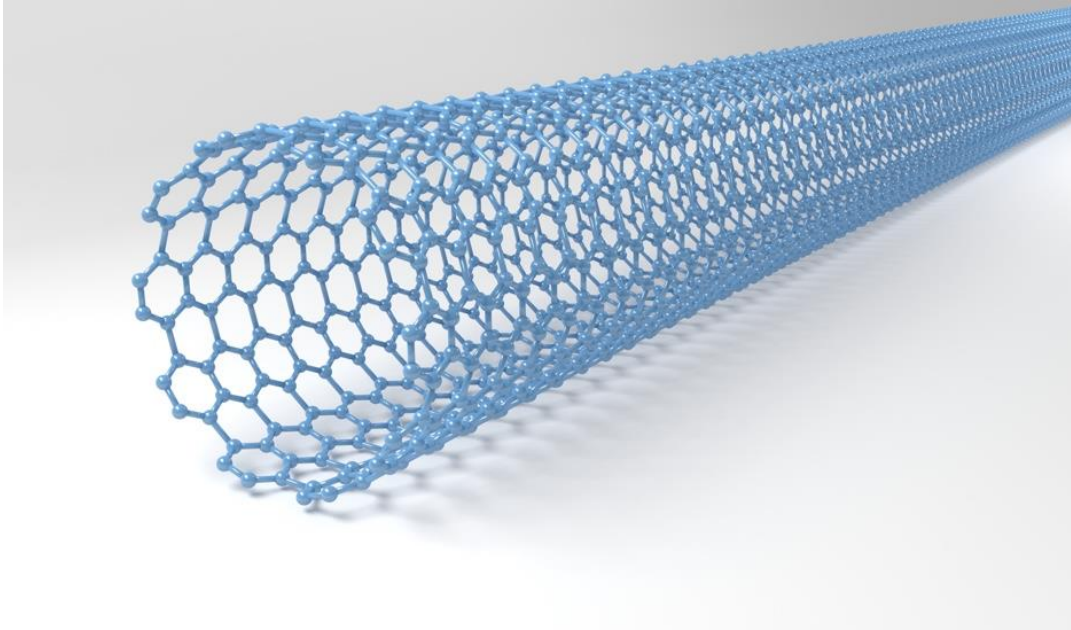


Figure 4. Carbon nanotubes. Source: www.nanomateriales.lineaprevencion.com

Its main applications on site are as follows:

- **Structures:**
 - Concrete and Cement: in concrete improves mechanical properties.
 - Steel: it has been identified as a possible replacement for steel wires by this nanomaterial for future use.

COPPER OXIDE (CuO)

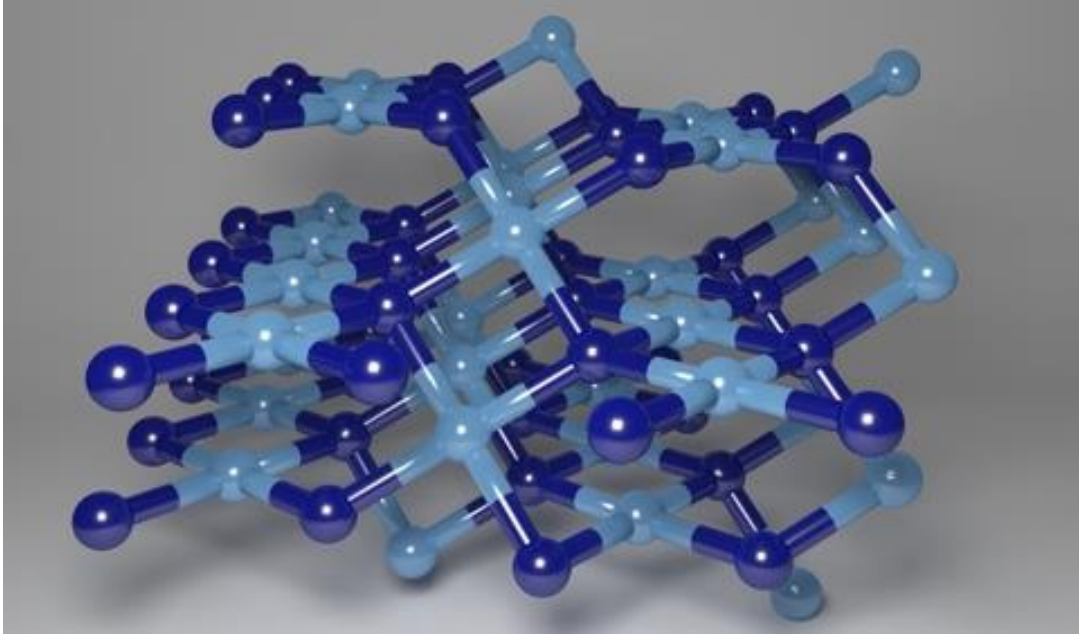


Figure 5. Copper oxide. Source: www.nanomateriales.lineaprevencion.com

Its main applications on site are as follows:

- **Structures**
 - Steel: produces corrosion resistant steels and facilitates weldability.

SILVER (Ag)

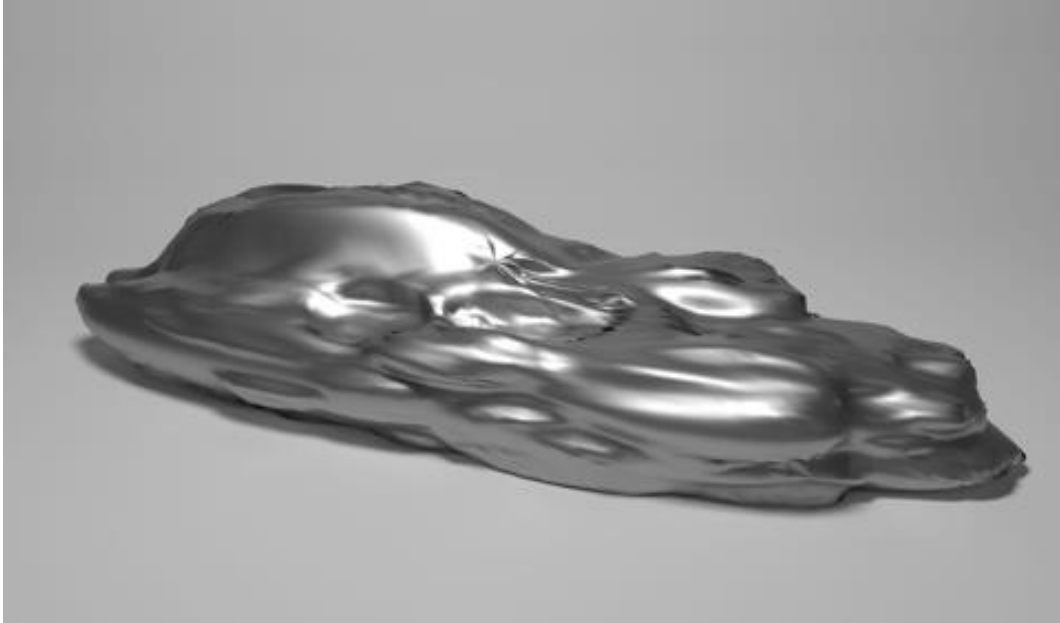


Figure 6. Silver. Source: www.nanomateriales.lineaprevencion.com

Its main applications on site are as follows:

- **Finishes and coatings:**
 - Paints: the nanomaterials in this material, applied as paint, have antibacterial properties.
- **Insulation/Enclosures:**
 - Windows/Glass: has self-cleaning properties on glass.



4. NANOMATERIALS IN STONE SECTOR

In the natural stone sector, there are numerous situations of exposure to nanoparticles. These situations range from the cutting of stone material, the application of paints or varnishes to the application of nano-treatments.

Cutting stone material with a saw, polishing, sweeping away dust, etc., generate the suspension of nanoparticles capable of penetrating the body through the respiratory tract and even the digestive tract, as in the case of the application of varnishes or paints.

Because of their greater complexity and innovative interest, we will focus on nano-treatments. Numerous treatments are currently available on the market to treat stone against deterioration. The most popular treatments today are consolidants and water repellents, and in addition to conventional treatments, nanoparticulated treatments have recently appeared on the market.

In addition to consolidants and water repellents, we can also find, although to a lesser extent, oil repellents.

4.1. Consolidants

Consolidation is the treatment aimed at decreasing the porosity and increasing the cohesion of the stone and thus increasing its mechanical strength. For consolidation to work as intended, the consolidant must be applied homogeneously and penetrate deeply, the latter requirement depending on factors such as the porous structure of the stone, the chemical properties of the consolidant and the application system.

The characteristics that a consolidant must meet are as follows (Wheeler G., 2005):

- It must increase the mechanical strength of the material.
- It must penetrate into the interior of the rock material.
- The alterability of the consolidated rock must be lower than that of the untreated rock.
- Must allow the passage of water vapour through the rock to prevent the accumulation of both water and salts.
- It must be compatible with the rock, avoiding the formation of harmful compounds or compounds that may react with the rock components.
- From a physical point of view, the properties of the treated material should be similar to those of the untreated material to avoid the occurrence of stresses between the treated layer and the internal substrate.
- A good consolidant should not change the appearance of the stone. The stone should not suffer variations in colour or gloss as a result of the treatment. Furthermore, over time, it must remain resistant to environmental agents, especially ultraviolet radiation.

The rise of nanomaterials has led to their adaptation to all fields, including the natural stone sector. In recent years, nanomaterials with a consolidating effect have been developed in an attempt to overcome many of the disadvantages of conventional consolidants.

The improvements have been made possible by the nanometric size of the nanoparticles (1-100 nm), which gives them a greater specific surface area and, therefore, greater reactivity (Miranda, 2006; Berlanga, 2013).

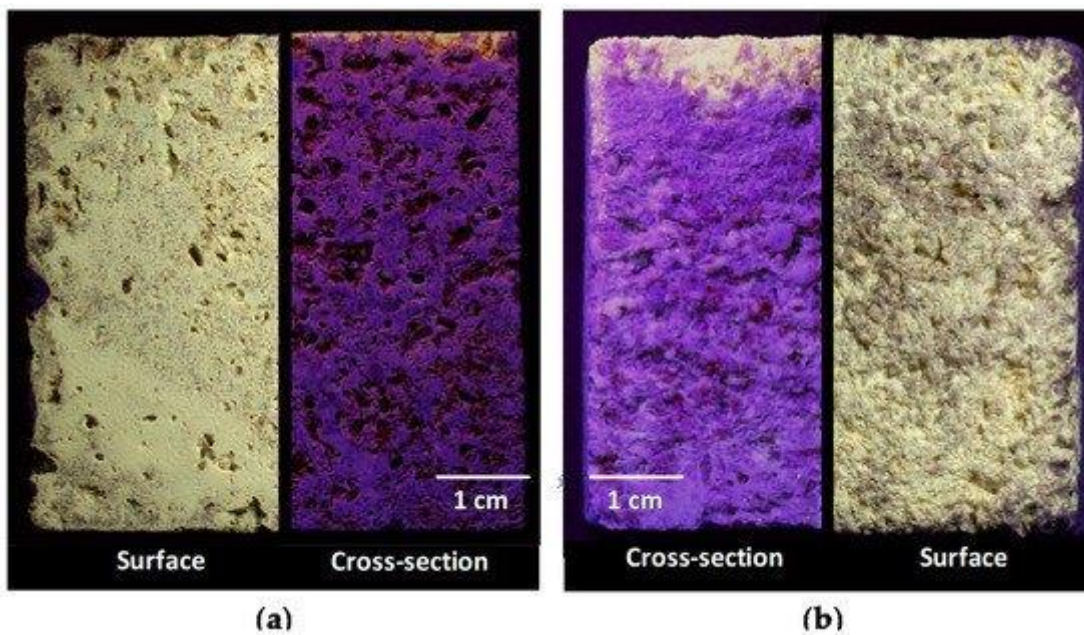


Figure 7. Natural stone treated with $\text{Ca(OH)}_2/\text{ZnO}$ NPs under UV light. Source: Cultural Heritage—Science, Materials and Technologies

Among the characteristics of the consolidants that are improved by the fact that the particles are nanometric are the increase in the penetration capacity of the products (D'Armada and Hist, 2012), greater capacity to react with the substrate, greater coating capacity, without negatively altering its breathability and avoiding the cracking of the consolidant. Among the most widely used consolidants currently in use are:

LIME NANOCONSOLIDANTS

The addition of colloidal calcium hydroxide nanoparticles whose solvent is an alcohol, favours a higher carbonation speed, a complete conversion and a higher concentration and depth of penetration of calcium hydroxide in the treated material (De Rosario, I., 2017).

SILICA NANOCONSOLIDANTS

Another type of nanoparticulate treatment is silica nanoconsolidants. These binders are formulated based on a colloidal dispersion of nanosilica in an aqueous dispersion. After the



water evaporates, the silica nanoparticles aggregate to form a silica matrix (Ripoll, A., 2020). Basically, these are colloidal dispersions of nanometric silicon dioxide, which on drying form silica gels similar to those produced when ethyl silicate reacts with the stone material, giving rise to adhesive properties.

4.2. Water repellents

Water repellents reduce the absorption of water through the surface of the stone by modifying the surface tension of the stone, preventing the penetration of water at depth, but still allowing water to escape from the inside to the outside.

A good water repellent should have the following characteristics (Villegas et al., 2003; Amoroso and Fassina, 1983):

- Null or minimal influence on the optical properties of the stone material.
- Stability to weathering agents and UV radiation to ensure a certain effectiveness of the treatment over time.
- Good adhesion to the substrate and resistance to washing.
- Ease of application.
- Impermeability to water in liquid state.
- Permeability to water vapour. So that, if the water in liquid state manages to penetrate the interior of the stone, it can evaporate.
- Reversibility or re-treatability.
- No harmful by-products when applied.



Figure 8. Natural stone treated with water repellent. Source: CSIRO.

Like consolidating nanoproducts, water-repellent nanoproducts have appeared in recent decades and, again, being nanometric particles, their penetration capacity improves, giving them better performance than conventional treatments.

With the addition of nanoparticles, water repellency is sometimes improved, and superhydrophobicity can even be achieved.

The addition of inorganic nanoparticles such as silica, aluminium, tin and titanium oxides to commercial polysiloxanes causes, after their application to the stone, the appearance of a certain surface roughness and a reduction in surface energy, which gives the stone hydrophobic properties (Manoudis, 2009).

In addition to inorganic particles, silica nanoparticles are also of particular interest. They have proven effective as consolidants and water repellents applied on siliceous rocks, granites and sandstones (Pérez, N., 2017). These nanoparticles, added to a mixture of organic and inorganic silica oligomers in the presence of a surfactant, allow superhydrophobic surfaces to be obtained (Facio and Mosquera, 2003).

Other nanoparticles used to achieve the water repellent effect are nano-hydroxyapatites, which, when added to TEOS, considerably improve the mechanical properties and resistance to accelerated ageing tests (De Rosario, 2017).



4.3. Oil repellents

In recent years, the application of materials that provide anti-graffiti protection together with hydrophobic properties has been strongly encouraged in order to reduce maintenance costs and minimise restoration interventions. For these applications, coatings must be manufactured that simultaneously exhibit hydrophobic and oleophobic properties to prevent or limit the penetration of stains into the pores of the stone. Such materials have been successfully made with long hydrocarbon side chains or fluorinated compounds, the latter providing the oleophobic properties. Other effective strategies have involved the addition of nanoparticles in fluorinated polymers. Although the importance of stone coatings capable of repelling not only water but also other substances is recognised, the current literature emphasises the protective behaviour against water, while the oleophobicity of the surface is much less investigated.



5. APPLICATION OF NANOPRODUCTS

The effectiveness of the application of a treatment depends on the depth of the treatment, the distribution pattern generated in the porous structure and other factors such as the adequacy of the treatment applied, the type of material, the concentration of the treatment, the contact time, the working conditions, etc.

Two types of application methods can be distinguished:

5.1. Laboratory application

If the stone material can be moved and transported to a laboratory, application methods are often more effective than in-situ application methods. Laboratory application methods include:

5.1.1. Immersion

A method of applying treatments in immersion. This process involves complete immersion of the stone material in the treatment. It is usually carried out at ambient pressure and temperature, although variations can be made in these parameters. Different conditions of pressure and temperature. It is advisable to add the treatment solution gradually to allow the air to escape from the porous system.

A variant of this method is to perform it under vacuum, which usually results in a higher penetration. In this method, it is necessary to make use of a vacuum vessel, a solution tank and a pump. When a sufficiently low pressure is reached, the penetration of the solution is facilitated. When the object is completely covered, the valve is closed, maintaining the pressure for a while, and then the pump is closed, returning to atmospheric pressure.

5.1.2. Capilarity

Another method of applying the treatment is capillary action. In this case, the stone material is placed inside a container that can be covered to prevent evaporation of the solvent. The solution penetrates the material through the porous structure. As in the previous case, the solution is added slowly to allow air to escape from the porous system.

5.2. On site application

When the application has to be carried out in situ, it is generally more difficult to achieve high penetration. Among the most frequently used types of in-situ application are:

5.2.1. Sprayed or aerosolised solutions

This method achieves a good penetration depth. The pure solvent or a very dilute solution must be vaporised so that diffusion is favoured and therefore penetration is increased. Penetration is increased by using hot solutions and progressively increasing their concentration.



5.2.2. Application by brush or roller.

Application by brush or roller does not generally allow good penetration.

5.2.3. Direct application

Direct application aims at a high contact time. For this purpose, tampons covered with plastic material are used to prevent evaporation. This method allows application over large surfaces provided that a mechanism is available to allow recovery of the excess solution.

This system can be improved by generating pressure conditions below atmospheric pressure so that, once the excess solution has been applied, the air is extracted so that the solution adheres to the surface of the stone material.



6. ASSOCIATED RISKS.

Scientific data on the health and safety effects of nanomaterials on workers are scarce. Therefore, consideration needs to be given to whether the nano-sized particle poses a different risk than non-nano-sized particles of the same composition.

As the particle size decreases, the specific surface area increases and thus the reactivity of the particle increases. reactivity increases. Due to this increase, nano-sized particles can cause adverse effects on the cause different adverse health effects in the body than those caused by non-nanosized particles of the same composition. particles with the same chemical composition, as they may interact in the body in different ways. organism in different ways. If nanoparticles exhibit novel physico-chemical properties in comparison to the same particles, there is a possibility that this may be accompanied by new toxicological properties. toxicological properties. Therefore, the risks associated with nanomaterials will be mainly related to particle size. mainly related to particle size.

6.1. toxicological proprieties.

Some of the toxicological properties of nanomaterials are:

-Translocation: Given their nanometric dimension, nanomaterials can reach parts of biological systems that are not normally accessible to larger particles. This includes an increased ability to cross cell boundaries, or to pass from the lungs into the bloodstream and from there to all organs of the body, or even through deposition in the nose, to pass directly into the brain. This process is known as translocation, and in general, nano-objects can translocate much more easily than other larger structures.

-Toxicity: Nanoparticles have a much larger surface area than the same mass of large particles. To the extent that surface area is a factor in toxicity, this clearly implies a possible increase in the toxic effects of nano-scale particles.

-Biospersistence: some nanoparticles (e.g. nanowires), show a high ratio of biopersistent appearance, with similar morphology and durability to asbestos fibres, and are therefore likely to persist in the lungs if inhaled, causing inflammation and ultimately disease.

-Solubility: Size reduction in some nano-objects has been shown to be associated with increased solubility. This effect could lead to increased bioavailability of materials that are considered insoluble or poorly soluble at the large particle size.

6.2. Toxicological effects.

The toxicological effects of nanomaterials on the body depend mainly on:



Factors related to exposure: routes of entry into the organism, duration and frequency of exposure and environmental concentrations. The deposition and absorption of nanoparticles into the body occurs mainly via three main routes: the inhalation, dermal and digestive routes.

Through the respiratory route, depending on the form and chemical composition of the nanomaterial, it can penetrate and be deposited in different parts of the respiratory tree. This is the main route of exposure for construction workers, especially during machining work on nanomaterials in which dust [cutting, sanding, drilling, boring, drilling, etc.] or mist [paint spraying] is generated.

The dermal route has to be taken into account as smaller particles are more likely to pass through the skin, so this route becomes more important in tasks where a large part of the worker's body is in contact with nanomaterials.

Nanomaterials can also enter the body via the digestive tract as a result of poor hygienic practices during the handling of nanomaterials or by swallowing those retained in the upper respiratory tract.

Factors related to the exposed worker: individual susceptibility, physical activity in the workplace, deposition site and the route activity in the workplace, site of deposition and route taken by nanomaterials once they enter the body. penetrate the body.

Factors related to the nanomaterials: intrinsic toxicity of the nanomaterial.

Although there is very little information on the safety hazards that nanomaterials may pose, the risks of fire and explosion are known to be of most concern.

Particle size or specific surface area is one of the factors involved in the ease of ignition and explosive violence of a dust cloud. Because of their size, they can remain airborne for long periods of time, thus increasing the possibility of creating potentially explosive dust clouds, and because of their larger surface area, nanoparticles can be easily electrostatically charged, thus increasing the risk of ignition.

However, particulate nanomaterials in the form of dust may pose explosion risks, while their corresponding materials may pose an explosion risk. explosion risks, while their corresponding materials may not. As a general rule, the quantities handled are generally small, so the risk of explosion is greatly reduced. to a large extent.

Some nanomaterials have to be considered as having the potential to cause an explosion and therefore require special working conditions, therefore require special working conditions (inert atmospheres).

Studies on the toxic implications of nanomaterials show, for example, that titanium dioxide and zinc oxide nanoparticles used in sunscreens could cause DNA damage in mice.

One of the first cases of death from exposure to nanoparticles was reported in 2009 when two female employees at a factory in China died from pulmonary fibrosis caused by the presence of nanoparticles of acrylic resins.

Some of the health risks posed by nanomaterials used in construction mentioned above are outlined below.

- **TITANIUM DIOXIDE (TiO₂).** Inhalation may produce inflammatory and genotoxic effects. The inflammation, which can sometimes be reversible, depends on the surface area per unit mass ratio and the duration and concentration of exposure. Studies show that the toxicity of the anatase form of TiO₂ is greater than that of the rutile form. In in vitro studies, TiO₂ anatase induces oxidative stress in human lung tissue with DNA damage. In long-term exposures of TiO₂ anatase, carcinogenic effects have been observed. TiO₂ is not absorbed through intact skin.
- **ZINC OXIDE (ZnO).** Studies show that it causes oxidative stress reactions in lung tissue and DNA damage. By inhalation, inflammatory effects on the lung and systemic effects have been observed; distribution in the body is affected by the solubility of the particles. Genotoxic effects have been observed in in vitro studies, whereas in vivo studies were negative. Dermal absorption is limited and no local effects have been observed.
- **SILICON DIOXIDE (SiO₂).** Toxicity depends on the crystalline structure present. Amorphous silica, unlike crystalline silica, has low toxicity and does not produce progressive fibrosis. Silica fume is mainly composed of amorphous silica, although it may contain a higher or lower percentage of crystalline silica, depending on the production process.
- **CARBON NANOTUBES (CNT).** They can be single-walled (SWCNT) or multi-walled (MWCNT). They exert pulmonary toxicity: inflammation, fibrosis and epithelioid granulomas. CNT toxicity is related to the type of nanotube (SWCNT or MWCNT), the stiffness and its length/diameter ratio. Toxicity is also influenced by the synthesis process and the presence of active groups, e.g. carboxylic acids. During synthesis, catalysts such as iron and nickel are used, which can remain as small impurities and increase toxicity. Similar reactions to asbestos can be assumed for nanotubes of any composition that are in the form of loose fibres, not as short or entangled fibres. CNTs longer than 20 µm have been found to be associated with mesothelioma.
- **COPPER OXIDE (CuO).** Nanometric CuO particles are more toxic than stabilised metallic copper. The solubility of this nanomaterial and the release of copper are responsible for the toxic effect, producing an inflammatory response.
- **SILVER (Ag).** The toxic effects produced by nano-sized silver particles are poorly understood. Upon inhalation, they are distributed through the blood and can



accumulate in various tissues and produce effects on the liver and the immune system. Through the olfactory nerve they can reach the brain. Nano-sized silver is known to have a lethal effect on bacteria and fibroblasts.



7. PREVENTION MEASURES

The collection of information to identify the hazards of each nanoproduct should focus on the search for data on its physico-chemical characteristics and properties. Information can be obtained from labels (pictograms), safety data sheets, European Commission recommendations and other sources such as databases or scientific literature.

The preventive measures to be put in place will be adapted to each work situation according to the nanomaterials used and the available information on exposure. For the appropriate selection of these measures will require knowledge of the type of process, the characteristics of the nanomaterials present, and the characteristics of the nanomaterials present, the potential exposures (frequency and duration of operations), the procedures duration of operations), the procedures, the characteristics of the workplace, etc.

Exposure to hazardous substances shall be avoided whenever possible, preferably by eliminating the substance, avoiding exposure or substituting the material with a less hazardous material. If the use and generation of nanomaterials cannot be eliminated or replaced by less hazardous materials and processes, exposure of workers shall be minimised by technical source control measures, organisational measures and personal protective equipment as a last resort.

In the implementation of preventive measures, it is advisable to follow a well-established hierarchy of control hierarchy of control:

- Process modification: to minimise exposure, changes can be made to work procedures, such as reducing the amount of nanomaterial in certain activities or replacing nanomaterials in powder form with another form of presentation in which the nanomaterial is in a liquid medium or embedded in a solid matrix.
- Isolation/confinement: operations involving a potential release of nanomaterials in the workplace shall be carried out in separate facilities or in facilities where the handling is carried out from a protected area.
- Technical control measures: these are aimed at reducing the emission of the pollutant at the source of emission by creating a physical barrier. source by creating a physical barrier between the worker and the nanomaterial. Among Technical control measures include localised extraction systems.

7.1. Organisational measures

- Minimise the number of exposed workers.
- Reduce exposure time.
- Delimit and signpost work areas with pictograms indicating the possible presence of nanomaterials and the protective measures to be taken.
- Minimise the amount of particulate nanomaterial in use at any given time.



- Regularly train and inform exposed workers of the potential risks, as well as the preventive measures to be taken.
- Maintain the work premises in proper conditions of order and cleanliness. Clean regularly cleaning floors, equipment, tools and work surfaces using damp cloths or a vacuum cleaner equipped with a filter. or a Hoover equipped with a very high efficiency "absolute" air filter group H (HEPA) class H14 or higher (ULPA). Pressurised air, brooms, brushes or powerful water jets must not be used. or powerful water jets must not be used.

7.2. Collective protective equipment:

The design of the fume cupboard and the flow rate will be critical for proper operation. In relation to these control systems, it is important to consider the following aspects:

- Use fume cupboards that enclose the source as much as possible and are located as close to the source as possible.
- Use filtration collection systems with high efficiency HEPA class H14 or ULPA filters or ULPA.
- The ducting of the extraction system must be resistant to the nanomaterials handled, as these can be handled, as these can be more reactive than their non-nano scale counterparts, paying special attention to the joints to avoid possible leakage. Localised extraction systems are probably the most frequently used measures in industry. The aim of a localised extraction system is to capture the pollutant as close as possible to the point where it is generated (source), preventing it from spreading to the worker's exposure zone. The selection of the most appropriate ventilation system will depend on the process, the hazardousness of the pollutant, the source to be controlled and the exposure limits of the corresponding nanomaterial.

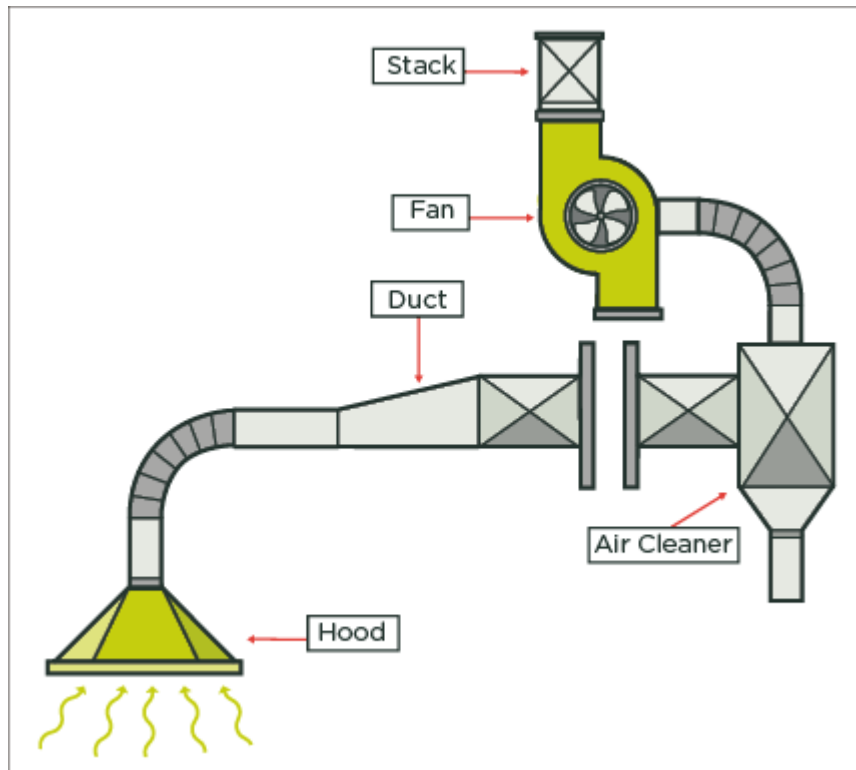


Figure 9. Localised extraction system. Source: ECL

- Use sticky mats outside the areas of use to avoid dispersion of nanomaterials. nanomaterials



7.3. Personal protective equipment:

For routine short-term work, full masks, half masks and quarter masks, incorporating P3 particulate filters, which can be incorporated into interchangeable filters, can be used as respiratory protective equipment. For prolonged exposure, powered filtering devices with P3 particulate filters are used.



Figure 10. Full mask. Source: ISEM



Figure 11. Half mask. Source: Grupo Casa Lima

For hand protection, the use of protective gloves against chemicals and microorganisms is recommended, which must comply with EN 374-1:2016, and in the case of using disposable gloves, the use of two pairs of gloves overlapped is recommended to confer greater resistance against mechanical deterioration of the gloves.



Figure 12. Gloves I. Source: TG Medical



Figure 13. Gloves II. SW Safety Work



If the nanomaterial is in powder form, protective clothing should be worn.



Figure 14. Protective clothing. Source: <https://www.segutecnica.com/>

Protection of the mucous membranes of the eyes shall be provided by the use of different types of eye protection depending on the form in which the contaminant is present.

- Safety glasses: laboratory goggles with universal frames.



Figure 15. Safety glasses. Source: www.walmart.com

- Safety goggles: "diving" type, tight-fitting eye protection held in place by a rubber band around the head.



Figure 16. Safety goggles with rubber. Source: <https://www.freeimageslive.co.uk/>

- Face shields: extending from the eyebrows to under the chin and across the full width of the employee's head.



Figure 17. Face shield. Source: <https://www.faceshield.com/>

Growing concerns about the health and safety impact of the use of nanopowders and other nanomaterials are almost exclusively focused on the potential toxic effects, but the fire and explosion risk of nanopowders must also be taken into account.

On the other hand, the production and use of nanomaterials inevitably emit significant quantities of nanoparticles into the environment, which, through a wide variety of routes, can reach humans and other organisms.

In addition, it inevitably leads to the emergence of nano-waste, for which knowledge about its management is very limited and the legislative landscape is insufficient.



8. BIBLIOGRAPHY

- Adlakha-Hutcheon, G., Khaydarov, R., Korenstein, R., Varma, R., Vaseashta, A., Stamm, H., and Abdel-Mottaleb. (2009). M. NANOMATERIALS, NANOTECHNOLOGY applications, consumer products, and benefits. *Nanomaterials: Risks and Benefits*.
- Amoroso, G. y Fassina, V. 1983. Stone decay and conservation: Atmospheric pollution, cleaning, consolidation and protection, *Materials Science Monographs*, vol. 11, Elsevier, Amsterdam, 453 pp
- Bartos, P. J. M. (2009). In Bittnar, Z Bartos, PJM Nemecek, J Smilauer, V Zeman,J. (Ed.), *Nanotechnology in construction: A roadmap for development*
- Becerra, J., Zaderenko, A. P. and Ortiz, P. (2019). Basic Protocol for On-Site Testing Consolidant Nanoparticles on Stone Cultural Heritage.
- Berlanga Mora, I. 2013. Síntesis y caracterización de nanomateriales 0D, 1D y 2D. Tesis Doctoral. Universidad Autónoma de Madrid Facultad de Ciencias. Departamento de Química Inorgánica.
- Broekhuizen, F. V., Broekhuizen, P. V. (2009). Nano-products in the European Construction Industry. European Federation of Building and Wood Workers and European Construction Industry Federation.
- Bystrzejewska-Piotrowska, G., Golimowski, J., & L. Urban, P. (2009). Nanoparticules: their potencial toxicity, waste and environmental management.
- Chih-cheng L., Chun-hsien W., Pei-Yu C., Chien-Wei H. (2012). An empirical study of commercialization performance on nanoproducts.
- European Commission. (2012a). Policies. Retrieved from http://ec.europa.eu/nanotechnology/policies_en.htm
- Facio, D.S. y Mosquera, M.J. 2013. Simple strategy for producing superhydrophobic nanocomposite coatings “in situ” on a building substrate. *ACS Appl Mater Interfaces*.
- Golanski L, Guillot A, Tardif, F. (2010). "Experimental evaluation of individual protection devices against different types of nanoaerosols: graphite, TiO2 and Pt", Special focus: Safety of Nanoparticles, *Journal of Nanoparticle Research*.
- Hanus, M. J., & Harris, A. T. (2013). Nanotechnology innovations for the construction industry. *Progress in Materials Science*.
- INSST. Exposición potencial a nanomateriales en el sector de la construcción. [en línea]. Instituto Nacional de Seguridad y Salud Trabajo (INSST), 2018.
- Kumar A, Vemula PK, Ajayan PM, John G. (2008). Silver-Nanoparticle-embeded antimicrobial paints based on vegetable oil.



Manoudis, P.N.; Tsakalof, A.; I. Karapanagiotis, I.; Zuburtikudis, I.; Panayiotou, C. 2009b. Fabrication of super-hydrophobic surfaces for enhanced stone protection. *Surface & Coatings Technology* 203. 1322–1328

Miranda, R. 2006. Efectos de tamaño cuántico y su importancia para la reactividad y estabilidad de nanoestructuras. *Revista Sistema madri+d, Especial Nanociencia y Nanotecnología. Monografía 15: 19-25*

Nasibulina, L. I., Anoshkin, I. V., Shandakov, S. D., Nasibulin, A. G., Cwirzen, A., Mudimela, P. R., . . . Kauppinen, E. I. (2010). Direct synthesis of carbon nanofibers on cement particles.

Ripoll Casas, Alba (2020). Piedra de Novelda: evaluación de consolidantes nanoparticulados.

Schmidt M, Amrhein K, Braun T, Glotzbach C, Kamaruddin S, Taenzer R.(2013). Nanotechnological improvement of structural materials - Impact on material performance and structural design

Quintil, M. (2012). Nanociencia y Nanotecnología... un mundo pequeño

Ugwu OO, Arop JB, Nwoji CU, Osadebe NN. (2013). Nanotechnology as a Preventive Engineering Solution to Highway Infrastructure Failures. J

Villegas, R.; Baglioni, R.; Sameño Puerto, M. 2003. Tipología de materiales para tratamiento. En: Metodología de diagnóstico y evaluación de tratamiento para la conservación de los edificios históricos. Villegas, R. y Sebastián Pardo, E. Instituto Andaluz del Patrimonio Histórico. Sevilla 2003. Cuadernos técnicos; 8. ISBN: 84-8266-370-4

Wheeler G. Alkoxysilanes and the consolidation of stone. (2005). The Getty Conservation Institute.

WHO guidelines on protecting workers from potential risks of manufactured nanomaterials. ISBN 978-92-4-155004-8