

SAFE PRODUCTION OF NANO MATERIALS (NANO SILVER DOTTED SILICA)

1. Case metadata

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Poland

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2. Organisations involved

POCH S.A. ul. Sowińskiego 11, 44-101 Gliwice

3. Description of the case

3.1. Introduction

POCH S.A. produces and supplies laboratory chemicals under the Labscan, POCH and POCH BASIC brand names. Its markets include pharmaceuticals, food and feed, chemical and petrochemical industries, environmental protection, and research and analytical chemistry.

The development of nanotechnology at POCH S.A. focuses on the manufacturing, engineering and application methods of nanomaterials on inorganic carriers. In 2007, POCH launched a modern production line of nanopowders. Currently, POCH produces nanomaterials on inorganic carriers (nano silver dotted silica - $\text{SiO}_2\text{-Ag}$) (Figures1-2). This material, by weight, contains 20% metallic silver (confirmed by Scanning Electron Microscopy and Energy Dispersive Spectroscopy) and amorphous silica. 95% of the silica grains have a diameter in the range of 450 nm – 650 nm, however 90% of the silver particles have a diameter of 10 nm (confirmed by Transmission Electron Microscopy method, carried out in Institute of Non-Ferrous Metals in Gliwice).

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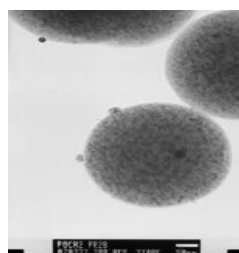
The manufactured material is characterised by a multipoint BET-method¹ specific surface area of 3.840 m²/g, and single point BET-method specific surface area of 3.303 m²/g (confirmed by nitrogen adsorption tests at 77K, at the Zakład Chemii i Technologii Paliw Politechniki Wrocławskiej (Wrocław University of Technology - Department of Fuel Chemistry and Technology)).

Tests confirming the physical/chemical properties of the nanomaterials are performed according to the guidelines published by the Scientific Committee on Emerging and Newly-Identified Health Risks (SCENIHR) in 2007 [1].

Figure 1: Nano silver dotted silica (the final product)



Figure 2: SiO₂-Ag (TEM x 100 000)



This nanomaterial has a wide application as an anti-microbial agent in various industries, such as textile, plastic, paints, paper and timber, among others. The Company's final products containing nanomaterials are marketed under the NAVIA™ brand name [2].

POCH is focused on providing safe working conditions for their employees. To this end, POCH has implemented the Safety at Work Management System complying with all guidelines of the PN-N-18001 Standard (which implements the provisions of the ILO-OSH 2001 document and PN ISO 9000 series) [3].

Antimicrobial (i.e. antibacterial, antifungal, antiviral and anti-drug resistant pathogens) properties of silver have been known for several years. In recent years, there have been reports of possible harmful effects of silver nano-sized particles. It is believed that silver nanoparticles can create new (poorly studied) hazards in the workplace.

POCH is aware of the possible risks associated with silver nanoparticles. Knowledge of the risks is derived primarily from literature studies. The company stays up-to-date with information available on the web pages of the European Commission, the appropriate Offices/Agencies regarding potential

¹ BET method – Brunauer, Emmett and Teller method

risks related to the 'nano' scale, and derives information from databases of scientific magazines, such as Scopus or Web of Knowledge.

POCH is interested in creating safe workplaces and making efforts towards preventing injury to workers and reducing any potential risk from the use of nanomaterials (SiO₂-Ag).

3.2. Aims

All actions have been taken with the intent to ensure the safety of workplaces that have contact with nanomaterials and the formation of safe products for final users.

3.3. What was done, and how?

The Company, at the beginning stage of the research and development, has analysed the physical/chemical properties of the potential nanomaterial as well as a methods of its production and deliberately made the decision to develop such production method that would reduce risks related to exposure of employees or users to the free nano-particles to a minimum. In the developed method nano-scale silver is created during reduction of the specific silver salt (in the form of a suspension) in a hermetically sealed and automated oven. During that process, the nano-scale silver is **permanently** deposited on silica.

Then, a modern technical production line was designed. Separate segments of the manufacturing line were manufactured to order, based on projects done by engineers and process engineers projects at POCH S.A.. They feature the highest quality safety standards, while integrating all obligatory safety standards. The most important element of the technical production line (loading the oven) is automatic and hermetically sealed. This allows for reduced exposure to nanoparticles 'at the source'.

In order **to improve** the safety of production of nanomaterials and a safe final product, POCH has taken several steps, described in the following.

- Identification of areas particularly at risk.

As part of the mastering of the safety management and occupational hygiene system (risk assessment analysis), areas of high exposure to the **powder form of the material** were identified, where **it is suspected** that **nanoparticle agglomerates** can occur during the work process. The probable exposure routes are the respiratory system, and less frequently the skin.

Workers may be exposed to nanomaterial dust during such processes as:

- removing the product from the reduction furnace,
- grinding and crushing of nanopowders (where nanoparticles are standardised),
- packaging,
- preparing suspension of the final product (weighting),
- technical and personal precautions

In the above mentioned areas, the processes are conducted with adequate general and local exhaust ventilation (in anti-explosive versions).

The processes are carried out in the presence of the appropriate pressure/exhaust ventilation, in explosive-protection conditions, and with the use of local ventilating hoods.

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Being aware of the probable harmful effects of powder forms, additional employee protection during the work processes was established. During the manufacturing phase, employees use personal protection equipment (PPE) for the respiratory system, eyes and skin mucous membranes, such as: masks and half-masks, goggles, protective clothes, gloves (Figures 3 and 4).

Figures 3 and Figure 4: Packaging of nanosilver dotted silica.



- Exposure assessment

Measurements of silver and silica amorphous concentrations in the air were done according to current standards of measurement of harmful agents at work. The airborne levels of silica and silver were below recommended exposure limits (OELs). An exposure assessment of workers is hampered by a lack of threshold values for nano-sized form of silver and silica.

Evaluation of employee exposure is difficult due to lack of normative values for nano-size substances, and lack of any reference values.

- Organisational measures

Organisational remedies were also applied. The manufacturing room is marked as shown in Figure 5. Restricted access protection was applied – see solution shown in Figure 6.

Figure 5: Manufacturing room markings

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Figure 6: Restricted access protection



Employees are trained in working with nanopowders, they have knowledge about the dangers of nanoparticles and are familiar with the various routes of exposures (via the respiratory tract, skin and eyes).

The manufacturing rooms are equipped with two types of instruction manuals: Health & Safety Instructions regarding operation of devices, and operating instructions regarding the production processes. The manufacturing room is covered by a special hygiene plan.

- Risk assessment of workers

Occupational risks for employees in contact with nanomaterials were evaluated. The risk assessment included the following:

- physical/chemical properties (permanent bonding of the nano silver with the silica), and harmful effects of the nanomaterials (see next paragraph);
- employee exposure time (the time of direct contact of an employee with the powder of product is about 1.5 hours within 8 working hours);
- remedies applied (technical, personal, organisational).



Results of the risk assessment indicated that the employed remedies are sufficient to ensure a safe working environment.

- Providing safety of the final product

POCH conducted a study confirming the **permanent** binding nano silver with silica in both internal laboratories, as well as externally (Institute of Physical Chemistry, Polish Academy of Sciences)

The nano silver is **permanently** deposited on silica (tests performed by the Laboratorium Kontroli Jakości POCH S.A. {Quality Control Laboratory} and Instytut Inżynierii Materiałów Polimerowych i Barwników {Institute for Engineering of Polymer Materials and Dyes} confirm lack of silver migration). Laboratories of POCH have authorizations and certificates as follows: Accreditation Certificate of Testing Laboratory meeting requirements of the PN-EN ISO/IEC 7025:2005 standard. Accredited activity is defined in the Scope of Accreditation No AB 1015; GMP, Certificate No. GIF-IW-N-4022/34/10.

The final product is tested for **toxicity and irritation** at the Zakład Badań Toksykologicznych (Toxicity Tests Institution) in the Instytut Przemysłu Organicznego (Organic Industry Institute). The subject of tests was to determine: oral acute toxicity according to guidelines OECD nr 420; skin acute toxicity according to guidelines OECD nr 402; acute irritation of skin according to guideline OECD nr 404; acute eye irritation according to guideline OECD nr 405. Test results confirm that silica with silver nano particles does not show toxic properties, nor irritative properties, in the doses under examination (LD50>2000 mg/kg).

Dermatological tests of nanomaterial were conducted in the Specialised Testing Laboratory ITA-TEST (Warsaw, Poland). The Scope of the research was to: determine human skin tolerance to the tested preparation based on the results of dermatological research by a semi open contact test, European Cosmetic Directive 76/768/EEC (with amendments). The method of research was conducted in accordance with Research Procedure 07/DA by a dermatologist using a semi-open contact test on a group of 60 volunteers sensitive to allergens. Results confirmed that of 60 subjects with demonstrated sensitivity to allergens, no positive reactions were observed. This proves that the raw material does not possess any irritating or sensitising properties, thus the product fulfills requirements regarding the safety of human health according to Directive.

The Company is also aware of information regarding ecotoxicity of free nano silver particles. POCH S.A. is planning to perform ecotoxicity tests according to OECD guidelines (OECD 201, 202, 203, 209).

- Risk communication to customers

Accurate information on the composition and structure of the nanomaterials is provided to potential clients in form of presentations, MSDSs, and data sheets regarding the specific product application. According to client requests, reports with specific tests results are provided.

3.4. What was achieved?

- The entire production installation for nanosilver dotted silica was constructed using the highest quality safety measures regarding the protection of workers. Safe working conditions have been ensured.
- A high level of worker protection has been assured, reducing the risk of exposure to nanoparticles. Dermal and inhalative exposures have been limited as much as possible.
- The safe and tested final product was manufactured.

3.5. Success factors

- Implementation of the Quality, Environment and Safety at Work Management System.

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- Implementation of GMP (Good Manufacturing Practice).
- Involvement of the workforce in the development of the company.
- Commitment to creating safe workplaces.
- Orientation towards Customer.

3.6. Further information

POCH S.A..

ul. Sowińskiego 11,
44-101 Gliwice

tel.: 32 23-92-000, fax: 32 23-92-370, e-mail: poch@poch.com.pl; www.poch.com.pl

Contact person: helena.czepelak@poch.com.pl; bozena.malinowska@poch.com.pl

3.7. Transferability

Most of the abovementioned practices concerning health and safety at work (especially risk management) may be implemented in the company having a corporate profile similar to POCH S.A.

4. References, resources:

1. Opinion On The Appropriateness Of The Risk Assessment Methodology In Accordance With The Technical Guidance Documents For New And Existing Substances For Assessing The Risks Of Nanomaterials Scientific Committee on Emerging and Newly-Identified Health Risks, SCENIHR, 2007, Link to resource 1:
http://ec.europa.eu/health/ph_risk/committees/04_scenihhr/docs/scenihhr_o_010.pdf
2. <http://www.navia.com.pl/EN/index.html?a=wlasciwosci>
3. [Quality Policy, Environmental Policy and Safety at Work Policy.](#)
4. http://www.poch.com.pl/1/wysw/msds_clp.php?A=4d624a55e7cf1ba60001
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