This project is implemented through the CENTRAL EUROPE Programme co-financed by the ERDF

Material Safety Data Sheet

DATE: 29/05/2013

1. Identification of substance and of the company/undertaking

1.1 Product identifier

Substance Name: Silver (powder)

EC No.: (EINECS) 231-131-3

REACH Registration No.: NA

CAS No.: 7440-22-4

1.2 Relevant identified uses of the substance and uses advised against

Relevant identified uses: Use of the powder to formulate antibacterial additives for varnishes to be applied on plastic.

Industrial use (SU3), Professional uses (SU22), Use in closed batch and other processes (synthesis) where opportunity for exposure arises (PROC4), Coatings and paints (PC9a), Biocidal products (PC8), Formulation of preparations (ERC2)

Uses advised against: Consumer use (SU21)

Reasons why uses advised against: The use of powder by the general public is advised against due to the high risk of human end environmental exposure in uncontrolled environments.

1.3 Details of the supplier of the Safety Data Sheet

Manufacturer/Supplier: NA

Street address/P.O. Box: NA

Country ID/Postcode/Place: NA

Telephone number: NA

Email address of competent person for the SDS: NA

National Contact: NA

1.4 Emergency telephone number

NA

2 Hazards identification

2.1 Classification of the substance

Silver as such is classified as H400 and H410, according to ECHA (http://clp-inventory.echa.europa.eu/DetailsOfNotifAndLabelling.aspx?SubstanceID=99642&NotificationID=14308365).

Ag NP in the environment release Ag ions: it behaves more as a soluble salt than an insoluble metal. Therefore, both the classification of silver metal and the classification of silver nitrate can be used to propose a classification for nano silver, also taking into account available nano-specific literature, and the fact that this a powder product.

2.1.1 Classification according to Regulation (EC) No 1272/2008 [CLP]

Risk Phrase: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Aquatic Acute 1[1]: H400

Aquatic Chronic 1: H410

Irritant 2[2]: H315

STOT SE 3: H335

2.1.2 Classification according to Directive 67/548/EEC

N; R50-53: dangerous for the environment

2.1.3 Additional information

NA

2.2 Label elements

Labelling according to Regulation (EC) No 1272/2008 [CLP]

[1] Ashgari et al., 2012. *Journal of Nanobiotechnology* 2012, **10**:14.
[2] Koohi et al., 2011. Journal of Physics: Conference Series 304 (012028)

Hazard pictograms*:* 

Signal word: GHS09, GHS07

Hazard statements:

H410: Very toxic to aquatic life with long lasting effects

H315: Causes skin irritation

H335: May cause respiratory irritation

Safety statements:

P102: Keep out of reach of children
P280: Wear protective gloves/protective clothing/eye protection/ face protection
P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
P314: Get medical advice/attention if you feel unwell
P501: Dispose of contents/container to …
P273: Avoid release to the environment

2.3 Other hazards

Nano Ag, as a powder, during handling can form dust. To measure this parameter, dustiness is measured. However, it is a value not easy to find. According to the value reported in section 9, the **dustiness class** established by the software Stoffenmanager nano[3] is **medium** (lowest possible value in the software).

3. Composition/information on ingredients

3.1 Substances

Name	Index number in CLP Annex VI	Weight % content (or range)
Silver	**N.A.**	**99%**

[3] http://nano.stoffenmanager.nl/

4 First aid measures

4.1 Description of first aid measures

General notes: The main exposure routes are inhalation and dermal contact. Ingestion is very much less likely.

Following inhalation: Supply fresh air. If required, provide artificial respiration. Keep patient warm. Seek immediate medical advice.

Following skin contact: Immediately wash with water and soap and rinse thoroughly. Remove contaminated clothing and shoes. Seek medical attention if irritation develops or persists. Wash clothing before reuse. Thoroughly clean shoes before reuse.

Following eye contact: Rinse opened eye for several minutes under running water. Then consult a doctor.

Following ingestion: If conscious, wash out mouth with water. Seek medical treatment.

Self-protection of the first aider: The first responder should wear appropriate personal protection devices, at least a mask to avoid inhalation of powder in air.

4.2 Most important symptoms and effects, both acute and delayed

Following inhalation: Material may be irritating to nasal septum, throat, mucous membranes and upper respiratory tract

Following skin contact: May cause skin irritation or ulceration

Following eye contact: May cause eye irritation or blue-grey eyes

Following ingestion: May cause gastrointestinal irritation with nausea, vomiting and diarrhoea.

4.3 Indication of any immediate medical attention and special treatment needed

No special treatment needed

5 Fire fighting measures

5.1 Extinguishing media:

Suitable extinguishing media: fire extinguishing powder, dry sand

Unsuitable extinguishing media: water

5.2 Special hazards arising from the substance or mixture:

Hazardous combustion products: Combustion of silver powder may cause the release of toxic metal

oxide fume

5.3 Advice for firefighters:

Wear self-contained respirator.

Wear fully protective impervious suit.

6 Accidental release measures

6.1 Personal precautions, protective equipment and emergency procedures:

Wear protective equipment. Keep unprotected persons away. Ensure adequate ventilation.

6.2 Measures for environmental protection:

Do not let this chemical enter the environment

6.3 Measures for cleaning/collecting:

Evacuate area, shut off all sources of ignition and pick up mechanically using non-sparking tools.

6.4 Reference to other sections:

See Section 7 for information on safe handling
See Section 8 for information on personal protection equipment.
See Section 13 for disposal information.

7 Handling and storage

7.1 Precaution for safe handling:

Protective measures:

Measures to prevent fire: Protect from physical damage, ignition sources and electrostatic discharges.

Measures to prevent aerosol and dust generation: handle in closed systems, under fume hood and/or in glove box. Don't handle/operate open containers outside fume hoods/glove box. Use appropriate filters (use filters HEPA > H13).

Measures to protect the environment: handle in closed systems, under fume hood and/or in glove box. Don't handle/operate open containers outside fume hoods/glove box. Use appropriate filters (use filters HEPA > H13).

Advice on general occupational hygiene: Keep container tightly sealed. Store in cool, dry place in

tightly closed containers. No special precautions are necessary if used correctly.

7.2 Conditions for safe storage, including any incompatibilities:

7.2.1 Technical measures and storage conditions:

Do not store together with acids.
Do not store together with alkalis (caustic solutions).

7.2.2 Packaging materials:

NA

7.2.3 Requirements for storage rooms and vessels:

Store in a tightly closed container in a cool, dry, ventilated, and dark area. Keep container tightly sealed.

Storage class: NA

7.2.4 Further information on storage conditions

NA

7.3 Specific end-uses:

Silver powder used for the preparation of varnish. Specific ES reported in Annex I.

8 Exposure controls and personal protection

8.1 Control parameters

Occupational exposure limits values (http://limitvalue.ifa.dguv.de/WebForm_ueliste.aspx):

Substance	Silver, metallic
CAS No.	7440-22-4

	Limit value - Eight hours		Limit value - Short term	
	ppm	mg/m³	ppm	mg/m³
Australia		0,1		
Austria		0,01 inhalable aerosol		

Belgium		0,1		
Canada - Ontario		0,1		
Canada - Québec		0,1		
Denmark		0,01		0,02
European Union		**0,1**		
France		*0,1*		
Germany (AGS)		0,1 inhalable aerosol		0,8 inhalable aerosol (1)
Germany (DFG)		0,1 inhalable aerosol		0,8 inhalable aerosol
Hungary		0,1		0,4
Italy		0,1		
New Zealand		0,1		
Poland		0,05		
Singapore		0,1		
Slovakia				0,1
South Korea		0,1		
Spain		0,1		
Sweden		0,1		
Switzerland		0,1 inhalable aerosol		0,8 inhalable aerosol
The Netherlands		0,1		
USA - NIOSH		0,01		
USA - OSHA		0,01		
United Kingdom		0,1		

Remarks	
European Union	Bold-type: Indicative Occupational Exposure Limit Values [2,3] and Limit Values for Occupational Exposure [4] (for references see bibliography)
France	Italic type: Indicative statutory limit values
Germany (AGS)	(1) 15 minutes average value
Germany (DFG)	STV 15 minutes average value

Poland	Silver dust and fume

Information on monitoring process:

N.R:

8.2 Exposure controls

8.2.1 Appropriate engineering controls:

Substance/mixture related measures to prevent exposure during identified uses: NA

Structural measures to prevent exposure: NA

Organisational measures to prevent exposure: NA

Technical measures to prevent exposure: Properly operating chemical fume hood designed for hazardous chemicals and having an average face velocity of at least 100 feet per minute. Filtering cabinet connected to ventilation system to the outside. General ventilation of laboratory environment.

8.2.2 Personal protection equipment: The usual precautionary measures for handling chemicals should be followed. Keep away from foodstuffs, beverages and feed. Remove all contaminated clothing immediately. Wash hands before breaks and at the end of work.

8.2.2.1 Eye and face protection: Safety glasses

8.2.2.2 Skin protection: Protective work clothing

8.2.2.3 Hand protection: Impervious gloves

Other skin protection:

8.2.2.3 *Respiratory protection*: Use suitable respirator when high concentrations are present.

8.2.2.4 *Thermal hazards*: NA

8.2.3 Environmental exposure controls:

Substance/mixture related measures to prevent exposure during identified uses: NA

Structural measures to prevent exposure: NA

Organisational measures to prevent exposure: NA

Technical measures to prevent exposure: Filtered ventilated air before release to the outside

9 Physical and chemical properties:

9.1 Information on basic physical and chemical properties:

a) Appearance:

Physical state: Solid powder (nanomaterial);

Colour: Black gray

Granulometry:

i) Average size: 37 ± 16.5 nm (TEM)
Note: maximum diameter 133 nm, but 99% of the sample below 100 nm.

ii) Aggregation/agglomeration: Z average 151 nm (PDI = 0.210). The whole sample is between 100 and 300 nm
Note: nanoparticles dispersed in culture media + FBS at a concentration of 20 μg/mL nanosilver

iii) Shape: round (smaller particles) to elongated (larger particles) (TEM picture)

b) Odour: Odourless

c) Odour threshold: NA

d) pH: Not Relevant

e) Melting point/freezing point: 961.3 °C[4]. Melting point for nanosilver is expected to drop with size below 20 nm, with a predicted melting temperature of 550 °C at 2 nm[5]

f) Initial boiling point and boiling grange: 2210 °C[3]

[4] Nanomateriasl under REACH. Nanosilver as a case study. RIVM report 601780003/2009
[5] "Silver Nanoparticles", Ed. David Pozo Perez; ISBN 978-953-307-028-5

g) Flash point: NA

h) Evaporation rate: NA

i) Flammability (solid, gas): Fine powder: highly flammable

j) Upper/lower flammability or explosive limits: ND

k) Vapour pressure: Not relevant (solid)

l) Vapour density: Not relevant (solid)

m) Relative density: (at 20 °C) 10.491 g/cm^3

n) Solubility(ies):

Ag particles release ions in water.

In DI water: 20% after 24h, 50% after 120 d (initial concentration 4 mg/L Ag);[6]

In natural water (with NOM): 10% after 48h, 60% after 90d.[7]

o) Partition coefficient: n-octanol/water: Not Relevant for nanoparticles

p) Auto ignition temperature: ND

q) Decomposition temperature: ND

r) Viscosity: ND

s) Explosive properties: Product does not present an explosion hazard.

t) Oxidising properties: it is a reducing agent.

9.2 Other Information:

u) Dustiness: 17 mg/Kg

The value is a read-across between a method applied to nano Ag that overestimate dustiness by 1000 times[8] with respect to the usual methodology. The reported value of 17000 mg/Kg was then

[6] Liu and Hurt, 2010. Environ. Sci. Technol., 44, 2169–2175.
[7] Gao et al., 2012. Chemosphere, 89:96–101.

divided by 1000.

10 Stability and reactivity

10.1 Reactivity:

NA

10.2 Chemical stability: No hazardous reaction when handled and stored according to provisions.

10.3 Possibility of hazardous reactions: Silver may react with acetylene or ammonia to form shock sensitive compounds.

10.4 Conditions to avoid: Dust generation and incompatibles.

10.5 Incompatible materials: Acids, Bases. I.e. Acetylene, ammonia, strong hydrogen peroxide solutions, strong acids, oxalic acid, tartaric acid, bromoazide, chlorine trifluoride, and ethyleneimine.

10.6 Hazardous decomposition products: Metal oxide fume

11 Toxicological information

11.1 Information on toxicological effects

Acute toxicity: No LC_{50} or usual benchmark found for nano Ag. However, current in vitro studies have shown that Ag NPs have potential to induce cytotoxicity in cells derived from a variety of organs, with concentrations variable from 10 μg/mL, also depending from cell lines.[9]

Few *in vitro* and *in vivo* inhalation studies are available. The results show that EC50 cytotoxic effects of coated Ag particles on A549 epithelial cells[9] ranged from 50 to 100 μg/mL (PI staining test), after 72h exposure. The EC50 MTS test on **A549 for the TS particles** showed an EC50 of 56 μg/mL at 48h exposure, with a time dependent and dose dependent response. Cytotoxicity on NR8383 rat cells showed a much lower EC50, around 1.7 μg/mL after 48h exposure.

In vivo inhalation exposure of rats and mice for 28[10] and 14 days[11] did not cause appreciable toxic effects up to an exposure of 1.9E7 particles/m^3.

[8] O'Shaughnessy et al., 2012. J Occup Environ Hyg. 9(3): 129–139. Ahamed et al. Clinica Chimica Acta 411 (2010) 1841–1848

[9] Lankoff et al. Toxicology Letters 208 (2012) 197– 213

[10] Hyun et al. Toxicology Letters 182 (2008) 24–28

Chronic toxicity: The literature shows that absorption of silver compounds by ingestion, inhalation or through broken skin can cause argyria, a permanent bluish-grey discoloration of the skin, conjunctiva and mucous membranes. Studies have shown that the lungs and liver are major target tissues for prolonged Ag NP exposure.[8]

Skin corrosion/irritation: Powder, irritant effect

Serious eye damage/irritation: Powder, irritant effect

Respiratory or skin sensitisation: No sensitizing effects known

Germ cell mutagenicity:

Carcinogenicity: Not carcinogenic

Reproductive toxicity: NA

Summary of evaluation of the CMR properties: Tumorigenic effects have been observed on tests with laboratory animals

STOT-single exposure:

STOT-repeated exposure:

Aspiration hazard:

Additional toxicological information: To the best of our knowledge the acute and chronic toxicity of this substance is not fully known. Tumorigenic data reported in NIOSH database are very old.

Oxidative stress was measured with GSH/GSSG ratio and Lipid peroxidation. GSH oxidation was observed from 25 μg/mL both after 6h and 24h exposure, but no Lipid peroxidation was observed. Gene expression showed oxidative stress, inflammatory response, and DNA damage in A549 cells from 25 μg/mL after 48h treatment, while some signs of stress started to be seen already at 10 μg/mL.

[11] Lee et al. J Nanopart Res (2010) 12:1567–1578

12 Ecological information:

12.1 Toxicity

Acute (short term) toxicity:

Fish: Different studies shows a lethal concentration (96h LC50) of 90 µg/L nano Ag (10 nm size) for *Pimephales promelas*[12], and of 1.4µg/L in Japanese medaka[13], while effects on development of early life stages of different species ranging from 0.5[13] µg/L in Japanese medaka and 180 µg/L[14] Ag (96h EC50) for *Danio rerio*. The studies used different Ag NPs (coated/uncoated, different size).

Crustacea: Two acute studies on daphnia species showed that 48h LC50 concentrations ranged around 4 to 30 µg/L Ag, depending on particle size (smaller particles more toxic)[12]. Exposure with Humic Acid to 50 µg/L Ag caused 90% mortality with 0 HA, while 10 mg/L HA decreased toxicity to 50%, and 20 mg/L HA decreased effect to ~ 15%[15].

Algae/aquatic plants: Ag NP caused decrease of photosynthetic efficiency of *R. subcapitata* at high concentration (i.e. ~21 mg/L, 4.5h EC50)[14], while *Lemna minor* showed significant effect on growth already at 5 µg/L at 14d, with a EC50 at 14d ~ 20 µg/L[16].

Bacteria: The exposure of soil to sludge containing low concentration of silver NP (0.14 mg Ag/kg soil) cause decrease of enzymatic activity (around 27% minimum) and biomass (35%) of bacteria[17].

Chronic (long term) toxicity:

Fish: Only one study showed that 14d exposure to *Cypronodon variegatus* at 2.9 µg/L in adults caused only proliferation of epithelial tissue in gills, decreasing significantly at day 35.[18]

12.2 Persistence and degradability

Abiotic degradation: Ag NP in wastewater[19] and in soil[20] tend to be transformed in AgS in presence of different levels of S.

Physical- and photo-chemical elimination: NA

[12] HOHEISEL et al. Environmental Toxicology and Chemistry, Vol. 31, No. 11, pp. 2557–2563, 2012
[13] Kashiwada et al. Environ. Sci. Technol. 2012, 46, 6278−6287
[14] Wang et al. Environmental Toxicology and Chemistry, Vol. 31, No. 10, pp. 2408–2413, 2012
[15] J. Gao et al. Chemosphere 89 (2012) 96–101
[16] E.J. Gubbins et al. Environmental Pollution 159 (2011) 1551-1559
[17] Colman BP, Arnaout CL, Anciaux S, Gunsch CK, Hochella MF Jr, et al. (2013) PLoS ONE 8(2): e57189.
[18] Griffitt et al. Environmental Toxicology and Chemistry, Vol. 31, No. 1, pp. 160–167, 2012
[19] Kaegi et al. Environ. Sci. Technol. 2011, 45, 3902–3908
[20] Levard et al. Environ. Sci. Technol. 2011, 45, 5260–5266

Biodegradation: NA

12.3 Bioaccumulation potential

Partition coefficient n-octanol/water: Not relevant

Bioconcentration factor (BCF): Not Available

12.4 Mobility in soil

Known or predicted distribution to environmental compartments: NA

Surface tension: NA

Adsoprtion/desorption: NA

12.5 Results of PBT and vPvB assessment

NA

12.6 Other adverse effects

NA

12.7 Additional information

NA

13 Disposal considerations

13.1 Waste treatment methods

13.1.1 Product/packaging disposal: Consult state, local or national regulations to ensure proper disposal.

13.1.2 Waste treatment-relevant information: NA

13.1.3 Sewage disposal-relevant information: The literature shows that nanosilver in model wastewaters treatment plants is almost entirely converted in Ag_2S[19]. In addition, according to simulations, the highest concentration expected in effluents for more stable coated Ag is < 0.24

μg/L[21]. Disposal via wastewater treated in a common wastewater treatment plant is preferred to disposal via landfill.

13.1.4 Other disposal recommendations: There are no specific information about disposal of wastes containing nano silver. However, it is suggested to avoid release of solid material into the environment.

14 Transport information

Not a hazardous material for transportation.

- **Land transport ADR/RID (cross-border)**
- **ADR/RID class:** None

- **Maritime transport IMDG:**
- **IMDG Class:** None

- **Air transport ICAO-TI and IATA-DGR:**
- **ICAO/IATA Class:** None

14.1 UN number:

14.2 UN proper shipping name:

14.3 Transport hazard class: None

14.4 Packing group:

14.5 Environmental hazards:

14.6 Special precautions for user:

14.7 Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code: Not dangerous according to the above specifications

15 Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture:

EU Regulations

[21] Hendren et al. Science of the Total Environment 449 (2013) 418–425

Authorisations and/or restrictions on use:

Authorisations:

Restriction on use:

Other EU regulations:

National regulations:

15.2 Chemical Safety Assessment

The use foreseen in this SDS is industrial, performed in confined location (e.g. under ventilated chemical fume hoods) and also with general ventilation of the production site, and using very low amount at a time (i.e. 20 g). Therefore, it was considered a negligible or absent environmental emission, and thus, no environmental exposure scenario was performed.

16 Other information:

(i) Indication of changes:

(ii) Abbreviations and acronyms:

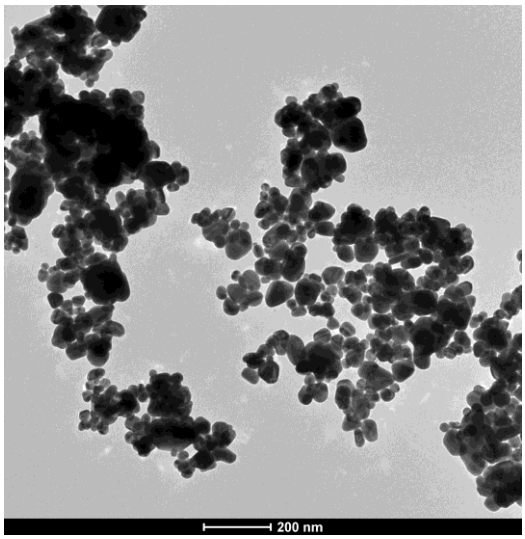
(iii) Phys-chem measurement details

The dustiness of nanosilver powder is a read across from dustiness for Ag nano in powder measured by using a methodologies that estimate dustiness 1000 times higher than the falling powder method, which is usually applied in literature. The comparison, made for TiO_2, was extended to Ag, thus reducing by 100 times the value of total dustiness of 17000 mg/kg, reaching 17 mg/kg.

Solubility in water: According to the literature, Ag releases Ag ions into water. The amount of Ag that enter water as ion is variable, and depends from the water chemistry (pH, NOM, O_2) and temperature. In Liu and Hurt[22] it was studied the kinetic of ion release of nano Ag in De-Ionized water. The ion release is slow, but constant. In 120 days, half of 2 mg/L Ag was in ion form. After 24h, 0.4 mg/L Ag^+ are released from 2 mg/L Ag. In Gao et al.[23], similar results were obtained in natural water with Natural Organic Matter for bare nano silver. After 48h, the lowest ion release was 10% of total silver, while after 90 days the lowest release was 60% (at NOM content around 8 mg/L).

[22] Liu and Hurt, 2010. Environ. Sci. Technol., 44, 2169–2175.
[23] Gao et al., 2012. Chemosphere, 89:96–101.

TEM picture



(iv) Classification and procedure used to derive the classification according to Regulation (EC) 1271/2008 [CLP]

Silver nitrate is classified in CLP according to GSH as: *H272 (May intensify fire; oxidiser); H314 (Causes severe skin burns and eye damage); H400 (Very toxic to aquatic life); H410 (Very toxic to aquatic life with long lasting effects).*

(v) Relevant R-phrases and/or H-statements (number and full text)

(vi) Training advice:

(vii) Exposure scenarios (…)

(viii) Details of Ecotoxicity data

(ix) Further information:

Hazard pictograms for silver nitrate

For silver nitrate:  , ,

This project is implemented through the CENTRAL EUROPE Programme co-financed by the ERDF

ANNEX I: Exposure Scenario

1. Exposure Scenario
Workers exposed to nano Ag during varnish additive preparation and use
2. Contributing scenarios
2.1 Contributing scenario (1): powder partitioning
2.2 Contributing scenario (2): powder dispersion (additive preparation)
2.3 Contributing scenario (3): further reactions in dispersion (additive preparation)
2.3 Contributing scenario (4): paint preparation
2.3 Contributing scenario (5): paint use
3. Exposure estimation and reference to its source
3.1 Contributing scenario (1): the arrived material, in a closed and sealed bag, is placed in a glove box, opened there, and the powder is weighted and distributed in containers with double cap. The containers are then extracted from the glove box and stored in a filtration cabinet. Exposure estimation: According to Stoffenmanager Nano, Inhalation Exposure Class is **Low**
3.2 Contributing scenario (2): the powder is extracted from the filtration cabinet, inserted in the glove box, and pre-dispersed into the appropriate matrix. The pre-dispersion is placed in sealed containers. Exposure estimation: According to Stoffenmanager Nano, Inhalation Exposure Class is **Low**
3.3 Contributing scenario (3): The pre-dispersion is placed under fume hoods, where further chemical reactions or energetic treatments (if needed) are done. The result of this phase is the production of the final product (additive), put in closed containers. Exposure estimation: According to Stoffenmanager Nano, Inhalation Exposure Class is **Low**
3.4 Contributing scenario (4): the additive is added to the paint under fume hood, or in the open, wearing protective equipment. Exposure estimation: According to Stoffenmanager Nano, Inhalation Exposure Class is **Low**
3.5 Contributing scenario (5): the paint is distributed on the surface using a close system, or by hand depending on the needs (e.g. coating thickness) Exposure estimation: According to Stoffenmanager Nano, Inhalation Exposure Class is **Low**

Disclaimer

We make no warranty of any kind regarding the information furnished herein. Users should independently determine the suitability and completeness of information from all sources. While this data is presented in good faith and believed to be accurate, it should be considered only as a supplement to other information gathered by the user. It is the User's responsibility to assure the proper use and disposal of these materials as well as the safety and health of all personnel who may work with or otherwise come in contact with these materials.

Corresponding Author:

Christian Micheletti - Veneto Nanotech S.C.p.A, Italy christian.micheletti@venetonanotech.it