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SAFETY RISK OF NANO-METAL ALKOXIDES FOR THE CONSERVATION OF CULTURAL HERITAGE: RESULTS FROM NANOMATCH PROJECT

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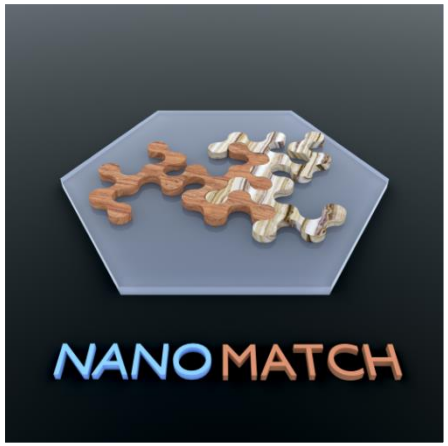
NANOMATCH Project



Nano-systems for the conservation of immoveable and moveable polymaterial Cultural Heritage in a changing environment

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cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Project partners

13 partners from 6 European Countries

Public Research Centres
Private /No profit Research Centres
Conservation Centres
SMEs

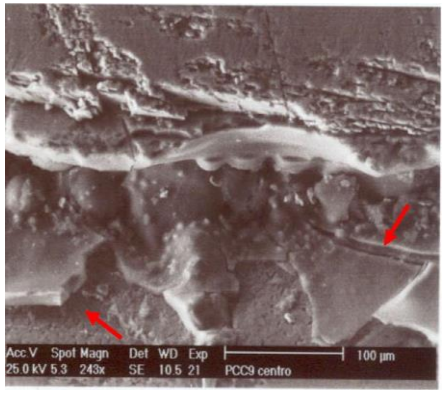
1	CONSIGLIO NAZIONALE DELLE RICERCHE (COORDINATOR)	CNR	Italy
2	NEDERLANDSE ORGANISATIE VOOR TOEGEPAST NATUURWETENSCHPPELIJK ONDERZOEK - TNO	TNO	Netherlands
3	FUNDACION TECNALIA RESEARCH & INNOVATION	TECNALIA	Spain
4	Cercle des partenaires du patrimoine – Laboratoire de recherché des monuments historiques	CPP-LRMH	France
5	FRAUNHOFER-GESELLASCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V	FRAUNHOFER	Germany
6	ASOCIACION DE INVESTIGACION DE LAS INDUSTRIAS DE LA CONSTRUCION	AIDICO	Spain
7	R.E.D. SRL	RED	Italy
8	BOFIMEX BOUWSTOFFEN BV	BOFIMEX	Netherlands
9	METROPOLITANKAPITEL DER HOHEN DOMKIRCHE KOLN DOMBAUVERWALTUNG	HDK	Germany
10	OPERA DI SANTA CROCE	OSC	Italy
11	ESCHLIMANN ATELIER DE RESTAURATION-PEINTURE SAS	ESC	France
12	TOP OBERFLACHEN GMBH	TOP	Germany
13	DUCT SRL	DUCT	Romania

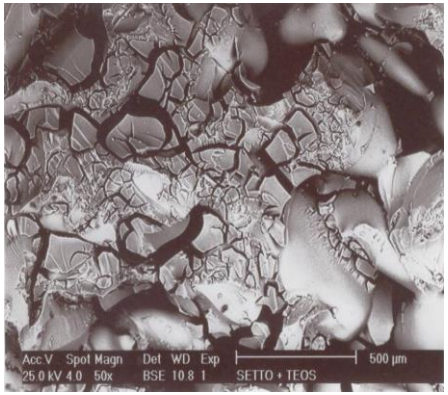
State of the art

Cultural Heritage is threatened by a great variety of natural deterioration agents and pollutants which can affect very seriously materials and precious surfaces

Actually, the same factors acting on the historic substrates are effective also on the products used for conservation, i.e. organic polymers, reducing their efficacy and removability

SEM image of cracking and detachment of siloxane coating from a stone substrate





SEM image of cracking and detachment of SiO_2 coating on a glass substrate

Urgent need to DEVELOP NEW OR TO IMPROVE ACTUAL PRODUCTS AND CONSERVATION METHODOLOGIES as alternatives to conventional ones for Cultural Heritage

Aim of the project

In NANOMATCH two alkoxides have been developed:

calcium alkoxides, precursor of corresponding carbonate, have a strengthening effect on stone and provide an alkaline supply on wood

aluminium alkoxide, precursor of Al_2O_3, for the consolidation of micro - fractured glass (development in EU project CONSTGLASS)

Requirements of the new products:

- **evolving to nano-structured adherent coatings**
- **compatible with the substrates**
- **ensuring enhanced sustainability, durability and efficiency compared to conventional conservation products**

Advancement in the state of art

- The final products are new advanced compatible and sustainable nano-structured materials starting from the same class of compounds
- Their common base simplifies the process of the synthesis and the subsequent production of the final products
- An appropriate tailoring of the precursors tunes the final properties of the resulting nanostructured materials to be effective towards the environmental change
- They have no detrimental effect on polychromy
- Although not reversible, they fulfil the most important requirements i.e. compatibility, durability and retreatability
- They are low cost products and simple in the application
- They respect environment & human health

Project strategy

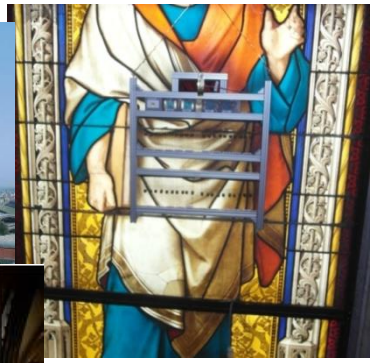
- **Developments of Ca/Mg alkoxides:**
  - ✓ selection of appropriate reagents
  - ✓ test of different synthesis routes
  - ✓ complementation with nanoparticles (Zn/Cu, TiO_2) or organic molecules to obtain a biocide effect for wood
- **Optimization of A18 glass-in-glass consolidant:**
  - ✓ optimization of the sol-gel process deposition
  - ✓ improvement of the viscosity of A18 in order to allow penetration also on smaller cracks (< 5µm)
  - ✓ to obtain a low rate of hydrolysis process in order to improve its adhesion

Project strategy

- **Laboratory experimentation** to assess:
  - ✓ applicability and workability of solutions
  - ✓ compatibility of nanostructured materials with the substrates
  - ✓ performance regarding the specific properties to be improved
  - ✓ durability
- **Field exposure experiments:**
  - ✓ performed on untreated and treated substrate models sound and artificially weathered and on weathered historic real surfaces
  - ✓ evaluation of on going deterioration processes, surface appearance, variation of thermal and hygroscopic behaviour

  The results have been compared to the current commercial products
- **Evaluation of safety hazards** towards **man and environment**
- **Production on small scale** of the **best performing and safe products** for the **introduction in the market**

Experimental sites

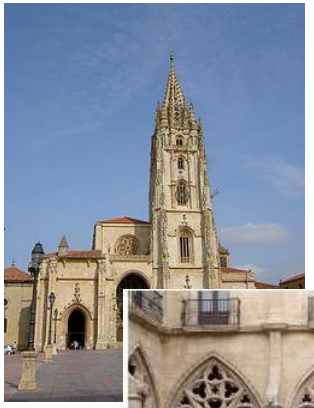

Cologne Cathedral (DE)



S. Croce Cathedral, Florence (IT)



Stavropoleos Monastery, Bucharest (RO)



Oviedo Cathedral (ES)

Risk assessment

D 5.1 Assessment of risk for health & environmental effects when using metal alkoxides solutions and sols

D 5.2 Assessment of risk for health & environmental effects related to potential nanoparticles dispersion

Risk assessment of stone/wood consolidant

Activity	Planned
1. Literature review	"State of art" on risk assessment and nanotoxicology of alkoxides and Ca-based nanomaterials
2. Risk for health	Occupational exposure to nanoparticles
3. Risk for health	Characterization of nanoparticles released in occupational scenario
4. Risk for environment	Environmental exposure to nanoparticles
5. Exposure after treatment	Characterization of nanoparticles released in outdoor scenario
6. Guidelines	Report with the guidelines
7. Risk of alkoxides	Study of the MSDS of the different components of the Ca alkoxides and related risks

Literature review

Concerning the toxicity of calcium alkoxides

The formulations does not have any CAS number

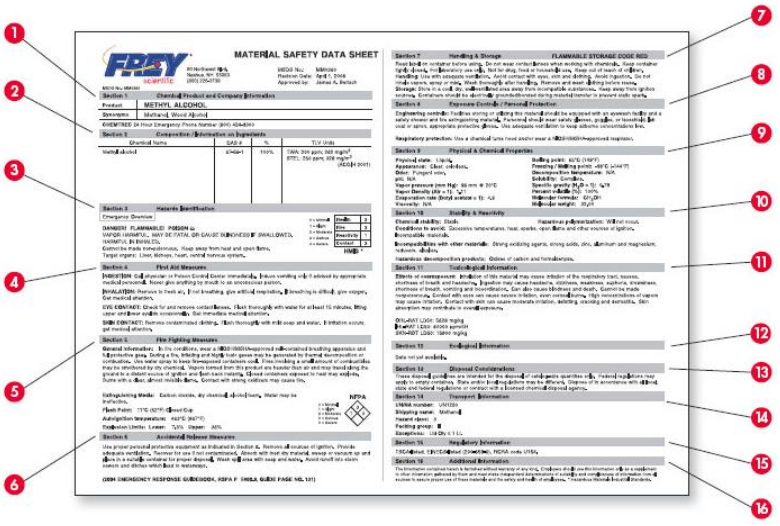
No toxicity data for the substance are available. It was also not possible to find any physical-chemical property

Therefore, in order to evaluate the hazardousness of the compound we considered the classification of two hydrolysis compounds, i.e. $Ca(OH)_2$ and the alcohols

Literature review

To collect a comprehensive state of the art on the toxicity profile of calcium carbonate nanoparticles and chemicals used as reactive precursors:

- ✓ **Accurate review of the available scientific literature**
- ✓ **Use of the most important databases of research literature and web sources**



Occupational exposure - Methodology

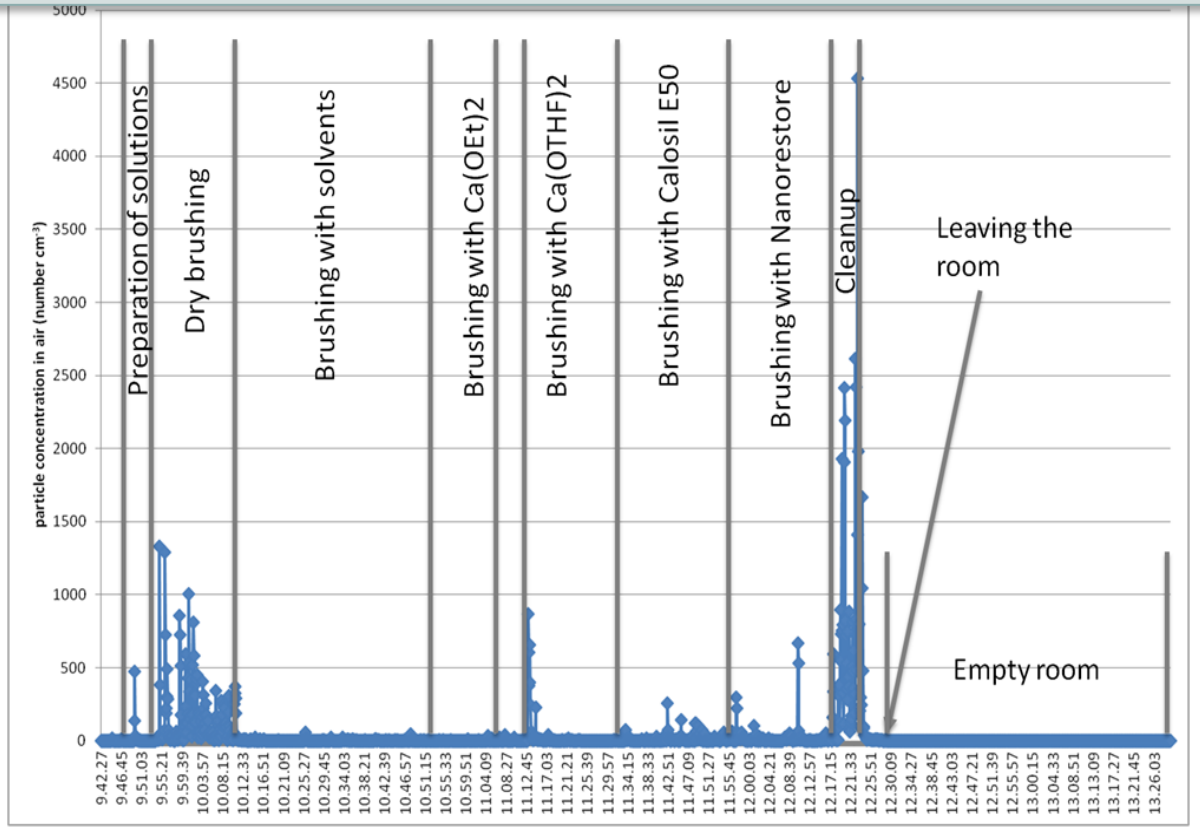
Estimation of exposure to nanoparticles by inhalation during application procedures of alkoxides on stone samples:

- ✓ **Monitoring of the number particle concentration in air with a Condensation Particle Counter (CPC)**
- ✓ **Sampling activities in a clean room class 1.000**
- ✓ **Identification of particle size: 0-375 nm**

Instrumentation	CPC mod. 5.403, Grimm
Condensation liquid	1-butanol
Sampling frequency	6 sec
Sampling range (D_{50} aerodynamic diameter)	4.5 – 370 nm
Distance from the operator	10-15 cm
Room temperature	22.6 ± 0.2 ° C
Room relative humidity	42.1 ± 1.2 %

Occupational exposure - Results

- ✓ The highest particle concentration in air were detected during dry brushing and cleanup activities
- ✓ During application of solvents and Nanomatch treatments the increase of particle concentration was very low



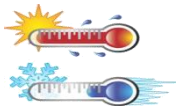
Characterization of nanoparticles released in occupational scenario

Classification of particles dimension in the range 0-100 nm according to EU standards

The emissions from restoration activities are negligible in environmental conditions, where background concentration are about one order of magnitude higher than observed emissions

Environmental exposure

Evaluation of Calcium release (ions, nanoparticulate or both) from the Nanomatch treatments **after exposure to aging processes,** to simulate the outdoor weathering:

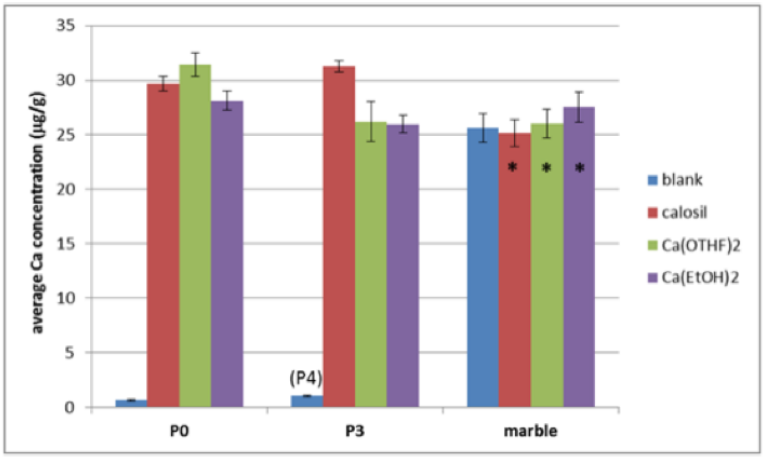
- ✓ exposure to UV rays 
- ✓ sinking in acid solution: pH 3 
- ✓ temperature turnover: 

  7 days at +20° C + UV rays;

  7 days at -20° C at dark; two cycles

Characterization of leached solutions released in outdoor scenario

- ✓ The released Ca concentration is comparable for all tested restoring solutions and it ranges from 25 to 31 µg/mL



Average Ca concentration

- ✓ In real exposure scenarios the Ca contribution from the products is negligible for marble specimens due to the high calcium background in the matrix.
- ✓ Dynamic light scattering measurements demonstrated the fully absence of nanoparticles leached either by marble untreated and treated probably due to their dissolution in the acid water (rain)

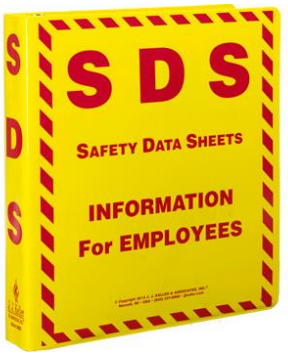
Risk assessment of glass consolidant

- ✓ **Nanoparticles are not present neither in the solution nor in the microcavities of the glass**
- ✓ **Risks from the hydrolysation of methoxysilane (additive used to stabilize the product under high humidity levels), which causes the formation of methanol**
- ✓ **So far, the required quantities keep the methanol content below 3% and therefore below the amount relevant for declaration.**

Conclusions

Production of application guidelines

- ✓ **Evaluation of the risk** related to the application and use of the Nanomatch treatments
- ✓ General **information on safe handling** for precursors, solvent, powder and finished product
- ✓ Production of **Material Safety Data Sheet (MSDS)**



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