Project NANOMATCH

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

environment and health

PROJECT DESCRIPTION

The problem of deterioration of heritage materials has become increasingly urgent due to:

- the increase of weathering caused by climate change and atmospheric pollution (as studied in several European Projects as for VIDRIO, Teach and NOAH'S ARK);
- the current use of inappropriate commercial products and their fast deterioration;
- the need of a more sustainable management of the built heritage.

Therefore, there is the demand to improve the current products and methodologies or to develop new valid alternatives for the conservation and preservation of monuments, safeguarding their cultural values and improving their future usability.
NANOMATCH project addressed these issues combining the most recent advances in the fields of nanotechnologies and conservation science. The overall objective of NANOMATCH has been the development of alkaline earth metal and semimetal alkoxides which evolve to nanostructured conservation products, compatible with the main materials used in built heritage like stone, wall paintings, wood and glass, ensuring enhanced sustainability, compatibility and efficiency, compared to conventional conservation products.

OBJECTIVES

The starting idea was that alkaline earth metal and semimetal alkoxides are suitable molecular precursors of consolidants since, when applied, they create a nano-structured coating adherent to pore walls (stone, stone-like and wood) or to the internal cracks (glass). Particularly, calcium alkoxide can be considered as strengthener for stone and as alkaline supply for wood. The project addressed the development of a new class of highly competitive and performing products and the assessment of their performance with respect to the most used conservation products. With this aim, workability, efficacy, compatibility and durability were assessed in comparison with commercial products both in laboratory and through exposure of treated model samples (sound and artificially weathered) and degraded historical surfaces in four sites: Cologne Cathedral (DE), Santa Croce Basilica in Florence (IT), Oviedo Cathedral (ES), Stavropoleos Monastery in Bucharest (RO).
NANOMATCH, payed specific attention to the development of suitable products for the treatment of historical materials as alternative to the inappropriate use of several commercial products, especially polymers.
Core of the project is the synthesis of molecular precursors, nano-coating deposition and assessment of their conservation properties leading to the production of innovative products able to replace unsuitable traditional ones in the market of conservation. In fact, in recent years, most of these products have shown deterioration processes, which, not only led to a loss of their functionality, but often gave rise to detrimental effects, provoking further damage to the treated material.
Essential for bringing the developed NANOMATCH prototypes to the market was the study of any possible hazardous impact of the metal alkoxides on environment and human health during production, application and after conservation treatment, by considering the transformation that the compounds would undergo and the possible environmental release of nanoparticles from the treated substrates. Finally, a considerable number of aspects were taken into account: the development, evaluation and production of these compounds, their optimal formulation, their performance evaluation, the risk assessment and environmental impact, and, finally, the development of business plans for the market uptake and the writing of the guidelines for end-users.

PROJECT PHASES

The first important step was the selection of the materials to be used as representatives for weathered historic substrates for laboratory testing and/or field-exposure, among the typologies considered in the project. The materials' identification was based on: type of sample stone (lithotypes, porosity and water absorption coefficient, shape and dimensions of models), wall painting replicas (binders, pigments) , kind of wood and glass to be used in the laboratory tests and comparative commercial products (organic and inorganic) selected to be tested. Apart from fundamental parameters and criteria to be taken into account, methods to be used for the laboratory tests and field-exposure measurements were defined and protocols established for the assessment of the properties and features of the new products and of the treated materials.
After these preliminary activities, the second key stage was dedicated to synthesize calcium alkoxides products and to optimized the aluminium alkoxide complex already developed in the EU project CONSTGLASS. Different synthetic routes to obtain Ca/Mg alkoxides were analyzed, and two Ca alkoxides were finally selected (calcium ethoxide and calcium tetrahydrofurfuryloxide) and their production process optimized up to Kg lab-scale. An in-depth study of the different parameters (starting alcohol features, solvent polarity and concentration, coordination capacity,…) that may have an important effect on the final compound characteristics was carried out. Aluminium alkoxide optimization led to a better formulation of the product, which show a good stability also with medium-high humidity conditions.
In the third project's stage, after an accurate selection of the optimal application conditions based on preliminary test, the model sample and the real historical samples were treated with the products. All the planned test were then carried out on all the samples (untreated, treated with NANOMATCH products, treated with commercial products) in order to assess the performance before and after treatment.
In the fourth stage, some samples (treated and untreated model samples, real historical samples) were exposed in the four different sites (Cologne Cathedral (DE), Santa Croce Basilica in Florence (IT), Oviedo Cathedral (ES), Stavropoleos Monastery in Bucharest (RO)). They were positioned into racks designed to have different exposure to environmental factors. In this case the positioned samples were monitored before and after treatments in order to assess the products reaction to the atmospheric agents and their durability.
In the last stage to provide a risk assessment evaluation, the release of nanoparticles in outdoor scenario tests was studied, particularly during the application (occupational scenario) and after the treatment (environmental release scenario). The final document covers guidelines and MSDS sheets on the products risks. MSDS data sheets was required in order to study the new product's commercialization. At this scope, the market potential assessment was essential to develop the business model and was evaluated through questionnaires to end-users and stakeholders.

PROJECT RESULTS

The main target of the NANOMATCH project was to synthesize, test and finally identify innovative materials with improved

consolidation effect on stone and stone like materials, filler/pH stabilizer effects on wooden materials or filler for the nanofissures in ancient glass.
Two types of products have been obtained:

- Aluminium alkoxide with added triethanolamine, very efficient in the treatment of microfissures of historical glasses and glass windows;
- Two alkoxides treatments (calcium ethoxide and calcium tetrahydrofurfuryloxide) with the aim to obtain a carbonate matrix compatible with stone and stone-like substrates.

Results showed good penetration (up to 25 mm in most porous stone) and microcrystalline crystallization of the consolidant within porous stones, with consolidation effect but without significant aesthetical change. Thanks to the fast alkoxide reaction time, a good surface cohesive effect was rapidly achieved and after exposure it further increased in the deeper layers. In stone-like materials the treatment performances were quite similar but strictly related to the type of binder and pigment. In wood samples, an effect of preservation against fungal attack and pH acidification was attained in combination with a biocide.
The product developed for the glass ensured high transparency even after long-term exposure outdoors and stability under medium relative humidity conditions indoors.
Finally, risk assessment of nanoparticles exposure was performed. Measurements successfully demonstrated that any nano-particles release took place neither in their manipulation nor after treatment.
During the three years of the project, a considerable number of aspects were taken into account, moving from the development, evaluation and production of these compounds to the formulation, the performance evaluation, the risk assessment and environmental impact , and finally to the development of business plans related to entry in the market for those products and the writing of the guidelines for end-users.
These new advanced products offer a variety of possible applications starting from the same class of compounds, tailored in relation to the specific conservation needs. Hence, they mark a new generation of restoring inorganic products, compatible with the original materials, easy applicable to indoor and outdoor Cultural Heritage and low-cost.

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