PANNA Project – Plasma and Nano for New Age Soft Conservation. Development of a Full-Life Protocol for the Conservation of Cultural Heritage

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Abstract. EU PANNA project started on November 2011 and aims at integrating a novel atmospheric plasma technique for surface cleaning and two innovative coating typologies (self-diagnostic protective coatings and identification marker coating) in a full-life protocol spanning surface cleaning, deposition of coatings and their complete removal. The validation of the protocol will be achieved through the cooperation between conservation scientists and technological companies. In the project, the development and testing of the protocol will be performed on two categories of substrates: metals (bronze and silver) and stone and stone-like materials (limestone, sandstone and wall paintings). The development will be performed on laboratory prepared samples (dummy or replica or mock ups) and also on real objects.

Keywords: EU-PANNA, Atmospheric plasma, Coating, Cleaning, Silver, Bronze, Limestone, Sandstone, Marble, Wall paintings.

1 Introduction

Key conservation principle relates to reversibility of treatments. There is a wide range of excellent organic and inorganic conservation materials that, in principle, could be used as protective coatings. Unfortunately, many of them are barely removable after weathering with sustainable cleaning techniques (e.g. organic solvents or laser ablation).

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The present challenge is not only to develop new protective coating materials with improved properties, but also to provide a solution for their complete removal. The atmospheric plasma technique is proposed for surface cleaning and coating removal as alternative or complementary to other non-contact techniques such as laser cleaning. This device should be both compatible with the cultural heritage asset and portable, allowing easy handling by the conservators.

Protective coating formulations will be developed with features which include the possibility to bestow self-diagnostic properties into the coating. Invisible tags for identification and anti-counterfeiting purposes will also be developed.

The aim of this project is therefore to establish a full life protocol, described in the following chapter.

2 The "Full-Life" Protocol

The full-life protocol will offer the cultural heritage conservation field the possibility to use a validated completely reversible technique for the application of a protective coating for preventive conservation. The "full-life" concept is even more restrictive in respect to reversibility since it includes cleaning; surface preparation; coating deposition and then coating removal.

All the process is contactless and with no significant temperature increase, avoiding in that way any change in the physical and chemical properties of the substrates. As plasma treatment consists in a surface technique (in the nanometre range), any loss in substrate toughness and consistency will be avoided.

2.1 Atmospheric Plasma

Plasma is a partially ionized gas containing an equal number of negatively and positively charged particles and a different number of non-ionized neutral molecules [1]. From a macroscopic point of view, plasma is electrically neutral [2]. In other words, plasma is a medium full of reactive chemical species some of which are in excited unstable or metastable states. These species can interact with the surface they come in contact with and trigger chemical reactions.

For the aims of this project, *Atmospheric Pressure Plasma Jets* (APPJs) will be considered. In such devices the plasma is generated by the application of an electric discharge to a gas. The gas is fluxed through the area where the plasma is generated and the products of the excitation are carried through a nozzle to the zone that has to be treated. These devices are often regarded as "Plasma Torches".

In the case of plasmas operating in atmospheric environment, the plasma purpose is to oxidize (originating mainly oxygen ions, ozone and related radicals) or to reduce (originating hydrogen ions). The cleaning and removal effects of such devices are therefore not performed as in, for example, laser treatments by ablation of the surfaces, but by *surface chemical oxidation or reduction* and formation of volatile compounds (mainly CO_2 and H_2O).

Atmospheric plasma instruments are spreading as *"plasma torches"* in different industrial sectors from the late nineties. Nowadays there are different commercial torches and each plasma torch has very different features. The widest application field for these sources is the surfaces treatment. There are many ways to treat surfaces: cleaning, activation, etching, functionalization and coating application [3].

There are hence several atmospheric plasma technologies, developed for specific purposes of industrial needs worldwide (USA, EU, Asia). In the field of cultural heritage, individual requirements, beginning with portability and easy handling of the equipment, as well as the low plasma temperature, require the development and use of a specific and tailored technology. Actually there are no commercially available plasma torches dedicated to this application. Only from few EU groups appeared in literature the first applications in this field, such as the removal of organic coatings (Paraloid B72) or the cleaning of wall painting replicas covered with soot [4]. The obtained results are promising and can allow an EU leadership in the use of this technique for CH.

Moreover, the atmospheric plasma is proposed in the project for the *deposition* of innovative coatings. The developed plasma torch will also allow the deposition of nano-composites [5].

2.2 Self-diagnostic Coatings

The innovative protective coatings offer the possibility of checking, with a simple and instant *in-situ* measurement, if the coating is present and what is its state of degradation/preservation. Unlike what happens with standard protective coatings, this novel attribute will prevent unnecessary inspections and conservation works of artefacts and façades and increase monitoring points with no impact on tourist site accessibility.

Furthermore, the protective coatings should comprise the same qualities of the ones already on the market (transparent, hydrophobic, controlled or designed barrier properties, etc.) [6, 7].

The development of the coatings will start from the identification of a removable long-lasting matrix, considering *organic resins* [8] and *hybrid organic-inorganic materials* [9, 10, 11, 12]. Commercial products will also be used as a starting point.

The self-diagnostic properties of the protective coatings will be provided by the spectroscopic behaviour of selected probe molecules mixed in the coating formulations. Also in this case a dual approach is foreseen and two different typologies of additives will be considered: *IR-active additives* (absorb IR radiation) and *Photoluminescent additives* (absorb UV radiation).

2.3 Identification Marker Coating

The objective of this new coating material is to allow the possibility of marking directly the cultural heritage artefacts by means of a *fully transparent* (in the visible range) *inorganic coating*. The *millimetre size mark* will be deposited by the developed plasma torch and it will be visible only when exposed to UV light.

The inorganic nature of the coating will assure its wear resistance and unalterable behaviour. In order to obtain such coating by means of a plasma torch, a silica precursor with stably dispersed inorganic fluorophore nanoparticles [13, 14, 15] will be used in the feeding for the deposition.

The reading of the label will be easy and inexpensive: just an UV light source and a hand lens will be required!

3 Protocol Development and Testing

In the EU-PANNA project, a new technique, the *atmospheric plasma* for cleaning, removal and deposition purposes; a new *self-diagnostic long-lasting protective coating* and a new *identification marker coating* for cataloguing and authentication of artefacts will be developed. All the innovative solutions will be integrated in a *"full-life" protocol,* which starts with the conservation of the assets and goes until the complete removal of the conservation products themselves.

In order to cover all the necessary expertise, EU-PANNA proposes an important European consortium consisting of nine partners coming from four different European countries with a strong participation of small and medium enterprises (SMEs).

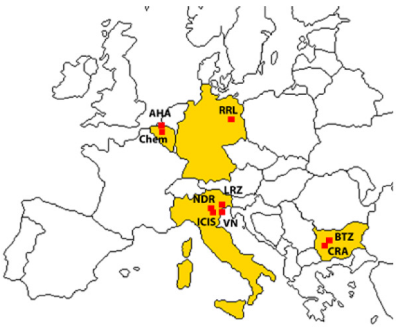

Fig. 1. PANNA consortium partners location

Table 1. Partners of the consortium involved in PANNA project

Partner	Acronym	Country	Institution Type
Veneto Nanotech scpa	VN	Italy	Research centre
CNR - Istituto di Chimica Inorganica e delle Superfici	ICIS	Italy	Research centre
Rathgen Forschunglabor – Staatliche Museen zu Berlin	RRL	Germany	Research centre
Artesis University College of Antwerp	AHA	Belgium	Research institute
Nadir srl	NDR	Italy	SME
Lorenzon Costruzioni srl	LRZ	Italy	SME
Center for Restoration of Artworks ood	CRA	Bulgaria	SME
Botega Z eood	BTZ	Bulgaria	SME
ChemStream bvba	CHEM	Belgium	SME

The consortium is well balanced and addressed to achieve the transfer of know-how from universities to the market with a strict and solid integration of knowledge among SMEs, industries and universities, favoured by the strong SME orientation. The five SMEs of the consortium are diversified and their fields of work cover all application topics considered in the project: atmospheric plasmas and related processes development (NDR), chemical coatings development and production (CHEM) and conservation interventions (CRA, LRZ, BTZ). The SMEs represent in this way technology manufacturers and conservation end-users, leading to an ideal complete chain for the aim of the project results exploitation.

The consortium is completed by four research institutions (university – AHA, conservation research laboratory – RRL and research centres – ICIS, VN).

The same project could not be run at national level, due to the unique nature of the partners, their expertise and the different conservation techniques considered. Moreover, the participation as a partner of the Rathgen Research Laboratory, part of the National Museums of Berlin, assures the possibility to have useful discussions and collaborations with museum associations and with international institutions and organizations, thanks to its contribution to ICOMOS, ICOM-CC and ICCROM.

The atmospheric plasma prototype and the new materials have to meet precise criteria according to end-product properties requirements, mainly due to the (historic) materials considered in the project and to the ethics and aesthetics of the conservation interventions. Three different end-user partners (CRA, LRZ and BTZ) supported by the research laboratories devoted to cultural heritage conservation (AHA and RRL) defined the suitable properties for each application. This work allowed a pre-evaluation of the new materials and technique design as well as planning a suitable road map for their development.

The development will be carried out by the technology manufacturers involved in the project. In particular the design, realization and testing of the plasma torch prototype will be performed by NDR in collaboration with VN. The torch prototype will be designed and developed satisfying two required configurations:

- cleaning and coating removal
- deposition of aerosol and vapour precursors

In a later stage the laboratory prototype will be transformed in a portable prototype in order to fit the needs of conservators for *in-situ* operation.

The self-diagnostic coatings will be developed in different stages throughout the project starting with the matrices design, then adding to them the ageing markers and finally developing their detection methodologies. The products development will be carried on mainly by CHEM and VN with the support of ICIS in the characterization and diagnostic development. For the diagnostic aging detection, two different solutions will be studied by VN and ICIS:

- FT-IR active additives
- Fluorescent additives

Their study will be combined with the acquisition of a portable FT-IR spectrometer (ICIS) and of a portable fluorescence detector (VN) in order to evaluate the detectability simulating *in-situ* methodologies.

The other partners will test the innovative solutions on different substrates. In order to better focalize the experimentation, each partner has been associated to a substrate: *Silver* (AHA), *Bronze* (BTZ), *Limestone* (ICIS), *Sandstone* (LRZ), *Marble* (RRL), *Wall Paintings* (CRA).

Each partner will buy (CRA, RRL, BTZ) or use (AHA, ICIS, LRZ) a different *commercial plasma torch* to carry on preliminary studies on surface cleaning and coating removal before the project prototype instrument is developed. This experimentation will supply useful information for the innovations development.

Actually the cost of such commercial devices is about 10.000-15.000 euros. The development of the prototype will take into account that the cost of the new plasma jet has to be less than 15.000 euros, in order to be competitive with existing commercial torches and to give to conservators an economically affordable device.

In a second stage the partners will apply the self-diagnostic coatings and will use the prototype plasma torch in order to evaluate their behaviour on the different substrates and suggest changes in coatings formulation or in torch design.

This cultural heritage assets testing of the innovative solutions with a feedback on their design, is fundamental for the success of the project. Therefore all the partners are active participants in the technical meetings.

The substrates used as test materials have been selected according to their susceptibility to weathering and diffusion in each country.

The efficiency of the plasma system will be tested in order to define:

1. the cleaning efficiency in removing deterioration products and aged/ineffective protective coatings without altering the substrate beneath
2. the conservation efficiency by the application of durable and compatible hydrophobic coatings.

Degradation products and protective coatings will be appropriately applied and aged in order to simulate real weathered surfaces. Artificial ageing methodologies were defined upon discussion between the partners in order to *reproduce the most relevant weathering phenomena* in the different European countries and according to European and national guidelines and norms.

The ultimate objective of this project is to provide a customized plasma jet prototype, a self-diagnostic coating and a marker identifier as described above, which have to be integrated in a demonstrator. The demonstrator will be provided with application protocols for at least one specific case for each substrate considered. The demonstrator will then be used for the dissemination of the results by participating in fairs dedicated to the sector of cultural heritage conservation and organizing training events for conservation operators.

4 Preliminary Results

From the cleaning tests, performed with the commercially available plasma torches, useful information was achieved.

The tested plasma torches, with power ranging from 8 up to 1000 W, were successful in the removal of organic dirt (e.g. soot and graffiti) and organic coatings (e.g. Paraloid B72 and Araldite) from the selected substrates.

In the case of inorganic materials, the action of the plasma is less effective. Inorganic sulphidisation products can be easily removed from silver but not from brass.

Moreover the plasma is not able to remove hydrophobic coatings with an inorganic backbone as siloxanes. In fact, after the treatment the protective loses its organic hydrophobic features, leaving the inorganic backbone coating fractured due to tensile stresses. This, even if the coating is not completely removed, allows to re-apply other transparent protective coatings on top.

These evidences were confirmed by the tests made on the new developed coatings: an organic matrix can be easily broken by plasma, but if inorganic additives are present or hybrid organic-inorganic structures are used, the coatings cannot be completely removed by the torch.

Moreover, when arc discharge plasma torches are used, the deposition of metallic particles eroded from the central electrode can be observed on the surface of the samples, together with a local surface temperature increase and some surface defects due to arcing. On the other side DBD torches seems to require too long treatment times.

The thermal effect of high power plasma torches can change the appearance of temperature sensitive substrates.

All these findings, gathered from the cleaning tests performed by conservation scientists, allow the technological companies to direct the efforts of their research in the right direction.

Starting from these results a specific plasma torch and protective coating are under development. The plasma torch will avoid central electrode and introduce improvements to standard DBD design in order to increase its efficiency. On the other side the development of specifically designed coating is showing the possibility to remove also hybrid organic-inorganic structures.

5 Expected Results

The project is expected to deliver results on three fronts.

- *Research and technology*: in the frame of the project, a true cold plasma torch will be tested, seeking the best compromise between treatment temperature and efficiency (plasma density and active species densities). The torch will also allow the deposition of nanostructured composite. Furthermore, the project will allow the creation of new smart hybrid low-cost protective coatings which will find application in different fields.
- *Cultural Heritage assets management*: the creation of a cleaning/deposition/removal combined protocol will provide conservators with a full set of tools. The protocol will be made available to the conservators in order to improve the technology of cultural heritage conservation. This will have a potentially high impact on restoration techniques by reducing conservation costs and changing the currently used techniques.

- *Advantage for business*: the collaboration between SMEs, conservation institutes and technological companies increases the opportunity of placing these new products on the market. The production of the protective coatings and the portable plasma torches will be implemented by the SME project partners.

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