Assessment of atmospheric plasma torches for cleaning of architectural surfaces

Stefano Voltolina[5]; Cristina Aibéo[1]; Tommaso Cavallin[2]; Ellen Egel[1]; Monica Favaro[2]; Veska Kamenova[3]; Luca Nodari[2]; Angel Pavlov[3]; Ivelina Pavlova[3]; Stefan Simon[1]; Paolo Scopece[4]; Emanuele Verga Falzacappa[4], Alessandro Patelli[5]

[1] Rathgen-Forschungslabor - Staatliche Museen zu Berlin, Berlin, Germany; [2] Istituto di chimica Inorganica e delle Superfici - Consiglio Nazionale delle Ricerche, Padova, Italy; [3] Center for Restoration of Artworks ood, Sofia, Bulgaria; [4] Nadir s.r.l., Padova, Italy; [5] Veneto Nanotech scpa, Venezia, Italy

1. Introduction

Cleaning of architectural surfaces is always a challenging task for restorers. Different methodologies were developed in time using mechanical methods, solvents and, more recently, laser. In a more recent time, atmospheric plasma began to be tested for such application. It represents a good alternative to abrasion methods, that often lead to the damaging of the original surface or chemical methods, which might carry the dirt/old coating deeper inside through pores, cavities or cracks. Nevertheless this technology is not used as widely as laser, due to the lack of knowledge about possible side-effects on artifacts. First applications of plasma in the field of Cultural Heritage were made for the conservation of archaeological iron artefacts [Patscheider J., 1986, 29-37] [Arnould-Pernot, P. 1994, 232-240] [Schmidt-Ott K., 2002, 81-87]. Disinfection and consolidation of paper by means of plasma was also tested [Vohrer U., 2001, 1069-1073] [L. Laguardia, 2005, 193-198]. Plasma found application also in cleaning of smoke-damaged paintings [Rutledge S.K., 2000, 65-74] and in the removal of organic coatings from the surface of paintings [Banks B.A., 1996]. Nevertheless, all these applications were carried out with vacuum plasma. Only a few cases using atmospheric plasma can be found in literature. One of the first patented atmospheric plasma devices was tested also in the removal of soot from canvas and marble [Banks B.A., 1997]. Later atmospheric plasma was used to improve the adhesion between polymer substrates and polymeric paints [Comiotto A., 2009] or in the removal of soot and organic polymers [Pflugfelder C., 2007, 516-521].

This work reports the results obtained in the frame of the EU project PANNA (Plasma And Nano for New Age soft conservation), dealing with the assessment of the atmospheric plasma torch as cleaning tool for the removal of alteration and deterioration products on stone and wall painting surfaces. The removal of gypsum and soot as well as of aged polymers and graffiti was tested on lab samples by different commercial plasma devices.

Materials and Methods

In order to establish a protocol for the use of atmospheric pressure plasma in cleaning of architectural surfaces, the first step was the selection of the test substrates and of the coating/dirt typologies to be removed.

The substrates chosen for the present study were Serena Sandstone (5x5x1

cm samples), Istria Limestone (5x5x1 cm samples), thermally aged Carrara marble (Marmo Cotto, 5x0,5 cm round samples) and wall-painting replicas (5x5x1 cm) with an egg tempera paint layer using Ultramarine Blue (Schmincke) and Yellow Ochre (Schmincke) as pigments.
The cleaning evaluation was assessed for the removal of epoxy resin Araldite AY103-1/HY 991 (Huntsman), hydrophobic siloxane SILRES BS 280 (Wacker), waterborne acrylic resin Acryl 33 (CTS), acrylic graffiti paint Deco Matt RAL 5003 (Dupli color), English Dark Red oil paint (Maestro PAN), soot, reproduced with the use of a wax candle and a mixture of gypsum, calcium carbonate and black carbon simulating the "degraded lime wash".
The commercial atmospheric plasma torches used for the tests are reported in Table 1.

Plasma Torch	Technical specifications
Kinpen by Neoplas	Dielectric barrier discharge (DBD) Afterglow temp.: 40 °C Power: 8 W Gas: compressed air Gas flow: 180 – 480 L/h
Plasmapen by PVA TePla	Arc discharge Afterglow temp.: 400 °C Power: 100 W Gas: compressed air Gas flow: 1275 L/h;
Blaster by Tigres Dr. Gerstenberg GmbH	Arc discharge Afterglow temp.: 350 °C Power: 250 W Frequency: 40 kHz Gas: compressed air Gas flow: 2400 L/h
PlasmaSpot by VITO	DBD; Afterglow temp.: 45 °C Power: 50-350 W; Frequency: 70 kHz; Gas: compressed air; Ar/O2 (98/2) Gas flow: 3000-6000 L/h

Table 1 - Commercial atmospheric plasma torches used for the experimentation and their technical specifications

For each device and each sample, the best parameters were determined in function of: power of the torch, gas, gas flux, distance between plasma nozzle and substrate and the exposure time.
Optical observation of the treated surfaces after cleaning was performed using an optical microscope Olympus BX51, using different magnifications 5x - 50x and 200x. Colorimetric measurements were made using a Minolta CM-2600d spectro-colorimeter. The results were collected in the CIE-L*a*b* system. Measurement window diameter is 4 mm and the error was estimated as 2% of the measured value. The water drop absorption rate is defined as the absorption time of a limited and definite amount of water (10 µL) by the surface of a material. It was determined according to the standard RILEM II.8 a. The error on the measurements was estimated as 60 s. The static contact angle, θ, between a water drop and the test surface of a specimen was me-

asured according to the norm DIN EN 15802 (2010). The error on the fitting procedure was estimated as 0.5% of the obtained value. FT-IR spectra were collected in total reflection mode by using a transportable FT-IR spectrometer ALPHA-R/BC from Bruker. When necessary a Nicolet microscope connected to a Nicolet 560 FT-IR system, equipped with a Mercury Cadmium Telluride (MCT) detector, has been used for spectra collection. With this instrument, the measured areas were about 150 μm2. IR spectra were recorded in the ATR mode in the 4000–650 cm−1 range, with 4 cm−1 in resolution. Morphological–compositional analyses were performed by using FEG-ESEM and an energy dispersive microprobe system (FEG-ESEM-EDS; FEI Quanta 200F). Samples were analyzed using an accelerating voltage of 20 kV in low vacuum condition, without any conductive coating.

3. Results and discussion

3.1. Effects of plasma on the substrates

To understand the effect of the torches on the substrates a preliminary set of experiments was performed on reference stone and wall paintings samples.
No macroscopic changes were observed in the properties of the different stone substrates. Only a minor darkening of the surfaces was observed for prolonged exposure times working with arc-discharge torches. This darkening effect has been correlated with deposition of metallic particles sputtered from the central electrode and from the nozzle of these torches.
In the case of wall painting replicas the same deposition was observed. Moreover, when the more powerful torches were used, a change in colour of the ochre pigment from yellow to red was observed. This is due to the temperature increase on the surface of the samples during the treatment, which causes the transformation of the yellow Goethite (FeOOH) to red Hematite (Fe_2O_3). Using the low-power Kinpen (Neoplas) device, no colour changes were observed even for long exposure times (up to 1 hour).

3.2. Removal of soot

Removal of soot from wall painting replicas was successful with all the tested torches.

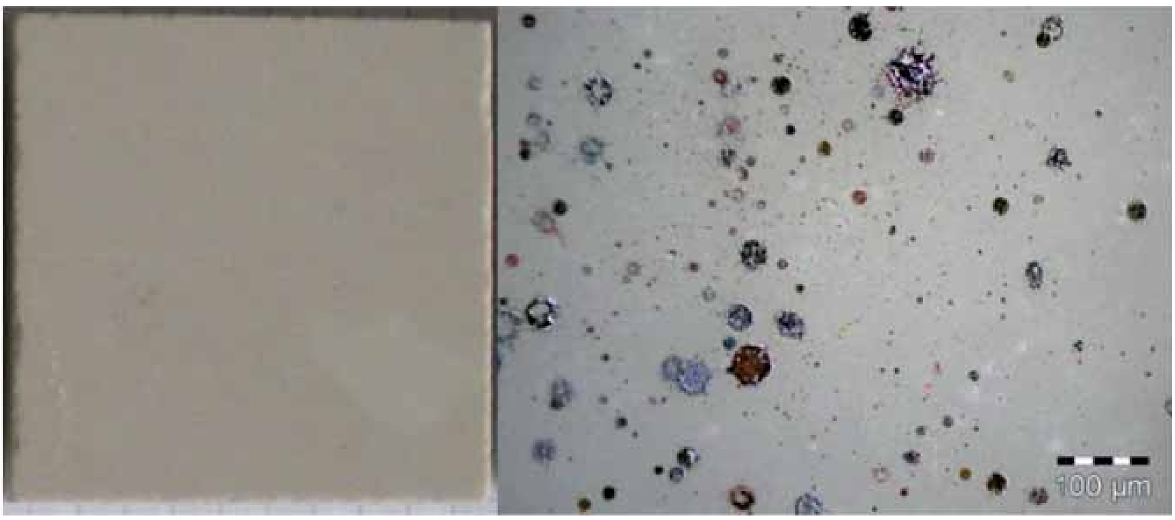

Fig.1 - Picture of Istria Limestone after the plasma treatment with Blaster from Tigres Dr Gerstenberg GmbH (left) and optical microscopy image of the surface after a treatment of 600 sec. with the same equipment (right)

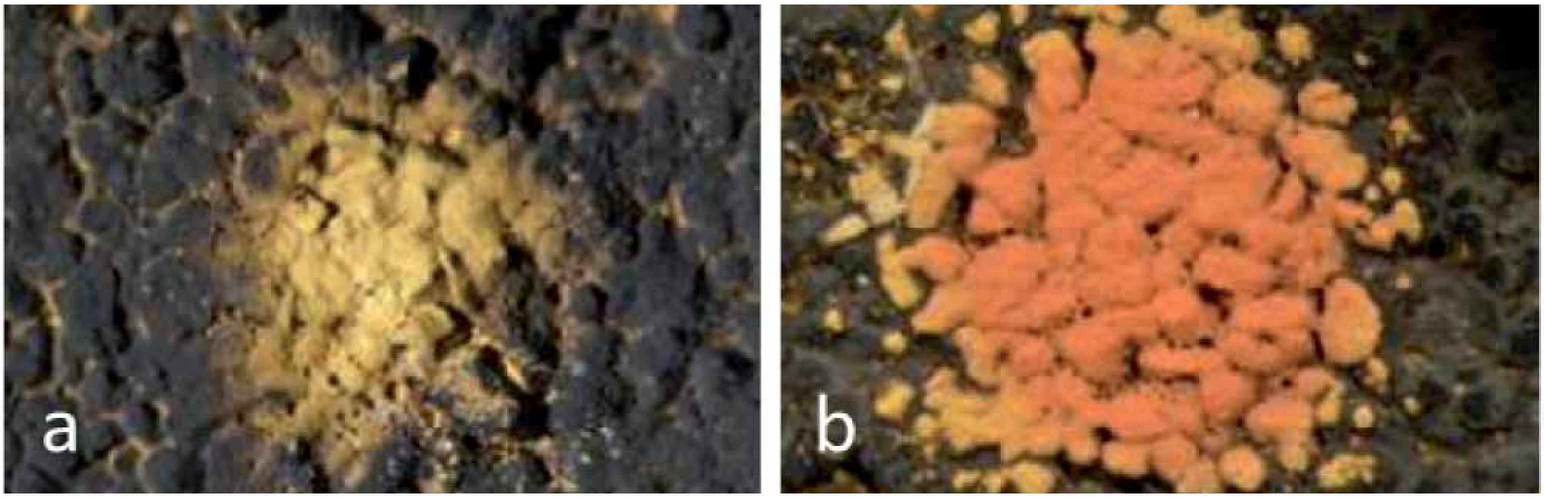

Fig.2 - Microscope images (magnification 7x) of the soot removal with a) Kinpen (20 minutes) and b) PlasmaPen (40 seconds). The colour change using PlasmaPen is clearly visible

With the low-power Kinpen (Neoplas) torch it was possible to remove soot only after long exposure times (approx. 20 minutes for a spot of 0.5 cm diameter). Using this torch no damages of the underneath pictorial layer nor colour change of the ochre pigment were observed.
With the two arc-discharge torches, PlasmaPen (PVA-TePla) and Blaster (Tigres), the soot removal took place at very short exposure times (approx. 30 seconds for a spot of 0.8 cm diameter) but a change in colour of the temperature sensitive ochre pigment was observed.

3.3. Removal of oil paint over-paintings

None of the tested torches could remove the oil paint over-painting layer directly. The oil paint was only partially removed by brushing after preliminary plasma treatment. Infrared analyses showed that plasma removes the organic binder from the oil paint layer, thus the residuals can be wiped off the surface.

3.4. Removal of degraded lime wash

In the case of layers composed by gypsum, calcium carbonate and black carbon, Kinpen (Neoplas) seemed to be not enough powerful to give visual results in the timescale of minutes. Only Blaster (Tigres) and PlasmaPen (PVA-TePla) have shown some results with whitening of the treated areas, due to the oxidation of the black carbon particles. For all the tested torches, removal of the inorganic part was not achieved. Moreover Infrared measurements performed on the surfaces treated with PlasmaPen (PVA-TePla) and Blaster (Tigres) showed that gypsum was converted to hemihydrate gypsum. The temperature of conversion from $CaSO_4 \cdot 2H_2O$ to $CaSO_4 \cdot 1/2H_2O$ is 128 °C.

3.5. Removal of epoxy resin

Plasmaspot (VITO) and Kinpen (Neoplas) did not affect the surface of the Araldite AY103-1/HY 991 (Huntsman) coatings even after prolonged exposure times (20 minutes). Using Blaster (Tigres) and PlasmaPen (PVA-Tepla) degradation (browning) of the coating was observed at first and subsequently the removal of the resin was achieved after some minutes of treatment.

3.6. Removal of waterborne acrylic coating

After the treatment with Kinpen (Neoplas) and Plasmaspot (VITO), the coated stone showed a slight opacification but no removal was achieved, as underlined by the subsequent Infrared analyses. Concerning PlasmaPen (PVA-TePla) and Blaster (Tigres), exceeding the exposure time of 30 seconds, an increase in temperature above the glass transition temperature of the polymer with its softening were observed. When the exposure time was further increased, degradation of the polymer started to become evident. Complete removal was not achieved: the softened polymer was blown away from the center of the treated area by the gas flux and penetrated in the pores of the stones.

3.7. Removal of graffiti paint

The power of Kinpen (Neoplas) is too low for a viable cleaning. A partial removal of the blue graffiti paint was possible: after 10 minutes a white spot of 7 mm could be observed. Nevertheless the paint layer was only partially removed: plasma was able to remove the polymeric component of the paint while the TiO2 particles used as filler in the paint are not affected by the action of plasma. They can be easily wiped off the surface with a tissue revealing the unaffected paint layer beneath.
The same behavior was observed also for Blaster (Tigres) and PlasmaPen (PVA-TePla) torches even if the treatment times necessary for the complete removal of the graffiti paint were in the range of seconds.

3.8. Removal of hydrophobic siloxane

In this case all the tested torches showed similar results. Plasma was able to decrease the hydrophobicity imparted to the stones by SILRES BS 280 (Wacker) but none of the tested torches could remove the siloxane even at long exposure times (more than 20 minutes). Infrared analyses on the treated areas showed that plasma removed the alkyl side chains (which imparted hydrophobicity) while the siloxane backbone of the coating is not affected by the action of plasma.

Conclusions

Commercial plasma torches were used to assess their efficacy as cleaning tools on different substrates and for different kind of dirt. Obtained results showed their potential as cleaning devices, especially for the removal of aged or deteriorated organic materials.
The main drawback encountered using commercial plasma torches, was the deposition of metallic particles from the ones working in arc-discharge configuration.
Although the most satisfactory results were achieved using arc-discharge torches, they are not suitable for cleaning cultural heritage objects, due to the problem of metal deposition. Moreover the better performances of these torches depends also upon the raise in temperature of the samples.
DBD torches don’t have the same performances as the arc discharge ones. Nevertheless, for long exposure times, satisfactory results of removal can be achieved without temperature increase and other detrimental effects on the

surfaces.
The conception of a DBD plasma torch, specially designed for cultural heritage purposes is therefore necessary.
The work performed in the first year of EU-PANNA project allowed to highlight main advantages and drawbacks in the use of commercially available plasma torches for cleaning purposes on cultural heritage materials. A novel plasma torch design has been developed avoiding the major drawback of metal deposition and keeping the balance between viable cleaning times and preservation of surfaces.

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Abstract
The use of plasma in the field of cultural heritage has been firstly applied for the conservation of archaeological iron artefacts and silver objects, for disinfection and consolidation of paper and more recently for conservation of polymers in modern art and cleaning of architectural surfaces. Notwithstanding these first applications, the plasma

is not a common element in conservation practices.
This work reports the results obtained in the frame of the EU project PANNA (Plasma And Nano for New Age soft conservation) dealing with the assessment of atmospheric plasma torches as cleaning tool for the removal of alteration and deterioration products on stone and wall painting surfaces. The removal of gypsum and soot as well as of aged polymers and graffiti was tested on lab samples and on real objects by different commercial plasma devices.
Among the positive features of plasma are the facts that the cleaning is contactless, precisely controlled due to the reduced diameter of the plasma plume and confined to the very first layers of the surface. Therefore it avoids undesired effects often encountered with traditional chemical cleaning, such as spreading or retention of solvents and undesired products inside the porous structure of the substrate.
It has been observed that the chemical effect of plasma is confined to nanoscale while the associated thermal effect is able to penetrate more in depth.
Regarding the chemical effect of plasma cleaning, the interaction of plasma is strongly dependent on the nature of the treated material. Oxidative plasmas are effective in the degradation of organic molecules or macromolecules while inorganic structures, like the siloxan (Si-O-Si) bonds in silicones or silicates and sulphate groups in gypsum, are more stable and reluctant to chemically interact with plasma.
The thermal effects induced by plasma on the samples can be controlled by choosing the appropriate parameters (power; gas; distance; etc.). Nevertheless, in the choice of the right parameters it has to be taken into account that while some substances, such as stone, are quite resistant to elevated temperature, others, such as oil paint retouches in wall paintings, might degrade and become more difficult to remove.
The main drawback encountered by using commercial plasma torches, was the deposition of metallic particles from the torch while using it in oxidative mode. This happens when the gas has to be ignited with an arc discharge with a central electrode, which is the case of all torches operating with compressed air.
Obtained results reported in this work will show in detail the described potentials and drawbacks of the commercial plasma devices as cleaning tool and set up the technological and functional requirements for the development of an innovative plasma device which could overcome the limits of current available instruments for their successful application in the field of conservation of cultural heritage.