PRELIMINARY ASSESSMENT OF ATMOSPHERIC PLASMA TORCHES FOR CLEANING OF ARCHITECTURAL SURFACES.

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ABSTRACT

This work reports the results obtained in the frame of the EU-funded project PANNA (Plasma And Nano for New Age soft conservation). In this project the use of an atmospheric plasma torch for cleaning alteration and deterioration products on stone and wall paintings is assessed. The removal of gypsum and soot as well as of fresh/aged polymers and graffiti by different commercial plasma devices was tested.

Plasma cleaning is a contactless method which can be precisely controlled by reducing the diameter of the plasma plume. Furthermore, the cleaning process is restricted 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 by-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 involves a greater volume of the treated area. Both effects will be described in detail regarding the different substrates and materials to be removed.

The main drawback encountered in using most of the commercial plasma torches, was the deposition of metallic particles from the torch while using it in oxidative mode. This happens when the gas is ignited using an arc discharge with a central electrode.

The results obtained will show the described potentials and drawbacks of the commercial plasma devices as cleaning tools and set up the technological and functional requirements for the development of an innovative plasma device, which could overcome the limits of the current available instruments for their successful application in the field of conservation of cultural heritage.

Keywords

Atmospheric plasma, Cleaning, Graffiti, Acrylics, Epoxy resin, soot, stone, wall paintings, PANNA project

1. Introduction

The use of plasma in the field of cultural heritage has been firstly applied for the conservation of metals, particularly for the treatment of archaeological iron artefacts and silver objects [1] [2] [3] [4]. Plasma treatment permits the removal of chlorides, facilitates a subsequent mechanical cleaning of archaeological objects and is able to reduce silver sulphide corrosion layers. The treatment of microbial infested paper by means of plasma for disinfection and consolidation purposes is also a subject of interest [5]. Nevertheless, all these applications were carried out under vacuum conditions. Only a few cases using an atmospheric plasma could be found in literature: for example the activation of polymeric surfaces in modern art in order to enhance the adhesion between a non-polar polymer substrate and a polar paint [6] or the removal of soot and synthetic/natural organic polymers used as consolidants [7].

The EU-PANNA Project focuses on the establishment of a conservation methodology for cultural heritage assets using atmospheric plasma. This includes the cleaning of a diverse range of materials, the application of a new reversible protective hydrophobic coating and its removal after ageing. Plasma is used for the cleaning step as well as for the application of the coating. The obtained results reported in this work will show the potentials and drawbacks of commercial plasma devices as cleaning tools for the removal of soot, graffiti paint, oil paint, black crust and aged protective polymers from architectural surfaces. The set-up of technological and functional requirements for the development of a Cultural Heritage dedicated innovative atmospheric plasma device were also reported. A prototype which could overcome the limits of current available instruments has been developed and its removal effectiveness is currently under evaluation.

2. Materials and Methods

For the assessment of a cleaning methodology by means of atmospheric plasma, several stone substrates and wall-painting replicas were chosen together with the "dirt" typologies to be applied on them.

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We focused our attention on Serena sandstone (5×5×1 cm), Istria limestone (5×5×1 cm), thermally aged Carrara marble (Marmo cotto, 5×0.5 cm) and wall painting replicas (5×5×1 cm) with an egg tempera paint layer using Ultramarine Blue (Schmincke) and Yellow Ochre (Schmincke) as pigments. Yellow ochre is very sensitive to heating since it dehydrates and turns to brown Fe_2O_3. The experimentation concerns the test of 4 different commercial plasma devices on different stone substrates, treated with epoxy resin, siloxane coating, acrylic protective, graffiti paint and black crust on stone and oil over-paint on wall paintings. The cleaning evaluation was assessed for the removal of fresh/aged epoxy resin Araldite® AY 103-1/ HY 991 Huntsman, of fresh SILRES® BS 280 (siloxane), a water emulsion of an acrylic copolymer: Acryl 33 from the company CTS and English Dark Red oil paint from Maestro PAN, as reported in table 1. Photo-oxidative ageing of coatings was performed according to the Italian standard UNI 10925:2001 [8]. Moreover, blue graffiti paint Deco Matt RAL 5003 from Dupli color (acrylic binder: butyl methacrylate-co-methyl methacrylate (BMA/MMA), a mixture of gypsum, calcium carbonate and black carbon simulating the "degraded lime wash" and soot, reproduced with the use of a wax candle, were used in order to simulate anthropogenic and natural alterations, as reported in table 1.

Table 1: Lithic substrate and applied coating

Substrate	Coating
Serena Sandstone	Waterborne Acrylic Coating Black Crust
Istria Limestone	Epoxy Resin Graffiti Paint
Carrara Marble (Marmo Cotto)	Siloxane Coating Graffiti Paint
Wall Paintings	Soot Oil over-paint on egg tempera

The commercial plasma apparatuses used for the experimentations are reported in table 2.

Table 2: Commercial Torches and working conditions used to test the effect of the devices on Istria substrate and the removability of epoxy resin and graffiti dirt.

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 from 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

After preliminary trials performed by varying the working distance and, where possible, the power, it was decided to perform cleaning tests with a fixed working distance of 1 cm for Plasma Blaster (Tigres), 0.1-0.2 cm for Neoplas and 0.5 cm for PVA Tepla (standard tip) and PlasmaSpot (VITO) and increasing the exposure time.

Optical observation of the stone surface 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 [9]. 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 measured according to the norm DIN EN 15802 (2010) [10]. 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 μm^2. 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. Data analysis and discussion

To understand the effect of the torches on the stone substrate a preliminary set of experiments was performed on untreated (hereafter reference) stones specimens, and then the removal of the different coating/dirt was investigated.

3.1 Results achieved on plasma treatment of reference stone and wall paintings

The experiments performed on the reference specimens showed that the macroscopic properties are slightly affected by the cleaning procedure. It is interesting to point out that sandstone, limestone and marble present the same modifications after the plasma treatment. The largest modifications are induced by Blaster from Tigres Dr. Gerstenberg GmbH and Plasmapen by PVA TePla. The results obtained on Istria limestone can be considered as representative of all the not treated stones under study. For the sake of brevity, therefore, only the Istria stone surface is discussed. Considering the variation in CieL*a*b* coordinates, only a minor darkening is evident when the exposure time is prolonged up to 300 s. This darkening effect has been correlated with deposition of metallic residues from the torch electrode and of carbon particles. This deposition seems to modify the surface properties of the sample, as underlined by the increase in water micro-drop absorption time and contact angle. No effect was observed on samples treated with the PlasmaSpot torch as demonstrated by measurements of water drop absorption that gave similar results both on untreated and treated samples.

As for stone, even on wall painting replicas, the deposition of metallic particles after the torch treatment was observed, Moreover, when the more powerful torches are 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. Using the low-power Neoplas/Kinpen device, no colour changes were observed even for long exposure times (up to 1 hour).

3.2 Results achieved on plasma removal of black gypsum layer and soot

3.2.1 Black gypsum layer

The trials on the removal of inorganic dirt from the Serena sandstone surface were unsuccessful, as the only observable effect was the whitening of the black layer due to the oxidation of the carbon black particles. IR measurements performed on the surfaces treated with the more powerful torches actually showed that the gypsum converts to emi-hydrate gypsum, thus confirming that the surface temperature reached during plasma treatment rises above 128°C, the temperature of conversion from $CaSO_4{\cdot}2H_2O$ to $CaSO_4{\cdot}1/2H_2O$.

3.2.2 Soot

The Kinpen was able to remove soot only after long exposure times (20 min) and from minimal working distance (0,1 cm) with diameter of the cleaned spot of 0,5 cm. It did not damage the pictorial layer nor impact the pigment's colour, but proved to be very inefficient for this application.

In comparison, the PlasmaPen removed the soot at very short exposure times (3 s) and distances of up to 0,8 cm, though it changes yellow ochre ($Fe_2O_3{\cdot}nH_2O$) into red ochre (Fe_2O_3) when used with compressed air. By using pure oxygen for the treatment, change in colour of the ochre pigment was not observed. The Plasmablaster's performance is comparable to that of the PlasmaPen.

The PlasmaSpot used with Ar/O_2 2vol% could also remove the soot successfully, but it damaged the pictorial layer. When used with compressed air, no effect was observed.

Both arc discharge torches deposit metallic particles on the surface. This deposition only becomes visible after long exposure times and in spot treatment mode. Increasing the treatment time or decreasing the distance makes the cleaning more effective. Long exposure times tend to impact the pigments' colours.

3.3 Results achieved on plasma removal of protective organic coatings

The success in removing acryl 33 from sandstone surface is strongly dependent on the torch used. For example, DBD apparatus did not promote any removal, even for prolonged exposure time. After the plasma treatment with the Kinpen or Plasmaspot, the coated stone surface shows a slight opacification, underlined by a small variation in L* value. This opacification could be considered only as a "visual" effect. In fact, the subsequent surface analyses (water micro-drop absorption, contact angle and FT-IR) have shown that acrylic coating was not removed or modified by plasma plume. The experiment using an arc discharge apparatus showed different results. With the PVA Tepla torch, the experiments showed that removal is not homogeneous. Exceeding the exposure time of 30s, a softening of the polymeric coating is observed. This phenomenon can be connected with the increment in temperature, due to the thermal effect of the plasma. An exposure higher than 30s involves an increase in temperature over the glass transition temperature of the polymer. When the exposure time is further increased, the degradation of the polymers starts to become evident. The effect on the CieL*a*b* coordinates is a shift of a* and b* towards high values, probably due to the burning of the coating. The physical properties of the surface change with increased exposure: water absorption decreases and eventually comes close to the water absorption rate of non-treated sandstone. A similar trend is observed in the contact angle measurements. Analogous results were obtained by using the Blaster from Tigres Dr. Gerstenberg GmbH.

As for the removal of epoxy coating, tests were performed by increasing the exposure time, i.e. Complete removal was assumed achieved when the physical properties of the surface were close to those of the non-treated stone surface. In general the Plasmaspot and Kinpen did not affect the surface at all, not even after prolonged exposure time (1380s), whilst the devices from PVA TePla and Tigres Dr. Gerstenberg GmbH were both successful in removing both fresh and aged epoxy coatings. The deposition of the metallic particles was also observed during the removal of epoxy resin. In fact, optical microscopy and SEM observations showed the presence of small metal particles in the specimens. The amount of these particles and their composition vary depending on the torch used, i.e. a higher number of particles were identified when using the Plasma Blaster and PVA Tepla rather than when using the Neoplas. Furthermore, the Plasma Blaster removes the coating faster than the PVA Tepla, while the Neoplas barely affects the coating surface.

Plasma was able to decrease hydrophobicity imparted by the siloxane coating, but not the coating itself. The best results were achieved by using the PVA TePla and Tigres Dr. Gerstenberg GmbH. Infrared spectroscopy revealed that the modification induced by plasma are connected with the oxidation of the alkyl side chains and not with the breaking of the inorganic polymer skeleton. Due to plasma treatments, the surface of the coated stone becomes therefore less hydrophobic, which can be confirmed by a decrease in the contact angle.

3.4 Results achieved on plasma cleaning of graffiti and oil paint

3.4.1Graffiti paint

In general atmospheric plasma, generated by arc discharge, was able to remove graffiti dirt from marble and Istria limestone substrates. As underlined by FT-IR analyses, the polymeric component of the graffiti is successfully removed. The experimentation on Istria limestone has shown that the exposure time necessary to remove the paint was higher than 30 sec for the Tigres and higher than 5 sec. for the Tepla when the working distance was 1 cm.

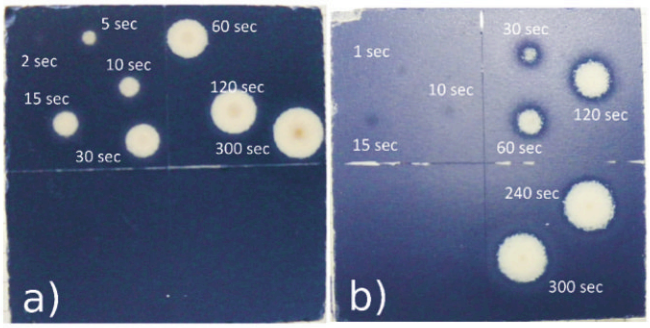

Figure 1 Samples of Istria limestone with graffiti treated with plasma - a) sample 02-058-36 (PVA Tepla); b) 02-019-31 (Plasma Blaster).

After the cleaning procedure, both contact angle and water absorption reached values close to those of reference stone. The device from PVA TePla and Tigres Dr. Gerstenberg GmbH also works successfully on Carrara marble.

In the treatment of thick Graffiti paint layers, it was noticed that the plasma cleaning leads to initial discolouration of the paint revealing the TiO_2 particles used as a filler. These inorganic particles have to be wiped away by means of a dry tissue.

In general, during the treatment, if an inorganic material is present, its removal by wiping off is necessary, otherwise the inorganic particles act as a shield against the action of plasma protecting the paint layers underneath. The best results were achieved using a combination of acetone followed by plasma. Acetone removes most of the graffiti and plasma is able to remove almost all of the residual particles, even in the pores.

Results with the both commercial DBD systems tested: viable cleaning was not possible using the low-power Kinpen device from Neoplas and the PlasmaSpot from VITO.

3.4.2 Oil Paint

Neither the Kinpen (at long exposures and narrow distances) nor the PlasmaSpot (used with compressed air and Ar/O_2 2%) could remove oil-paint. The Plasmablaster and the PlasmaPen had no direct effect on the oil-paint layer either. The oil-paint was only partially removed by brushing after preliminary plasma treatment. This, however, caused mechanical damage to the under surface.

The combined plasma + chemical treatment, even though more effective than plasma, damaged the pictorial layer. The preliminary plasma treatment does not enhance the action of the solvent.

4. Conclusion

The main drawback encountered using commercial plasma torches, was the deposition of metallic particles from the torch when using it in oxidative mode.

More than satisfactory results were achieved using arc discharge torches, but since these lead to metallic deposition, they are not suitable for cultural heritage objects. DBD systems are therefore necessary. However, the DBD torches do not have the same performance as the arc discharge torches. Therefore, a torch that combines the advantages of both torches would be desirable.

The conception of a DBD plasma torch, specially designed for cultural heritage purposes is therefore necessary.

The work performed in this first stage of EU-PANNA project highlighted the 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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