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A customised atmospheric pressure plasma jet for conservation requirements

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Abstract. In the last years atmospheric plasma has gained an increasing interest in the field of Cultural Heritage. Isolated experimentations that yet generated interesting results have drawn the attention of a wider community working on coating removal, oxide reduction and sterilization applications. Thanks to this growing multidisciplinary interest, the EU funded in 2011 the PANNA project, which includes the atmospheric plasma as a novel cleaning tool for cultural heritage. Plasma cleaning has some advantages compared to standard techniques because it avoids the use of solvents, it is contactless and differently from laser it works through a surface chemical action and not with mechanical shock or local heating. Moreover, atmospheric plasma has already shown good results in reducing mode for the conversion of corroded metal surface layers and in oxidation mode for biological cleaning and organic layer removal.

In order to fulfil the Cultural Heritage requirements a novel plasma torch has been developed with a new design which allows to overcome the actual limits of commercial atmospheric plasma devices. The new device permits fast and effective treatments at temperatures lower than 50 °C, even at room temperature, without any electrode material deposition. These performances will be presented in relation to the removal of epoxy coatings and daguerreotype cleaning as examples.

1. Introduction

1.1. *The novel atmospheric plasma jet*

Plasma processes have drawn the attention of cultural heritage restoration since the 80s, mainly because of their low temperature. Since his first article on the topic Daniels [1] identified the potential applications for plasmas: when the gases used are argon and oxygen, organic compounds can be removed from many substrates, while argon-hydrogen mixtures can be used in our apparatus to reduce several corrosion products back to their respective metals. Starting from this intuition, different experiments have been carried out by means of vacuum plasmas during the 80s and 90s. Daniels' preliminary work inspired other scientists to investigate this topic. Daniels tested the removal of some organic coatings in argon-oxygen plasma at a rate in the range of few micrometers per hour, while on metals only lead, copper and silver showed surface oxidation. On the other side argon-hydrogen plasma led to lead oxides and carbonates conversion to sub-oxides and to silver reduction. Silver reduction was identified as the more



efficient process, in particular when corrosion is confined in a thin surface layer. For this reason the more striking results can be observed on daguerreotypes [2]. The use of reducing plasmas has been tested also on archaeological artefacts in order to remove the corrosion layer [3,4]. For iron artefacts reduction plasma treatment at temperatures higher than 300 °C are needed for chlorides and oxides conversion after a preliminary mechanical cleaning [5]. These protocols are now in use for example at the Swiss National Museum. This protocol however shows the drawback of a potential surface cracking due to volume reduction from oxide to metal and potential phase transformations. Papadopoulou [6] tested the reduction process at lower temperature on bronze archaeological artefacts verifying that chlorides still remain on the surface. Therefore, the stabilization of objects with extensive Cl attack is not feasible without preliminary chemical treatment. The plasma vacuum processes offer also the possibility to deposit at room temperature protective layers such as silica and to improve their resistance to oxidation [7].

Vacuum plasma has been tested also on organic media such as photographs for oxides or sulfides removal or the etching of dust and greasy substances [8]. Soot has been also successfully removed on gesso, paint and paper [9]. On paper substrates these treatments can affect cellulose, therefore oxygen and hydrogen plasma effects have been widely tested for decontamination purposes [10,11]. Since plasma treatments seem not to de-polymerise cellulose, consolidation processes have also been evaluated through the deposition of a thin super-hydrophobic siloxane coating [12] or a polymethylmethacrylate plasma polymer film [13]. Despite the interesting results obtained by vacuum plasmas, their application is still limited because of some intrinsic technological features: the size of the treated artefacts is limited to the vacuum chamber, the whole surface must be treated and it is expensive, but the most important limit is that it cannot be continuously controlled by the restorers in-situ.

The atmospheric plasma technology allows to remove all these barriers to plasma processes. Its first application has been the improvement of surface wettability. Documented successful case studies are the activation of polypropylene wall tapestries for a following coating [14] or of paper surfaces for a following chitosan [15] or $\text{Ca}(\text{OH})_2$ nanoparticles [16] treatment. The use of atmospheric plasma treatments has been suggested for fungal decontamination on wood [17] or for varnish removal [18,19]. The efficiency of these processes is however still challenging because it leads to low organic coatings removal rate. At the same time, the use of more efficient plasma such as the arc torch devices could lead to high temperatures on the substrates and to the deposition of particles eroded by the electrodes [20].

An easier and faster application is represented by the silver surface cleaning by the atmospheric plasma in reduction mode, therefore using noble gas and hydrogen mixtures, which shows the most impressive results on daguerreotypes. The daguerreotype is the first example of photographic product that, around year 1850, reached a worldwide circulation. Each daguerreotype constitute an unique image which cannot be reproduced. The image is formed by silver-mercury amalgam particles produced by photosensitization and following development of a plate made of copper and silver, sensitized with silver iodide and developed with mercury vapours and eventually stabilized by gilding. Resulting artefact is particularly fragile and, if in contact with the environmental atmosphere, can be easily oxidized leading to the formation of silver oxides and silver sulphides. Typical cleaning techniques include the use of chemical reagents, of electrochemical processes or laser equipments [1,21,22]. However, such techniques present several drawbacks: they can leave residues which disfigure the image (chemical methods), require the use of electrolyte solutions (electrochemical methods) or may cause the partial removal of the outermost layer of the surface of the daguerreotype (laser methods). The atmospheric plasma jets can offer an interesting alternative as can be seen by results are already available in literature [23,24]. On silver alloys the effects are more complicated since they involve also the corrosion processes but some results in remote conditions have already

highlighted the potentialities of atmospheric plasma [25,26].

The use of atmospheric plasma is still a promising topic for Cultural Heritage applications but it needs a deeper experimentation through case studies in order to fully validate the technique, understand its effects and define protocols. However, in order to achieve this investigation stage the right tool must be available for the CH community. The plasma device needed for CH has specific requirements that standard commercial torches available on the market do not meet. In general, high efficiency torches like arc devices show the drawback of high temperatures and deposition of particles derived by electrodes erosion. On the other hand, dielectric barrier discharge (DBD) devices are developed for use on humans and are not efficient. Here we present an atmospheric plasma jet that has been developed following all the requirements of the CH field: it is applicable to any surface, including those temperature sensitive ($T < 50\text{ }^{\circ}\text{C}$); it does not generate electrodes deposition on the substrate; removal rate and cleaning costs are compatible with restoration works; it is suitable for localized treatment, it can be stopped at any time by the restorer and it is suitable for in-situ operation (portability).

The performances of this novel device are then shown in the two main applications: the organic layers removal in oxidizing atmosphere and the daguerreotype cleaning in the reducing atmosphere.

2. Experimental

2.1. *The novel atmospheric plasma jet*

The patented atmospheric pressure device [27] is a DBD plasma jet where no electrodes are in direct contact with plasma (Fig. 1). This configuration with electrodes hidden from plasma ensures clean processes with no undesired deposition since they can not be eroded. The electrodes are positioned externally and coaxially to an alumina tube where argon is fluxed and plasma is ignited. Two other ducts are present: an inner duct for precursors inlet in the vapour or aerosol phase and an outer duct for atmosphere control at the exit of the torch, where air or nitrogen are generally used. The main feature that characterizes the device is the use of a double couple of electrodes: a first upstream couple powered with an high voltage (HV) supply in the kilohertz regime ($\sim 17\text{kHz}$) and a downstream couple in radio frequency (RF) at about 27MHz.

The choice to work with argon noble gas, which avoids energy thermalization by molecular roto-vibrational motion and by dissociation/recombination reactions, allows to keep the temperatures of plasma as low as possible. The use of helium is not considered due to its cost. Furthermore, the RF regime with its fast oscillations avoids the formation of high current carrying streamers and enhances the generation of plasma in the volume and not on the surfaces leading to a more glow regime. The RF choice therefore goes further in the direction of reducing the thermal load on the treated surface without losing in plasma density. This is also the main design of different plasma jets used for human body applications [28]. The general drawback of this design is its ignition and stability in atmospheres when reactive species are added to the plasma. The upstream couple of electrodes solves this problem assuring ignition and stability also when high voltages are needed, without the need to increase the RF power. Basically the configuration allows to decouple plasma needs: the HV controls ignition and stability with low power, while the RF allows the control of plasma density. The coupling in fact is not just the overlapping of two different plasmas but they also interact with each other. The major effect is that the streamers created by the HV electrodes are blown up by the RF field that rapidly changes the polarity. As a consequence, if hundreds of mA streamers can be measured on a conductive substrate if HV is switched on when both power supplies are active, only a small current bumps of few tens of mA can be measured (Fig. 2b). Streamers that are current carrying channels are warmer because of their high charged species densities and fields gradients. The new design allows to avoid their propagation on treated surfaces reducing local heating. The

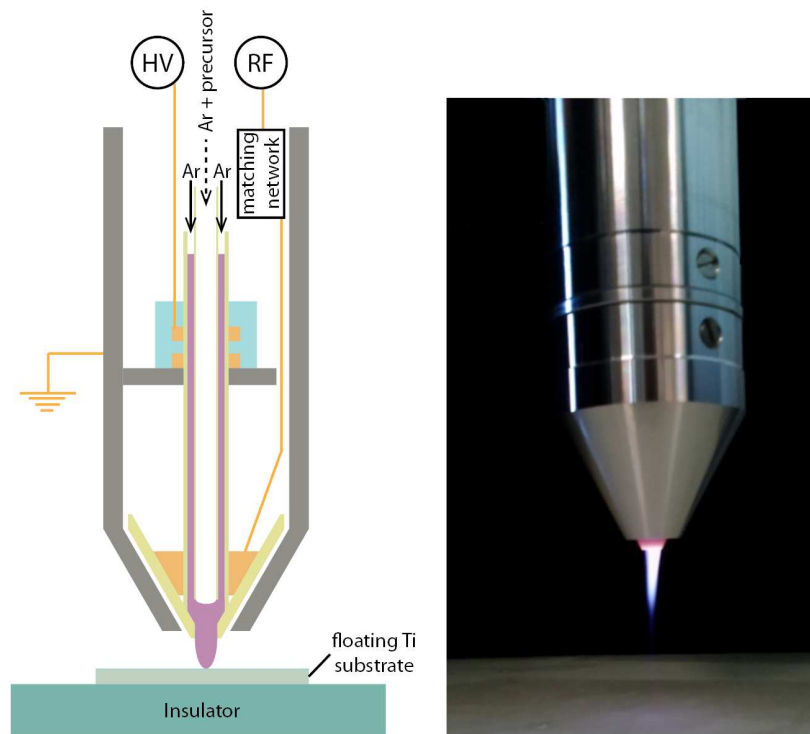


Figure 1. Scheme of the novel atmospheric plasma jet characterized by its three coaxial gas ducts and the double couple of electrodes RF and HV (on the left). On the right a photograph (time averaged) of the device.

low temperature of the novel jet design can be observed in Fig. 2a presenting a thermographic camera image after 5 minutes of treatment on a plastic substrate at 15W of RF power with argon as process gas. The image clearly shows that plasma has no emissions in the infra-red spectral region since it is not thermal. On the substrate the mirrored image of the jet can be observed.

2.2. Experimental conditions for the organic removal

An Istria limestone substrate sample was prepared by polishing and an epoxy coating (Araldite®) was applied on the surface [20]. The coating underwent photo-oxidative artificial aging according to the Italian standard UNI 10925. Photo-oxidation was carried out with a SolarBox 1500e apparatus (COFOMEGR, Milano I), equipped with a xenon light source filtered for $\lambda=295$ nm. Irradiation was kept at a constant power of 550 W/m^2 during the lamp operating life. The maximum temperature of the samples, during irradiation, was $45 \text{ }^\circ\text{C}$. Total exposure was fixed at 2000 MJ/m^2 (corresponding to 1000 h of exposure).

For the epoxy removal the plasma device has been used in oxidizing atmosphere with a mixture of Ar and O_2 at the 0.008% at a flux of 10 l/min. RF power was kept at 20 W and the HV at 8 W. Working distance was 3 mm, while in the outer duct there is fluxed compressed air. The treatment was performed in punctual mode without moving the jet on the surface as a function of the time. The results are characterized by optical imaging, FT-ATR spectroscopy (Perkin Elmer Spectrum One) and profilometry.

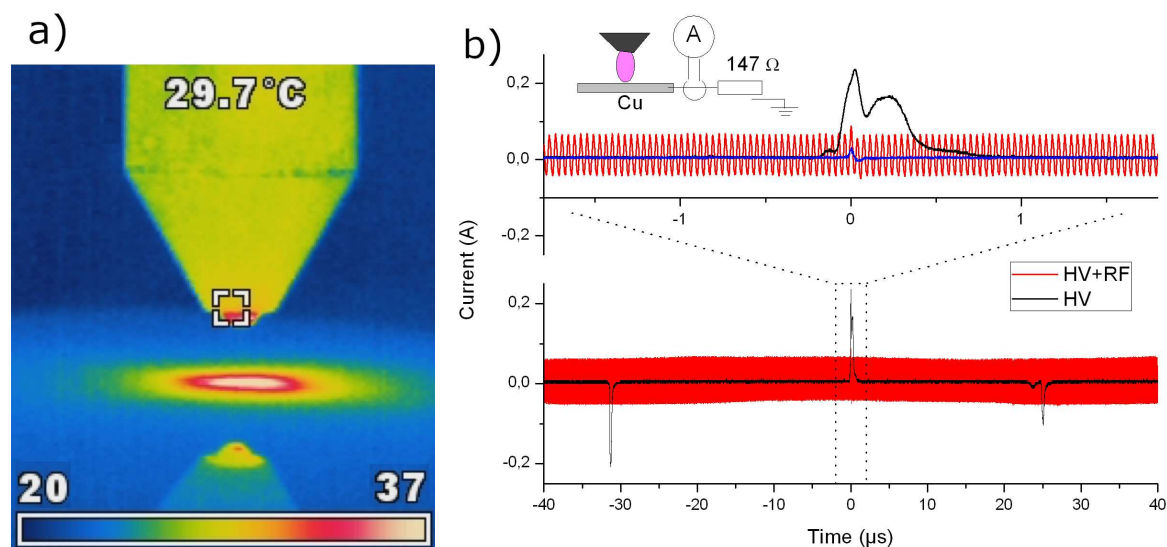


Figure 2. a) Image obtained with a thermographic camera of the plasma device on a plastic substrate in stationary conditions (after 5 minutes). b) Electrical characterization on a substrate of the coupling of the HV and RF plasmas.

2.3. Experimental conditions for the daguerreotype cleaning

The studied daguerreotype (6.7×4.8 mm) can be presumably dated around 1850–1860 and was provided by an American collector. According to the American style for daguerreotypes production, it was kept in a leather case, with a brass preserver and brass mat with an oval window, everything covered by a glass plate. Before treatment, the case was carefully dismantled, according to good restoration practice, in order to study and operate on the daguerreotype plate only, and remounted after the treatment.

The daguerreotype was in bad conservation state with scratches, deformations, imprints and surface chemical oxidation and sulfuration. The chemically damaged area appeared in different colours from blue to green, yellow or brown darkening as the thickness of the corroded layer increased. The cleaning process was performed gradually dividing the area in quarters. For each quarter the treatment time was set to 60 seconds and it was operated by hand. The distance of the jet from the surface was set to 5 mm, RF power was kept at 15 W and the HV at about 8 W. A mixture of argon and hydrogen at the 0.008% was used as process gas. The surface of the daguerreotype had been visually inspected before and after the treatment.

3. Results and Discussion

3.1. Aged epoxy layer removal

The coating applied on the sample surface has a thickness of about 50 μm. After the aging process the surface appears yellowish because of the reticulation process and C=C bonds formation. This aged layer is in fact only few microns thick and it is related to the penetration depth of the UV radiation. The surface does not appear smooth as the substrate but the coating deposited by aerosol presents a drop-like structure. After 25 minutes of treatment, as it can be observed in Fig. 3 it is fully removed under the plasma jet spot (∅ 8 mm) and the shiny stone surface is revealed without damages. The thickness profile of the eroded spot is also highlighted in Fig. 3. As it can be observed the treatment consists in a low temperature process where the epoxy is not carbonised or melted and no liquid epoxy displacement is visible on the border of the crater. The border is instead characterized by a gradual erosion by the creation of volatiles

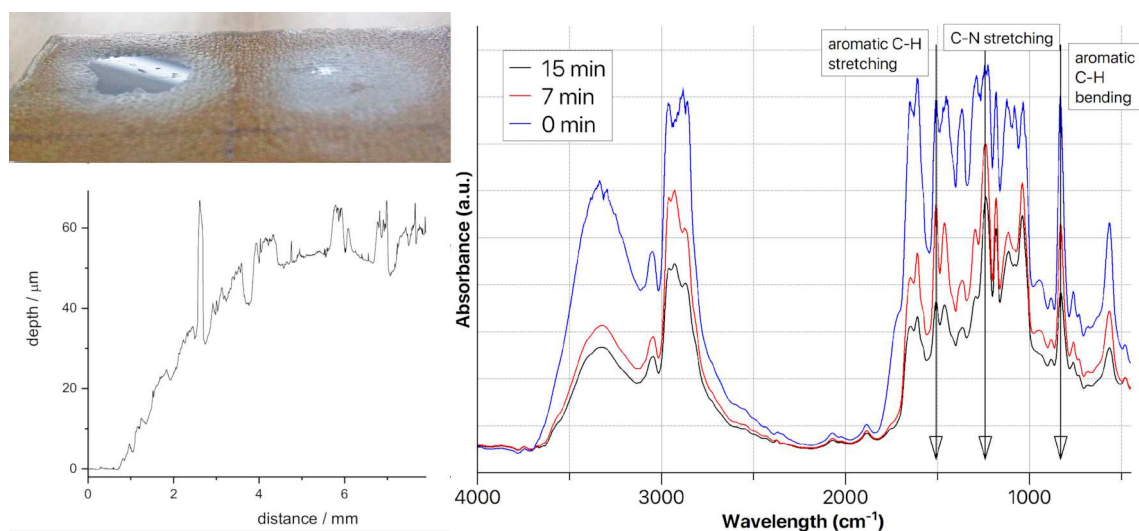


Figure 3. (top left) Photograph of the removed coating spot on the polished Istria limestone (left spot 25 min, right spot 10 min). (bottom left) Thickness profile of the removed spot. (right) FT-ATR spectra before and after 7 and 15 minutes of treatment.

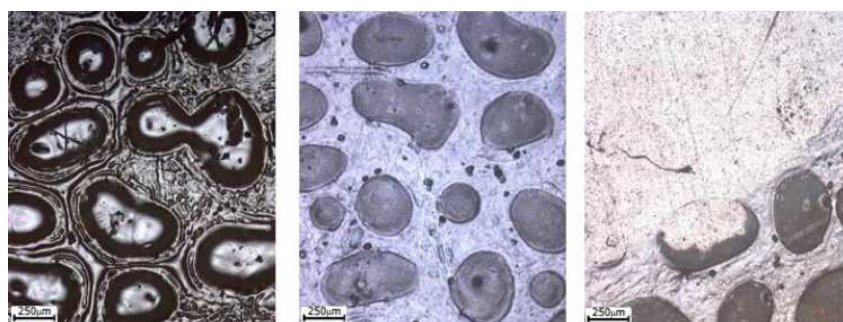


Figure 4. Optical microscope images of the epoxy coating at different stage of removal: before the treatment, after 10 min and after 25 min.

products. As the few microns thick aged layer is removed the not yellowed original epoxy is revealed. Plasma can often be used not to remove the whole thickness of the aged polymers but only to remove the first layer, allowing a subsequent easier action of the solvents. The removal of the coating is mainly a chemical oxidation. From FT-ATR spectra it can be observed that at first C-H bending out of plane of the aromatic ring are removed; then the bridge among the epoxy chains, made by the harder molecules, is broken; at the end, the fragments are oxidized, leading to H₂O, CO₂ and mono-nitrogen oxides (NO_x) (Fig. 3).

Optical microscopy clearly shows the gradual chemical etching of the surface that does not alter the morphology in a micrometer scale (Fig. 4). The droplets of the aerosol deposition are uniformly and gradually thinned. At a middle stage of the erosion process only the thicker parts of the droplets remain on the surface and after 25 minutes the whole coating is removed.

3.2. Daguerreotype cleaning

As shown in Fig. 5A, the studied daguerreotype presents some degraded areas. In particular, two types of oxidation can be noted, the first one is localized along the edges of the slab, characterized by an iridescent colouring, the second surrounds the oval window of contact with

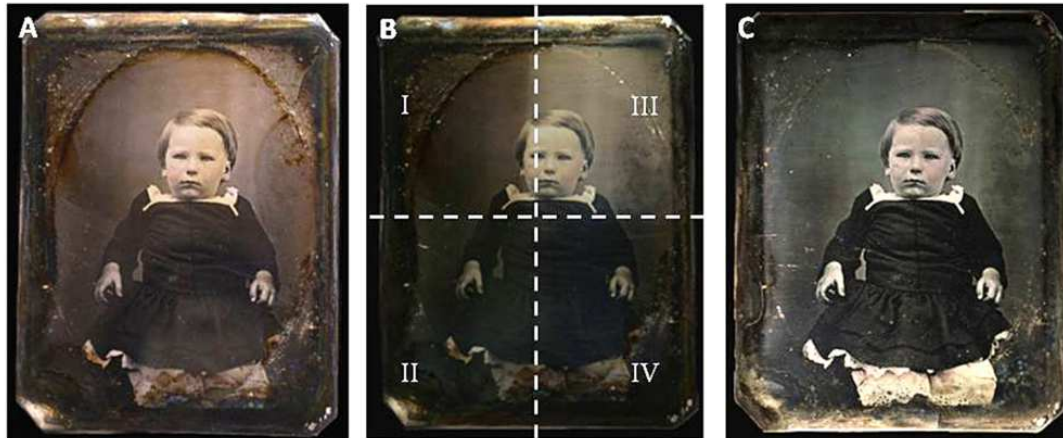


Figure 5. Photographs of the studies daguerreotypes, removed from the original case: (A) before, (B) during treatment optimization and (C) after final cleaning with plasma.

the brass mat. There are also alterations of a physical nature: the two corners on the right side show a detachment of the superficial layer, where the underlying silvery layer can be watched, while the lower left corner shows an obvious deformation. In the central area there are stains with jagged edges tinged to yellow, probably caused by previous cleaning operations, as supported by the presence of a pencil writing on the cardboard on the back of the plate with the words "Re sealed 17 March 99 L.M. Hodde". In order to optimize the cleaning, different plasma conditions were tested in four different zones, indicated as I-IV in Fig. 5B. Between the different sectors, the high voltage percentage was changed between 60% and 70%, with treatment time ranging from 60 to 120 seconds. On the basis of these preliminary tests, it was finally chosen to clean all the plate by setting the high voltage percent to 70%, using a treatment time spanning from 40 seconds, for less degraded areas, to 80 seconds for the highly oxidized zones. The final result is shown in Fig. 5C.

An evident attenuation of the degradation can be observed, particularly at the edges of the image, where rather thick and iridescent stains of oxidation products were initially present. The central spots, probably due to sulphurization phenomena, are also significantly attenuated after the treatment. Many details, particularly in the highlight zones, that previously were barely readable, are now very well defined and clear. In particular, the lower part of the picture, corresponding to the child's outfit, is finally well defined, the iridescent oxidation spots that previously overlapped the dress being no longer visible.

Preliminary surface characterization analyses performed by scanning electron microscopy, optical profilometry, macrophotography in grazing light, optical and metallographic microscopy indicated that the treatment didn't cause any major change in the morphology of the amalgam particles which constitute the daguerreotype image. Further detailed analyses are in progress.

The obtained results confirm that the novel proposed APPJ device can be used as a promising cleaning tool, particularly respectful of the delicate daguerreotype surface and of the silver and amalgam micro- and nanoparticles that compose the image, allowing the localized tuning of the cleaning procedure, depending on the degree of degradation of different objects or of different areas of the same object.

4. Conclusions

The newly developed APPJ offers safe tool for CH applications and with its patented design fully suits the CH requirements. It has a demonstrated room temperature operation mode,

does not deposit undesired material on the surfaces, it suits efficiency rates and costs of the restoration works and it is portable and can be used also in-situ. Its action is gradual, acts only on the topmost surface by chemical oxidation or reduction locally, therefore offers to restorers the possibility to control its action and to stop the process as desired. It can be used on organic and inorganic, insulating or conductive materials independently from their colour. Due to these features it is mainly focused on small areas or artefacts treatments where a soft and respectful treatment is needed. It can find interesting applications also in combination with other technologies, as for example in the presented case study on the removal of an organic coating: it is unbeatable for the removal of aged layers and after this stage solvents can act faster and are cheaper on the not aged polymer below the surface.

This atmospheric plasma technology is therefore ready to the CH community a new tool for deeper experimentation in case studies to fully validate the technique, understand its effects and define protocols. As potential applications, for the selection of case studies, the APPJ would fit better on sensitive materials as plastics as in modern art or as natural organics like for example silk like in textiles in particular where different materials are present or as support technique to clean metallic artefacts.

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