Using atmospheric pressure plasma as a tool in the cleaning of icon paintings

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Abstract. The removal of aged and unwanted layers from the surface of a work of art is one of the most significant operations in the conservation process, but it is also complex, risky and hard to control. The plasma cleaning procedure has been tested successfully on different materials representative in the field of cultural heritage and has proven its many advantages compared to mechanical and chemical cleaning techniques. Despite the success of atmospheric pressure plasma treatment in the cleaning of easel paintings (i.e. the removal of thin films of varnishes, resins, re-paintings or deposits) it is still a new research area. This paper presents the use of atmospheric pressure plasma (APP) for the removal of aged varnish, wax and soot from the pictorial layer of an icon painting. The case study is conducted on a 19th century wooden alms box with a painting of Saint John the Baptist and compares the influence of two different concentrations of the used gas mixture. Better cleaning result is obtained using APP Ar/O\textsubscript{2} 0.2%. The successful removal of the aged oil-resin varnish, wax and soot deposits, is assured without any mechanical and chemical modification of the underlying pictorial layer. The surface action of the plasma treatment is an important advantage compared to the use of aggressive solvents, mechanical shock, or local heating which is typical of traditional cleaning procedures. Furthermore, the non-contact treatment with plasma does not require preliminary consolidation of the treated surface, and avoids additional drawbacks. This method is a rare opportunity, especially in cases when the surface is protected by an organic material and could be neither safely, nor acceptably cleaned by the existing conventional techniques. Therefore, the use of plasma is proposed for the cleaning of icons as an alternative or complementary treatment to the existing techniques.

1. Introduction
The purpose of the treatments on the 19th century wooden alms box with a painting of Saint John the Baptist was to find out how to remove different undesirable layers (aged varnish/soot/wax) by a single process without harming the original paint surface. Based on the main conservation problem of this icon painting, the present study has dealt with the optimal plasma parameters for cleaning of icons. The half-length figure of Saint John the Baptist was represented on one of the sides of wooden alms box, true to the traditional method of icon painting [1]. The layer composition is as follows: wooden board, two ground layers, egg tempera/golden background and finishing protective oil-resin varnish. As a consequence of natural aging, the mixture of oil and resin has lost some of its protective qualities.
and transparency thus changing visibly the colour of the original painting. Moreover, organic materials, like soot and wax drops caused by candles, cover a big part of the icon surface. Soot is composed of ultrafine particles (~2.5 microns) smaller than most pigments (2.5 to 10 microns) which can penetrate interstices and become embedded in painted surfaces [2]. The contaminations and the aged varnish are a combination of materials with an unpredictable degree of interpenetration between the layers. They have become highly insoluble and presents a further complication for the cleaning process. The elimination of the black candle soot, wax drops and aged varnish was the main conservation problem, which was hindered by the mechanical sensitivity of the surface: cracks and weakened adhesion.

Conventional cleaning methods include abrasive techniques and wet-chemical procedures. Mechanical methods such as scalpels, erasers and sponges require physical contact to remove dirt from painted surfaces and the intervention is disadvantaged by minor accuracy and selectivity. Wet-chemical techniques bear the risk of the solvent’s uncontrolled penetration of dissolved materials through a substrate due to capillarity, or could result in solubilisation [3][4]. Conservators had to choose a solvent system that removed layers of dirt, varnish, and overpaint while affecting the original paint layer as little as possible. Conventional contact cleaning techniques are not only less effective, often dangerous and very slow, but also require preliminary consolidation of the surface. This treatment can actually transport undesired materials deeper into the substrate, trigger unpredictable chemical reactions and lead to additional drawbacks. Furthermore, whenever organic solvents, acids or alkali agents are to be used, danger to health and environment exists [5].

Recently, however, the potential benefits of emerging non-contact techniques have been investigated, including the use of laser radiation [6], carbon dioxide (CO₂) snow [7][8] and plasma cleaning [9][10]. The use of atmospheric pressure plasma (APP) as a device for surface cleaning has been investigated in several projects and case studies and demonstrates that it presents itself as a good alternative to many aggressive solvents and abrasive tools in use for cultural heritage restoration [5][11].

Our research into using APP as a cleaning technique in cultural heritage restoration started as a part of an EU-funded project (FP7/2007-2013, grant agreement n. 282998, project acronym PANNA). The efficiency of the plasma on coating/dirt removal was thoroughly investigated and a novel plasma torch has been developed fulfilling the Cultural Heritage requirements (Stylus Plasma Noble, Nadir Srl.) [11]. The possibilities for application of the plasma technology on icon cleaning were studied as one of the activities in the frame of this project. The comparison of the cleaning potential of APP with that of some solvents and mechanical treatments was performed by tests on laboratory substrates with different varnishes and on a real 18th century icon, where very thick, aged oil varnish was successfully removed. The demonstrated plasma method was the safest, but unfortunately, it was also time consuming [12].

Our previous experience and the results obtained on the 18th century icon were used as a base/starting point of the present study. In order to remove the aged varnish, soot and wax contamination by a single process without harming the original paint surface, the influence of two different concentrations of the gas mixture, was investigated. By controlling plasma conditions and gas mixtures APP was tested as an affordable and practical alternative process to chemical and mechanical cleaning methods. This technique is not a novelty, but it is still not part of the restorers’ everyday routine.

2. Materials and methods
 Initially, the experimental treatments were conducted on laboratory performed tempera samples covered with oil-resin varnish, soot and wax drops. Consequently, the treatment conditions that demonstrated better removal effect were applied on the real object - 19th century wooden alms box with a painting of Saint John the Baptist.
2.1. Experimental methods on Lab Samples

2.1.1. Samples. The icon painting lab samples (5×5×1.5 cm) were prepared following the structure and the materials of the 19th century wooden alms box with a painting of Saint John the Baptist (Figure 1). This object, used as “reference”, was painted true to the traditional method, in egg tempera on wood. Therefore, a mixture of animal glue and gesso was applied on the wooden board in several layers of decreasing thickness [13]. Powder X-Ray diffraction pattern of sample collected from the real object identified the red pigment from the frame as hematite Fe₂O₃ (Figure 5). We used English red light pigment (Kremer Pigmente) mixed with egg-yolk medium (1:3 volumes in water) to represent the tempera layer. IR spectra collected on the original varnish confirmed that the icon was covered with an oil-resin mixture. To represent the original varnish, a recipe of Dionysos from Fournas was used [14]. The coating with a thickness of approximately 30 µm was applied by brushing in one layer on polymerized egg tempera (4 months after the application of the paint layer). To represent the organic contaminations, some of the painted samples were coated with soot (thickness ~26 µm) using a wax candle, which was held against the tempera surface for a few minutes. Others were covered with wax (thickness ~36 µm) using drops from a lighted candle (Figure 1b). All contaminants were applied 3 months after the varnishing of the tempera surface.

2.1.2. Treatments. For the treatment of smoke-damaged lab samples commercial atmospheric pressure plasma jet (APPJ), with a coaxial dielectric barrier discharge (DBD) design and working in radiofrequency (kINPen10/11, Neoplas GmbH, Germany) was used. The influence of two different concentrations of the gas mixture on the removal of oil-resin varnish, soot and wax was investigated. In particular, gas mixtures of argon and oxygen - Ar/O₂ (98/2 %) and (99.8/0.2 %). The treatment parameters demonstrated better plasma cleaning on the 18th century icon were used as a base of the present study [12]. The samples were located at a constant distance of 1 mm from the jet-nozzle (the torch was fixed to a stand). At this working distance the Ar gas discharge plasma has a diameter of 8 mm spread over the treated surface [15]. The cleaning tests were performed at 8 W power consumption, 230 V, 50/60 Hz power supply, inlet pressure 1.5 bar and 5.5 L/min gas flow. The wax/soot/varnish layers were treated between 10 and 1200 s until a clean spot of 8 mm (the size of the spread on surface plasma) was observed.

2.1.3. Characterization. The first part of the study (tests performed on lab samples) was used the visible and measurable colour modification as single criterion to estimate cleaning success. All samples were examined under a zoom stereo microscope EMZ-8TR (Meiji Techno Co., Ltd.; ×7–
\( \times 180 \) magnification at \( \times 25 \) magnification), with both visible and UV light. Digital photos were generated with Nikon D5100 digital camera (AF-S Nikkor 18-55 mm). The colorimetric measurements were made using a Konica Minolta CM-700d spectrophotometer. The results are presented in the CIELab colour space (coordinates L*, a* and b* for a specific colour) and the colour variation was evaluated by calculating \( \Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \). Colour measurements were carried out to obtain relative colour modification. The uncovered tempera colour was measured and stored as reference. Afterwards the varnished and contaminated with soot/wax surfaces and the cleaned squares on the sooty/waxy and clean side were measured and set in proportion to the reference. The temperature at the surface was monitored by using an infrared thermometer. The measurements were performed on the spot during the plasma treatment and on the surface near the spot.

2.2. Methods on Real object

2.2.1. Treatments. The obtained knowledge allowed us to safely use the APP on the present real object. The effectiveness of cleaning oil-resin varnish, wax and soot from the 19th century icon of Saint John the Baptist was demonstrated using the same commercial APPJ (kINPen10/11, Neoplas GmbH, Germany). The treatments were performed at 1 mm working distance, 8 W power consumption, 230V, 50/60Hz power supply, inlet pressure 1.5 bar, \( \text{Ar/O}_2 \) (98.8/0.2\%) as working gas and 5.5 L/min gas flow. The treatment time was between 60 and 180 s on a spot by moving the torch.

2.2.2. Characterization. The surface of the icon was characterised before and after cleaning treatments by means of UV light inspection, optical microscopy, and IR spectroscopy. FT-IR spectra were collected by using an Alpha Bruker® portable spectrometer operating with external reflection geometry. The spectra were collected by using a 4 mm² window, accumulating 40 scan with a resolution of 4 cm\(^{-1}\) in the region from 4000 to 400 cm\(^{-1}\).

3. Results and discussion

3.1. Results on the lab samples

Surfaces of the contaminated paint samples were examined with the naked eye and under microscope, before and after cleaning, to evaluate the effectiveness of each treatment and any resulting alterations in surface integrity. Special attention was paid to surface defects potentially caused indirectly by plasma cleaning.

The investigations demonstrate the removal of the tested varnish, soot and wax contaminants by means of both gas concentrations without affecting the underlying pictorial surface. Distinct and fast removal, however, could be observed only with \( \text{Ar/O}_2 \) 0.2\% plasma. Figure 2 depicts a comparison of wax/soot/varnish before and after treatment with \( 
\text{Ar/O}_2 \) 0.2\% gas discharge plasma. The application of \( \text{Ar/O}_2 \) 2\% resulted in a clean spot of 8 mm (size of the spreaded plasma) only after long exposures: 18 min on wax, 13 min on soot and 15 min on the oil-resin varnish. The longer \( \text{Ar/O}_2 \) 2\% plasma exposure was performed with some breaks between the treatments. The test was effective but time-consuming. In contrast, the APPJ used with \( \text{Ar/O}_2 \) 0.2\% removed the same spot of wax (diameter of 8 mm, thickness ~36 \( \mu \)m) at very short exposures - 30 s. This diameter of cleaned spot was obtained after 20 s. treatments on soot layer and 60 s on varnish layer. The contaminants with a thickness of approximately 10 \( \mu \)m, was removed within 300 s plasma treatment when \( \text{Ar/O}_2 \) (98/2 \%) was used, whereas \( \text{Ar/O}_2 \) (98.8/0.2\%) was able to remove 10 \( \mu \)m for approximately 1 s.

The neutral gas temperature was below 25 \( \text{C}^\circ \) under the experimental conditions, preventing the surface from heating. There is a potential for removal of the organic binder located on top of the pigment particles but the process of cleaning can be stopped earlier so as to minimize or prevent removal of the binder if desired. Moreover the binder which is in between and underneath pigment particles will be not altered.
The colour deviations of the cleaned surface (Ar/O_2 2% and Ar/O_2 0.2% treatments) in relation to the reference (uncoated tempera surface) ΔE present values of 0.6 for Ar/O_2 0.2% and 1.28 for Ar/O_2 2%, which are not perceptible by naked eye (Table 1). Visual observations and colour measurements confirm the effectiveness of plasma treatments on the removal of oil-resin varnish, soot and wax. Both concentrations of the used gas mixture did not damage the pictorial layer nor impact the pigment’s colour, but Ar/O_2 2% demonstrated to be very impractical for this application due to its slow action.

![Image](image_url)

Figure 2: Lab samples before and after treatment with Ar/O_2 0.2% plasma: a) wax over soot, 2.5×; b) wax was removed and the soot layer is visible 2.5×; c) the soot was gradually removed (left part of the image) 2.5×; d) the contaminations were effectively removed only from peaks and flat paint surface, then - e) from valleys in the paint surface 2.5×; f) plasma cleaned spot.

Table 1: Colour variation of the lab samples with respect to the reference - uncoated tempera sample

| Sample                                              | L*     | a*     | b*     | ΔE*   |
|-----------------------------------------------------|--------|--------|--------|-------|
| Uncoated tempera (reference)                         | 35.16  | 22     | 16.28  |       |
| Varnished tempera                                    | 29.44  | 27.43  | 27.29  | 13.54 |
| Soot and Wax contamination on varnished tempera      | 29.96  | 6.86   | 19.07  | 16.39 |
| Cleaned surface Ar/O_2 2% ~ 60min on area of 1×1 cm | 33.94  | 21.78  | 15.94  | 1.28  |
| Cleaned surface Ar/O_2 0.2% ~ 2 min. on area of 1×1 cm| 34.98  | 21.56  | 16.12  | 0.6   |

3.2. Results on the real object

The original oil-resin varnish is smoke and heat damaged in the right part of the icon (Figure 1a). The removal of the varnish in this area was hindered by interpenetration between the layers (contaminations, varnish and paint) and mechanical sensitiveness of the surface: very thin paint and ground layers with weakened adhesion. Smoke and high temperature caused by candles led to the melting and burning of the oil-resin varnish and covering of the surface with soot. Several wax droplets, accumulated on the scorched surface presented a further complication for the cleaning process.

The aged oil-resin varnish which is not heat damaged was removed by plasma with success comparable to the result on lab samples. After 1 min of plasma treatment Ar/O_2 0.2% the topmost contamination (wax and soot) was completely removed (diameter of the cleaned spot 8 mm, Figure 3 a, b). Then the varnish layer was removed gradually, without disturbing egg tempera brush strokes (Figure 3 c, d, e). The plasma cleaning rate was not altered from the different pigments in the pictorial layer. The material (wax, soot and varnish) disintegration from the golden background was even faster and easier due to the less interpenetration between the layers (organic contaminants over inorganic surface Figure 4 a, b).
In the areas, where layers (contaminations, varnish and paint) were melted and burned, the plasma cleaning action was hindered, probably due to surface chemical interactions between the paint and the contaminants. The varnish is uneven and its lowest layer contains pigment particles (Figure 5). Therefore, on heat damaged surface the thick oil-resin varnish was only thinned to a different thicknesses, corresponding to the different original layer depths. The treated area was precisely controlled because plasma interacts only with the first layers of the surface and does not penetrate or spread like solvents.

Figure 4 c and d shows another problem on the destructed surface of the real object- deep cracks full with dark contaminations. The paint and varnish layer are broken along those cracks. This is a peculiar danger in case of traditional contact cleaning, because of the weakened adhesion. The plasma treatment does not interfere mechanically with the surface and the fact that it is contactless is an important positive feature. On the laboratory performed tempera samples the contaminations were effectively removed from both -peaks and valleys in the paint surface by APPJ Ar/O2 0.2% (fig. 2d and e). However, on the real icon painting, the plasma removed only part of the unwanted material from the depth of the cracks. The spreaded plasma plume was not able to reach and effectively remove the accumulated dirt (aged varnish, soot) from the lower parts in the cracks. At ambient conditions, humidity can influence the resulting stable species chemistry: chemical pathways involving water primarily originate from water molecule dissociation, forming hydroxyl radicals (OH). The OH radicals interact with air species generating further reactive species[15]. Therefore, a drop of deionised water was dripped in the cracks just before plasma treatment and the wetted dirt was again exposed to plasma. This step increased the depth of cleaning but even with longer treatment times with Ar plasma not all material contaminants were removed from the cracks. The tip of the used commercial plasma jet (kINPen) comes in contact with the sensitive icon surface and the plume cannot be directed deeper.

![Figure 3: a) Plasma treatment on wax contaminant over the sooty surface of the real object; b) cleaned spot on wax contaminant 2.5×; c), d), e) gradual removal of the aged varnish layer 2.5×;](image1)

![Figure 4: a) Aged varnish on golden surface before plasma treatment 2.5×; b) after plasma treatment 2.5×; c) aged varnish on painted surface with crack - before plasma treatment 2.5×; d) treatment with plasma was not able to remove all material contaminants from the cracks 2.5×;](image2)
ER-FTIR spectra were collected on the surface before and after plasma cleaning correspondence to the red frame of the icon. A rough estimation of the varnish removal was performed by these measurements because the morphology of the painted surface (e.g. surface roughness, multicomponents composition of the layer) complicate the assignment of the IR bands. The spectrum of the uncleaned surface (Figure 5 a), confirm that the surface of the icon is coated by an oil-resin mixture. In the spectrum also appear the signals corresponding to the red pigment layer, which confirm the visual observation. The spectrum of the icon surface after the cleaning (Figure 5 b) presents an increase in intensity of the inorganic absorption bands in the spectrum ascribable to the pigments in the painting layer, thus confirming the plasma removal of the varnish.

![Figure 5: ER-FTIR spectrum of the icon surface: a) before plasma treatment: C=O stretching band due to Linseed oil/mastic/dammar (1); the CO3\(^{-}\) stretching due to calcium carbonate (2); the Si-O stretching band due to silicate (3) and the Fe-O stretching band due to Fe2O3 (4); b) after plasma treatment: N-H stretching bands due to the egg (1), C=O stretching band to the varnish and to lipidic part of the egg (2); C-N=H stretching of the proteinaceous part of the egg (3); the CO3\(^{-}\) stretching due to calcium carbonate (4); the Si-O stretching band due to silicate (5) and the Fe-O stretching band due to Fe2O3 (6);](image)

4. Conclusions

In the present paper a case study of application of the atmospheric pressure plasma for the removal of aged oil-resin varnish, wax and soot from the pictorial layer of an icon painting is described. The tested layers are organic and were cleaned with two different concentrations of Ar/O\(_2\). The used treatment conditions were able to oxidise the organic material without having an effect on the inorganic pigment. Moreover, the process temperature is actually the room temperature. Plasma Ar/O\(_2\) 2 % was able to remove the tested wax, soot and oil-resin varnish, however it took a considerable amount of time: 1 h treatment time leaded to 1 cm cleaned area. In contrast, plasma Ar/O\(_2\) 0.2% obtained the same result for exposure of 2 min. By controlling plasma conditions and gas mixtures, fast and effective plasma cleaning was possible. The mechanism of plasma interaction with the contaminated icon surface and the alteration of the feed gas composition (changes between 0.2% and 2%) on the rate of plasma action is a topic for future studies.

The result on the real object was the gradual removal of the unwanted organic layers which permitted control of the amount of surface material disintegration (thinned or completely removed). The action of the plasma is limited to the first 1-2 nm of the surface and offers the possibility to control its action and to stop the process as desired. Moreover, the most positive feature of plasma- the fact that it is contactless, was used to avoid the need of preliminary consolidation of the treated surface. A single disadvantage was discovered to the used commercial APPJ (kINPen, Neoplas GmbH). It was unable to remove contamination effectively from the low spots of the surface cracks because the tip of the jet comes in contact with the sensitive and rough icon surface and the plume cannot be directed deeper.

The treatment performed on the real object - 19th century wooden alms box with a painting of Saint John the Baptist demonstrated plasma’s great potential for cleaning of paintings as well as an actual limit of the used commercial device. The process is a rare opportunity especially in cases when the
surface is protected by an organic material and could be neither safely, nor acceptably cleaned by the existing conventional techniques. It is proposed for cleaning of icons as an alternative or complementary treatment to the existing techniques. However, the correct application of this cleaning method in the restoration practice needs not only a vast amount of case studies but also a device which can overcome the actual limits of commercial atmospheric plasma tools.

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