The Evaluation of DBD Plasma Technique for Removing Carbon Stain from Leather Artifacts

MUHAMMAD EL-QUBAISY[1]*, USAMA MOHAMMAD RASHED[2] and GOMAA ABDEL-MAKSOUD[3]

[1] *Restoration Management Al-Azhar Library, Islamic Research Academy, Al-Azhar Sheikhdom, Cairo, Egypt*

[2] *Physics Department, Faculty of Science, Al-Azhar University, Cairo, Egypt*

[3] *Conservation Department, Faculty of Archeology, Cairo University, Cairo, Egypt*

Abstract

In recent years, plasma technology has been successfully used in the conservation of cultural heritage. The removal of soot from historical bookbinding surfaces through a cold plasma cleaning technique is an important application. This study aims to test the efficiency of using atmospheric pressure cold plasma on cleaning and removing soot from historical leather bookbinding surfaces. Atmospheric pressure Dielectric Barrier Discharge (DBD) cold plasma in an oxygen environment was applied to modern leather samples that were contaminated with carbon and artificially aged. The results have been evaluated using several techniques including visual assessment, digital microscopy, Scanning Electron Microscope (SEM) with (EDAX), Fourier Transform Infrared Spectroscopy with Attenuated Total Reflection (FTIR-ATR), mechanical properties, and colour change by UV spectrophotometer. The results have revealed that, the best removal of a soot stain through DBD cold plasma was found at 17.35W plasma power and 2 minutes exposure time.

1 INTRODUCTION

Leather artifacts are found in many places in Egypt (museums, libraries *etc.*), but in most of these places international standards of conservation are not applied. The most common types of damage sustained by leather artifacts are caused by poor handling, poor storage, inappropriate display methods, wear and tear from repeated use, chemical changes in the materials of the leather objects, chemical changes caused by atmospheric pollutants, chemicals in contact with the leather objects and a combination of any or all of these.[1] According to deterioration factors, some stains are found on the surface of leathers. One of the most common stains is a carbon stain, which comes from exposure of the leather surface to the ambient atmosphere.[2] It can be added that smoke is a common surface contaminant found on archaeological materials. Possible causes of smoke contamination include cooking over an open flame or burning candles and incense during religious ceremonies as well as kerosene lamps used in ancient times for lighting.[3]

Cleaning is one of the basic procedures in conservation.[4] The conservator is naturally tempted to apply new characterization techniques and new products. One of the most recent techniques is plasma treatment which represents a non-destructive method applicable in decontamination of cultural heritage objects.[5]

Plasma cleaning of solid surfaces is a rapidly evolving topic in plasma material processing and has already been carried out in many industrial fields. Surface cleaning is primarily done by wet chemical processes but, in general, wet chemistry fails when the surface cleaner needs to reach the atomic level.[2] Plasma cleaning is based on the plasma-wall interactions. It uses the interaction of ions, electrons, and radicals with the surface. Their interaction with a solid surface causes mainly three basic phenomena that lead to surface cleaning; heating (baking), sputtering, and etching. Taking into account the latest regulations on environmental protection and worker protection, the perspective of replacing some harmful treatments such as using biocides and organic solvents with cold plasma treatments for decontamination and partial cleaning is highly recommended.[6] Cold plasma has been extensively studied due to its application in bacterial inactivation and surface treatments, such as cleaning and functionalisation.[7] It is characterised by shorter treatment times, no harmful residues remain after treatment and no shrinkage or deterioration is noticeable.[7,8] Additionally, cold plasma provides a low temperature environment using electrical energy rather than heat to promote chemical reactions, eliminate many of the problems associated with wet chemistry and is environmentally friendly with no liquid waste and hence no expensive disposal.

Atmospheric pressure cold plasma sources have been widely used due to their important applications in various fields. It is a promising technology that is simple to set-up, easy and economical to operate, small size, low temperature, low electric power cost, high density ($>10^{13}cm^{-3}$) and does not require vacuum equipment.[9] Dielectric barrier discharge (DBD) is a cold gas discharge between two electrodes wherein at least one of the two electrodes is covered with a dielectric barrier layer. It is filamentary in nature with discharge channels or streamers forming at random locations along the dielectric due to the charge

* Corresponding author: E-mail: m.elkobasy@gmail.com

accumulation on the dielectric surface. The filaments carry the energy and the active species of the discharge. The filaments are essential for surface cleaning.[2] Within the different types of atmospheric pressure cold plasmas, dielectric barrier discharges (DBDs) are the most interesting solution. DBDs have been widely used in industrial applications like ozone generators, plasma display panels, excimer lamps, volatile organic compounds destruction and surface modifications.[10,11,12,13]

Many studies have been reported using cold plasma sources in surface cleaning. Okane and Mittal[14] used RF glow discharge plasma of pure argon (99.99%) and helium (97%)-oxygen (3%) mixture to remove organic contamination from the surface of iron-cobalt alloy and rhodium surfaces. Augur electron spectroscopy (AES) and surface wettability measurements were used to evaluate the plasma cleaning procedure and to provide a comparison with conventional solvent cleaning methods. Plasma cleaning was shown by AES to be more effective than organic solvents in the removal of sulfur and carbon contamination from the surfaces of rhodium and iron-cobalt alloys. The plasma surface cleaning was mild enough to avoid damage to the magnetic properties of a Fe-Co film. The surface oxygen levels observed by AES and the water wettability of the surfaces indicated the presence of an oxide layer on Fe-Co and rhodium surfaces.[14] When these surfaces were water wettable, the AES results indicated a lower carbon contamination level. Kirkland[3] used Fourier transform infrared spectroscopy with attenuated total reflectance sampling (FTIR-ATR) to examine changes in the chemical nature of the surface of representative modern and archaeological samples upon plasma treatment. Samples that were treated with destructive wet chemical methods, *e.g.,* treatment with sodium hydroxide solution, were compared to plasma-treated samples, as well. Plasma treatment was carried out using a 13.56MHz radio frequency to gently remove the soot and smoke from the surface of the textile, leather, and filter paper samples. In general, materials that have undergone plasma treatment are visually preserved with minimal chemical changes occurring on their surfaces.[3] Ioanid *et al.*[6] used high frequency (HF) cold plasma in a gaseous environment of oxygen/argon to remove the smoke sediment from Linden wood icon's surface. It was confirmed that HF plasma can be taken into consideration as a partial cleaning variant for removal of soot accumulated at the surface of pictorial layer of icons.[6]

Cools *et al.*[15] used a medium pressure (5kPa) dielectric barrier discharge operating in different atmospheres (air and argon) to develop a fast and easy way to remove adsorbed carbon contamination from Ti samples. The obtained results are compared with other chemical and thermal treatments typically used. This comparison shows that plasma treatment at medium pressure is able to remove up to 20% more of the adsorbed carbon compared to the classical cleaning methods, while at the same time being less aggressive, leaving the sub-surface chemistry unchanged.[15]

This paper presents for the first time, the efficiency of oxygen DBD plasma on cleaning and removing soot accumulated on leather surfaces.

2 MATERIALS AND METHODS

2.1 Samples

2.1.1 Preparation of new vegetable-tanned leather samples

New vegetable-tanned leather (from goatskin) has been prepared by the authors in accordance with Gustavson,[16] Pough,[17] Abdel-Maksoud[18] and Abdel-Maksoud.[19]

2.1.2 Application of carbon stain

Carbon powder (from natural charcoal) dispersed with water was prepared by the authors. Carbon stain was applied on the surface of leather by brush.

2.1.3 Accelerated heat ageing

Accelerated heat ageing was in accordance to Abdel-Maksoud and Marcinkowska,[20,21,22] and Abdel-Maksoud and Al-Saad.[23] The test of temperature, 70°C, for 10 days was performed in the laboratory inside the reaction oven using the dry air atmosphere. The accelerated heat ageing was applied on the stained samples.

2.2 General plasma reactor set-up

A dielectric barrier discharge (DBD) reactor, used in cleaning is schematically presented in Figure 1. The DBD reactor consisted of two parallel plate electrodes. The upper electrode is an Al- sheet of dimensions 25 x 25cm^2 pasted on dielectric glass plate of thickness 2mm and the lower electrode is a stainless steel plate of the same dimensions. The gap distance between the dielectric glass plate and the lower electrode is 2mm. Plasma discharges are generated by a 25kV/30mA AC power supply of 50Hz frequency which is connected to the upper electrode, while the lower electrode is connected to earth through a resistor R of 100Ω or a capacitor C of 3.35µf. The samples were placed in the gap between two electrodes. The working gas (oxygen) at 3L/m was fed through a gas flow meter to the space between the two electrodes where the electric discharge was generated in this space. Plasma cleaning was carried out with a gas flow rate of 3L/m and for several treatment times ranging from 30 seconds to 2 minutes and applied in stages of 8, 10, 12kV. The voltage across discharge electrodes has been measured using a resistive potential divider (1:1000) connected in parallel with the discharge electrodes. The discharge current was measured by measuring the voltage drop across the resistor R through a digital storage two channel oscilloscope (GWinsTEX GDs-1072-u,70MHz). The dissipated power during the discharge has been estimated using a capacitor C to calculate charge flow through the reactor.

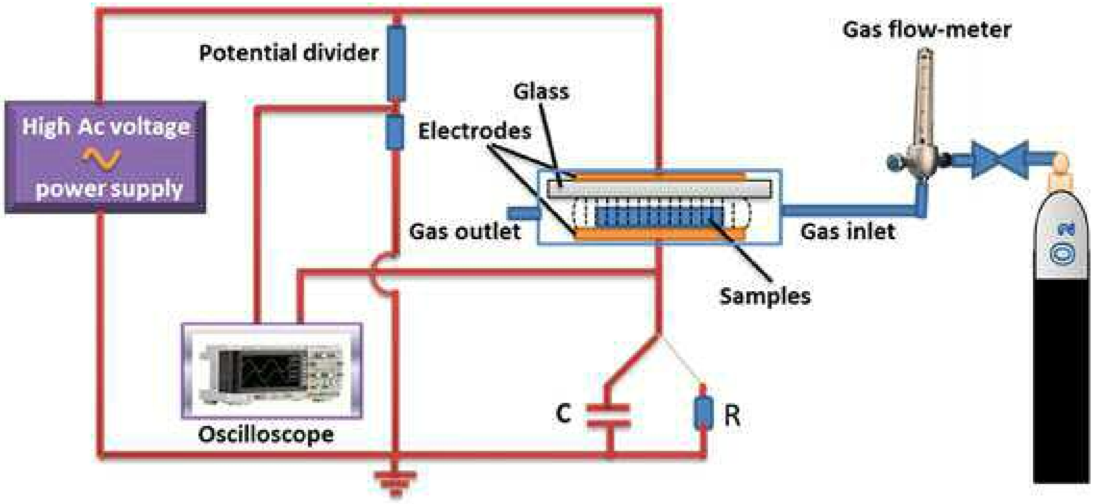


Figure 1. The schematic diagram of DBD reactor used in cleaning.

2.3 Investigation techniques

2.3.1 Visual assessment

Visual assessment has been carried out by the naked eye of the authors to evaluate the efficiency of DBD cold plasma technique for the cleaning process. The naked eye of conservator can also determine the effectiveness of analytical techniques, which should be applied for the evaluation processes.[1]

2.3.2 Digital microscope

Sample investigation has been carried out using a small handheld U500X Digital Microscope owned by the Conservation Department, Al-Azhar Library, Islamic Research Academy. The microscope was made in China with a maximum magnification up to 500x, focus range from 15mm to 40mm, image capture resolution 640 x 480 pixels. The Digital Microscope has been used for the investigation of the surface morphology of the samples before and after plasma cleaning process.

2.3.3 SEM-EDAX

The SEM used in this study is FEI Inspect-S50 supplied with Quantx Bruker EDS spectrometer. The samples have been observed at low vacuum and at 10-20KeV accelerating voltage. The (SEM-EDAX) has been used for assessing chemical proportions and surface morphology of the samples before and after cleaning process. The SEM analyses were carried out at the Scanning Electron Microscope Laboratory, Heat Treatment Department, Tabbin Institute for Metallurgical Studies, Helwan, Cairo, Egypt.

2.3.4 Colour values

Colour value measurements have been performed by the CIE L*a*b* system with L* defining lightness with a maximum value of 100 for white and a minimum value of 0 for black. a* is the coordinate of green (negative values) and red (positive values) and b* is the coordinate of blue (negative values) and yellow (positive values).[24] The measurements have been performed by a spectrophotometer (Ultra Scan Pro TRD/02/CL/VII), at a wavelength range between 350-1050nm, at Dyeing, Printing and Textile Auxiliaries Department, Textile Research Division, National Research Centre, Cairo, Egypt.

2.3.5 Mechanical properties (tensile strength and elongation)

An Asno Tensile Strength and Elongation at break Tester (Japan, 1987) loaded to100kg (10.19N) was used. The maximum tester speed is 30 inches/minute, extension range 200mm and gauge length 50: 200mm. The measurements have been carried out according to the ASTM-Standard Method D5035 - 2011 (2015), at Spinning and Weaving Engineering Department, Textile Research Division, National Research Centre, Cairo, Egypt.

2.3.6 Fourier Transform Infra Red Spectroscopy with Attenuation Total Reflection

FTIR-ATR was used for monitoring the existence and position of functional groups of the samples that were prepared at different times of stirring in the wave number region from 4000 to 400cm^{-1} on a JASCO FT-IR 6100, Japan. This method of analysis was used in accordance with Jadoul,[25] Dias[26] and Terinte.[27]

A significant advantage of the ATR technique is that the leather sample does not require any preparation, thereby minimising possible damage to the sample. FTIR analyses have been performed at the Laboratory of IR, Central Services Laboratory, National Research Centre, Cairo, Egypt.

3 RESULTS AND DISCUSSION

3.1 Electrical characteristics of DBD

Figure 2 shows waveforms of the applied voltage on the reactor and the associated discharge current measured in atmospheric oxygen at flow rate of 3L/m. When the AC applied voltage on the DBD reactor reaches the onset value, the streamer discharge starts in the gap inside the reactor in the form of discrete current spikes. These spikes are related to the formation of micro discharges (filaments) of tens of nanosecond (ns) duration in the gap space.[28] The filaments are randomly distributed over entire electrode surface. The streamers cross the discharge gap and spread on the surface of the dielectric barrier, building up surface charges, which produce electric field opposite to that of the applied voltage. After a short time (several ns), the streamer activity in that spot is extinguished, followed by streamer initiation in another location. The peak of each individual spike is related to the number of instantaneous microfilaments that were formed at this instant, and hence a high current spike indicates that a high number of micro discharges initiated almost simultaneously.

A simple method for obtaining the consumed power is using the discharge Lissajous figures, obtained when plotting transported electric charge Q through the discharge as a function of the applied periodical voltage.[29,30] The charge Q is delivered from the voltage drop across a measuring capacitor of 3.35μF. The average electric energy dissipated in a discharge cycle is then simply the area of the characteristic Lissajous figure, which in most cases is nearly a parallelogram.[31] Lissajous diagrams have been plotted at different applied voltages where the voltage difference between the two electrodes has been measured as a function of the charge on the electrodes. Figure 3 shows Lissajous diagrams applied at voltages 8, 10 and 12KV. It is noticed that, the area of parallelogram increases with the increase in applied voltage because; the energy dissipated in a discharge cycle is proportional to the area of the parallelogram. The dissipated power has been calculated by multiplying the area of the parallelogram by the frequency of the used AC power supply (50HZ). The change of the average dissipated power, calculated from the Lissajous figures with the applied voltage is shown in Table I. As can be seen from this table, the average dissipated power increases the increase in applied voltage, but remains relatively low even at higher applied voltage. This result may be referred to the characterised filamentary discharge behaviour where, the time of the filament is very short (few tens of nanoseconds).

TABLE I
Values of applied voltage and corresponding power values

V(KV)	8	10	12
PO_2 (Watts)	5.48	12.21	17.35

3.2. Visual assessment

Figure 4 (A, B and C) shows the leather samples before and after DBD plasma cleaning at different conditions of DBD plasma consumed power and exposure time. It is clear through visual assessment and photographic documentation that the soot stains were removed from the leather samples surface after oxygen cold plasma cleaning.

The difference between blank samples, control samples, aged samples, and treated samples treated by oxygen cold plasma is very clear. The leather surface looks visibly clear to the eye after cleaning. It is also obvious that, as both plasma consumed powers and sample exposure times increase, the cleaning efficiency of plasma increases.

3.3. Digital microscope

Digital photography provides a world of microscopy opportunities, providing an easy-to-use system for images that enable easy image storage, manipulation and management, and is increasingly applied to image capture of the microscope-an area that requires high accuracy, colour fidelity and precise management, often, limited lighting conditions.[32]

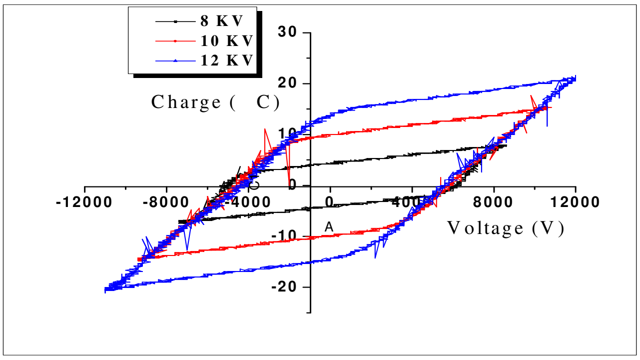


Figure 3. Lissajous diagrams at 8, 10 and 12KV.

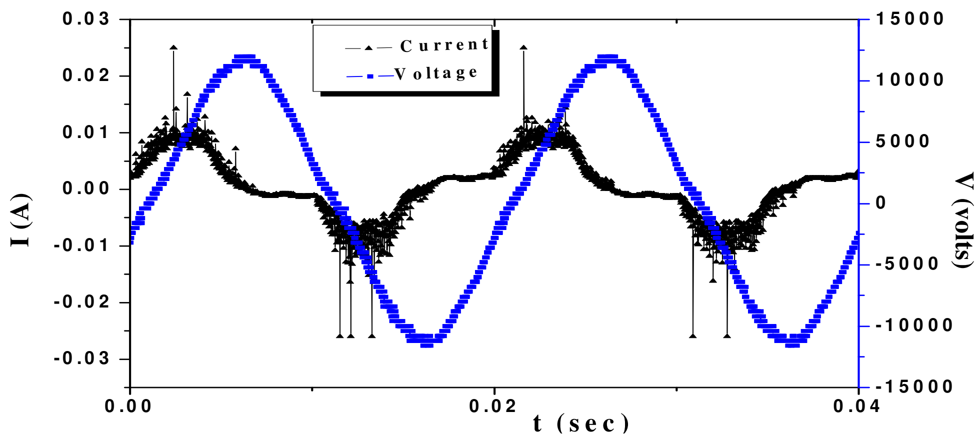


Figure 2. Waveforms of the voltage applied to reactor and associated current.

The results of the digital microscope investigation have been carried out at 500x magnifications. Figure 5 (A to L) shows the digital photos of leather samples before and after plasma cleaning at different conditions. The grain surface pattern gives a distinction of goatskin (Fig. 5A) and the surface is very clear and smooth. After the application of carbon stain (Fig. 5B) on the surface of leather, the grains of goatskin surface cannot be recognised and gives the characteristic of carbon soot stains, which covers the surface. After plasma cleaning (Fig. 5 D, E, F, G, H, I, K and L) with different powers, 5.48W, 12.21W and 17.35W and different times ½ minute, 1 minute and 2 minutes respectively, carbon stains disappear. The greater the power and exposure time of the plasma, the greater the removal of carbon stains from the surface of the sample. It is also clear that, although a large proportion of carbon stains have been removed, some are still present on the sample

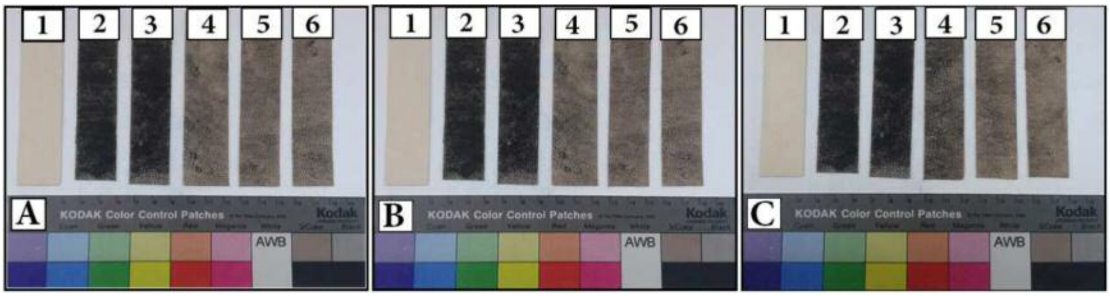


Figure 4. Leather samples after plasma cleaning with different powers: (**A**) Plasma cleaning with 5.48W; (**B**) Plasma cleaning with 12.21W; (**C**) Plasma cleaning with 17.35W. The cleaning above was for (**1**) Blank sample, (**2**) Stained sample, (**3**) Aged sample, (**4**) Cleaned sample after ½ minute, (**5**) Cleaned sample after 1 minute, (**6**) Cleaned sample after 2 minutes, respectively.

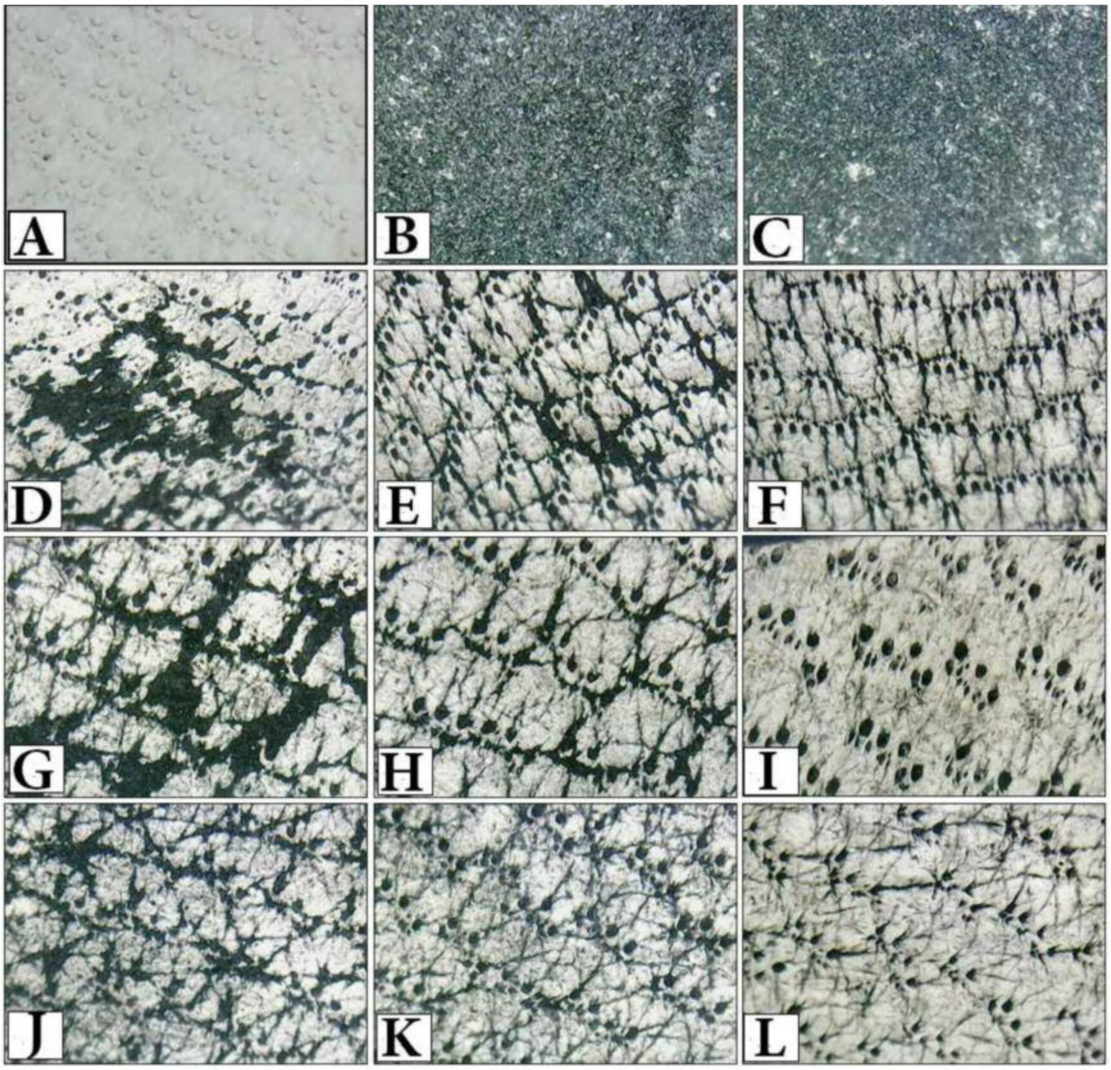


Figure 5. Investigation of the surface morphology by digital microscopy: (**A**) Blank sample, (**B**) Stained sample, (**C**) Aged sample, (**D~L**) Cleaned samples with different powers and time: (**D**), (**E**), (**F**) Cleaned sample with 5.48W after ½, 1 and 2 minutes, respectively, (**G**), (**H**), (**I**) Samples cleaned with 12.21 W after ½, 1 and 2 minutes, respectively, (**J**), (**K**), (**L**) Sample cleaned with 17.35W after ½, 1 and 2 minutes, respectively.

surface, especially in the areas of hair follicles. The best removal of the soot stain was found at 17.35W plasma power and 2 minutes exposure time.

3.4 SEM analysis

Scanning Electron Microscopy (SEM) constitutes one of the most important methods used for investigation of the surfaces.[5]

SEM was used to investigate the surface morphology of the latter samples before and after the plasma cleaning process. Figure 6A shows the blank sample with clear grain pattern of goatskin and smooth surface. Stained sample (Fig. 6B), shows carbon soot stains which cover the surface, the grain pattern of goatskin disappears and the smoothness cannot be recognised. The same observations are also noticed for aged sample (Fig. 6C). The treated sample in (Fig. 6D) at power 17.35W with time 2 minutes, shows that the grain surface pattern of goatskin reappears and the smoothness of the surface is recognised. The investigation of the surface morphology by SEM showed that particulate soot stains can be easily removed from the leather surface by oxygen plasma and appeared smoother and clearer after cleaning with plasma. This indicates that, layers of soot stain have been removed. Oxygen plasma did not act in modifying chemically and topographically the surface of the leather fibres and did not affect its interior. This reflects the efficiency of DBD plasma technique for cleaning and removing soot stains from the goat leather samples surfaces.

3.5 EDAX analysis

EDAX analysis was performed on goat leather samples contaminated with carbon before and after cleaning to detect any changes in elements due to contamination or removal of certain constituents of the leather surface. The EDAX results (Fig. 7A) show the stained sample before plasma cleaning.

Obviously from Figure 7A, there are carbon, oxygen and calcium elements in the stained sample. Carbon is found in a high percentage 87.45%. The presence of carbon is attributed to the contamination by carbon when the natural charcoal was applied on the leather samples. The oxygen percentage of 10.90% may have derived from the chemical structure of the leather itself or from the surrounding environment. Calcium was found at a small percentage of 1.66% and this may be due to the leather manufacturing process. After plasma cleaning (Fig. 7B), the results show a significant reduction in carbon percentage (58.90%) due to plasma cleaning process and the removal of carbon grains. The results also showed a significant increase in the oxygen percentage (39.96%). This increase of oxygen percentage may be derived from the oxygen plasma cleaning process. There was a slight decrease in percentage of Ca, 1.13% which is attributed to the plasma cleaning process.

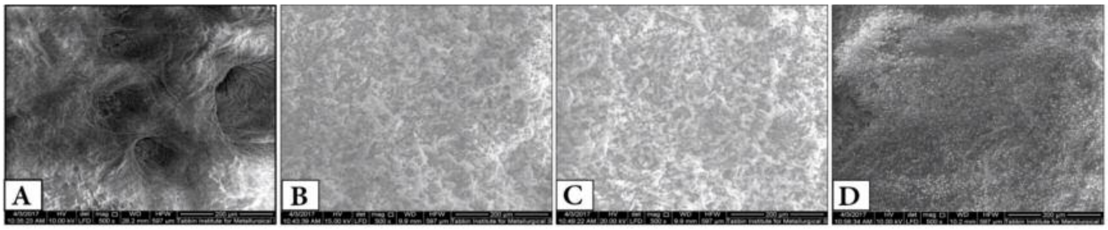
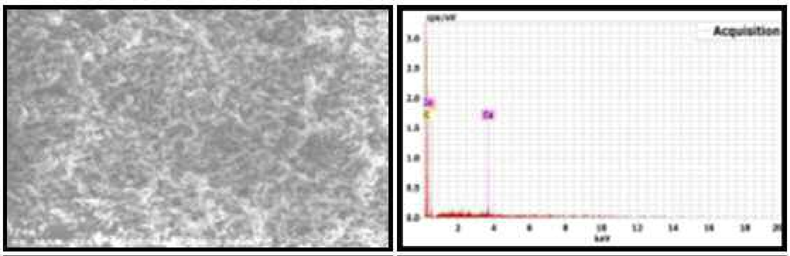


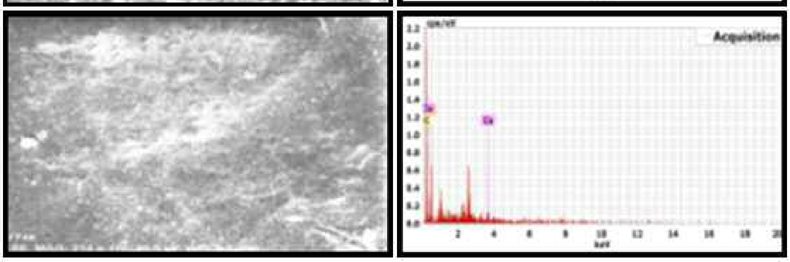
Figure 6. Investigation of the surface morphology by SEM: (**A**) Blank sample, (**B**) stained sample, (**C**) Aged sample, (**D**) Sample cleaned at 17.35W for 2 minutes.

A



Element	%
C	87.45
O	10.90
Ca	1.66

B



Element	%
C	58.90
O	39.96
Ca	1.13

Figure 7. EDAX analysis of stained leather before and after plasma cleaning: (**A**) stained sample before cleaning, (**B**) stained sample after cleaning.

TABLE II
Change of colour values for the soot stain before and after plasma cleaning

		Before cleaning			
Samples		L*	a*	b*	ΔE
Blank		84.54	5.54	10.31	–
Stained		33.66	2.75	5.30	51.21
Aged		24.04	0.53	2.00	61.27
		After cleaning			
Power (W)	Time (min)	L*	a*	b*	ΔE
5.48	½	47.57	5.34	9.12	36.99
	1	47.72	5.52	10.15	36.82
	2	49.67	5.47	9.61	34.88
2.21	½	53.43	5.76	10.33	31.12
	1	50.70	5.82	10.35	33.84
	2	52.30	6.51	12.29	32.32
7.35	½	43.87	4.62	8.76	40.71
	1	51.72	6.41	11.59	32.86
	2	50.33	6.16	11.99	34.26

TABLE III
Tensile strength and elongation of leather samples before and after cleaning

		Before cleaning	
Samples		Tensile strength (N)	Elongation (%)
Blank		21.00	28.33
Stained		20.33	20.00
Aged		13.67	13.33
		After cleaning	
Power (W)	Time (min)	Tensile strength (N)	Elongation (%)
5.48	½	22	32
	1	21	30
	2	21	25
12.21	½	21	25
	1	20	25
	2	19	24
17.35	½	18	24
	1	18	23
	2	17	21

3.6. Change of colour

Table II shows the change of components L*, a* and b* values and the total colour difference (ΔE) colour values for the different leather samples *untreated*: *Blank, Control, Ageing* and cleaned treated samples *Cleaning*. The colour difference values have been calculated as the comparison between the sample (blank) and the other samples. The results indicate that the addition of natural charcoal stains decreases the L* value, and this reduction increases with heat ageing. For the a* value, the results are for the red colour but the application of carbon stain and ageing leads to decreased red colour. For b* value, the colour was yellow and the yellow colour value also decreases after the application of carbon stain and heat ageing. This is due to the black colour of the natural charcoal. There is a significant reduction in the total colour difference (ΔE) for both stained and aged samples compared to the blank sample. The results after cleaning prove that, the cleaning with plasma at different conditions gives limited changes in the colour values and the total colour differences. The colour values (L*, a* and b*) increase with the increase in power (W) of plasma and time of cleaning. The cleaning at the conditions used revealed the aesthetic value of the samples. It is also noticed that the total colour difference reduces with the increase in power (W) of plasma and time of cleaning. Ioanid *et al.,*[33] used colour analysis for the evaluation of cold Radio-Frequency (RF) plasma in decontamination and cleaning treatments of paper documents. The results showed that 6 minutes of treatment are sufficient for sample decontamination. The colorimetric analysis showed a progressive increase in yellowing.

3.8. Mechanical properties (tensile strength and elongation)

Table III shows the tensile strength and elongation values of leather samples before and after cleaning. The results obtained reveal that the tensile strength and elongation of stained and heat aged samples decreases compared to the blank sample, but the reduction in tensile strength and elongation is higher in the aged sample. After plasma cleaning, the tensile strength and elongation increases after only ½ minute exposure time at all powers used. The increase in exposure time and plasma power leads to slight decrease in tensile strength and elongation. It can be said that the plasma enhances the mechanical properties of the leather samples. Li *et al.,*[34] used tensile strength tests to evaluate the plasma as a method for the deacidification of paper relics. The results showed that after aging, the tensile strength of the blank samples was reduced sharply to nearly 70%, while the plasma-treated samples still maintained more than 85% of their tensile strength. If we compare the aging measurements, the treated samples still have much better tensile strength, which means that the plasma treatment improves the mechanical properties, together with deacidification.

3.9 Fourier Transform Infrared Spectroscopy (FTIR-ATR)

Fourier Transform Infrared spectroscopy (FTIR) was employed to analyse the various components of the material and the possible induced changes after treatment with cleaning agents. The FTIR method can be used to investigate the effects of cleaning processes such as plasma or laser cleaning.[35]

Figure 8 (A to D) shows a typical FTIR profile of blank, stained, aged and cleaned (12.21W, 1min) samples respectively. It is clear from the data obtained (Fig. 8) that the intensity of the absorption band located at 2925cm^{-1} (-CH_3) decreases for both stained and aged samples more than blank sample as a consequence of oxidation processes and conformational changes. After plasma cleaning, the intensity of this absorption band was almost the same as the intensity of the blank sample. One can remark the appearance of an additional absorption band around 3070cm^{-1} in the stained and aged samples and which, again disappears after plasma cleaning and this may be due to the application of carbon stain.

In the (3650-3150cm^{-1}) ,-OH and -NH- regions, the band at 3360.63 wave number cm^{-1} indicated that N-H stretch decreases its intensity due to the application of carbon stain. The cleaned sample is very similar to the blank sample in the intensity and position of bands.

The main important change in FTIR spectra is found in the 1700-1450cm^{-1} spectral region, the amide I band (C=O stretch) at 1680 of the blank sample disappears due to carbon stain application before and after the ageing process and this band reappeared after plasma cleaning. The amide II band (N-H bending) of stained sample at 1560 becomes shifted for both carbon stained and aged samples explainable by the partial oxidation of carbon chemical bonds. This behaviour returns again to its origin but with less intensity. This illustrates that the cleaning by plasma did not affect the chemical stability of the treated sample.

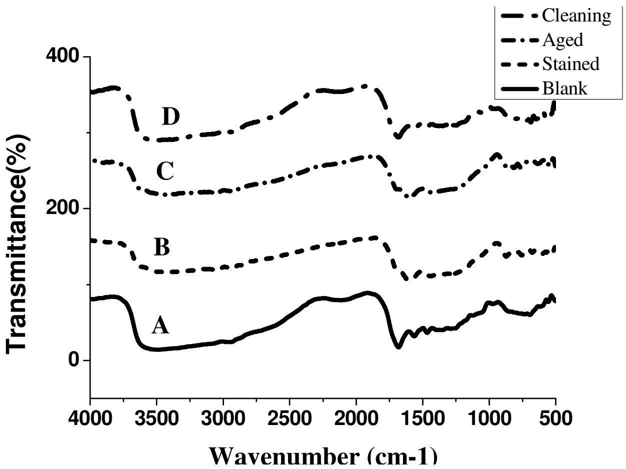


Figure 8. FTIR spectra of leather samples: blank, stained, aged, plasma cleaned.

4 CONCLUSION

Based on the results obtained from this paper, it can be concluded that atmospheric pressure Dielectric Barrier Discharge (DBD) cold plasma is a fast, effective method to remove and clean soot stain from the leather samples surfaces. DBD plasma is a simple maintenance reducing the risks of additional deterioration of brittle bookbindings, minimizing the manipulation required by the classical conservation-restoration procedures. It is a green method since it does not require the use of chemical reagents nor high amounts of energy. Finally, the lack of need for expensive vacuum equipment makes it a cheaper and more accessible technique.

Decontamination, removing and cleaning of soot stain from the leather samples surfaces is evident and complete after only ½ minute of treatment even in the samples with a high degree of contamination. Both bulk and surface investigation and analysis methods have been employed and the resultant data show that plasma acts only on the top nanometer layers of the sample and does not alter the bulk of the leather material. The action of cold plasma recommends that this method can be used for decontamination of the cultural heritage objects based on natural protein materials. Plasma does not imply a degradative effect and the integrity of the leather artifacts is preserved. All results confirmed that the increase in plasma power and exposure time increases the efficiency of plasma to remove carbon stain.

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