

Radio-Frequency Plasma Discharge Equipment for Conservation Treatments of Paper Supports

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Abstract—The application of cold Radio-Frequency (RF) plasma in the conservation of cultural heritage became important in the last decades due to the positive results obtained in decontamination treatments.

This paper presents an equipment especially designed for cold RF plasma application on paper documents, developed within a research project. The equipment consists in two modules: the first one is designed for decontamination and cleaning treatments of any type of paper supports, while the second one can be used for coating friable papers with adequate polymers, for protection purposes. All these operations are carried out in cold radio-frequency plasma, working in gaseous nitrogen, at low pressure.

In order to optimize the equipment parameters ancient paper samples infested with microorganisms have been treated in nitrogen plasma and the decontamination effects, as well as changes in surface properties (color, pH) were assessed. The microbiological analysis revealed complete decontamination at 6 minutes treatment duration; only minor modifications of the surface pH were found and the colorimetric analysis showed a slight yellowing of the support.

Keywords—Cultural heritage, nitrogen plasma, paper support.

I. INTRODUCTION

THE cultural heritage paper-based objects suffer various deteriorations in time due to natural aging, functional wearing, environmental factors (humidity, temperature, UV radiation) or degradation caused by microorganisms (bacteria and fungi) [1], [2]. The survival of paper documents is assured by restoration and conservation techniques consisting mainly in microbiological decontamination, cleaning, and reinforcement. The very brittle paper documents may also require a protective coating with appropriate polymers.

Non-thermal plasmas, characterized by relatively low neutral gas temperature, have been extensively studied due to their application in bacterial inactivation and surface treatments, such as cleaning and functionalization. The need of less noxious disinfection treatments of sensitive objects

based on natural polymers [3] led to the introduction of plasma in the field of cultural heritage conservation [4]-[7]. Additionally, cold plasma offers the advantages of lack of hazardous waste, low operating costs and short treatment times [8]. The use of various gases in plasma treatments of cellulosic substrates lead to improved surface characteristics such as mechanical (strength, hardness, abrasion resistance) and electrical properties (dielectric coefficient, conductivity) or to modification of surface chemistry (oxidation, wettability or water repellence, etc.) [9].

Cold plasma application in the conservation sciences was directed to decontamination of inorganic or organic materials [10]-[13], deposition of protective thin films on paper and paintings cleaning [14], [15].

Some of our previous studies have been oriented on plasma decontamination and cleaning effects on cellulose based materials, experiments performed on RF cold plasma or Corona discharge equipments [16], [17].

The preliminary findings indicate the possibility of using RF plasma discharge for modifying surface properties of paper within nanometer depth, thus rendering the paper better suited for subsequent coating with water-soluble polymer derivatives, without affecting its bulk properties.

The paper presents RF plasma discharge equipment designed for conservation treatments, consisting in decontamination, cleaning and protective coating.

II. EXPERIMENTAL PART

A. Materials

The experiments and the analysis have been performed on two types of paper:

- M₁— religious book, dated in XIX century, textile fibers hand-made paper – for microbiological, color and acidity analyses
- M₂ – industrial paper made of wood cellulose, beginning of XX century – for color and FTIR analysis after coating

B. Biological Analysis

The paper samples were soaked in sterile distilled water (5 mL) for a few seconds. The suspension obtained has been used to inoculate culture media prepared in advance and distributed in Petri dishes. In order to determine the two taxonomic microorganism groups, special culture media have been used namely nutrient agar broth for bacteria and Sabouraud media for fungi. The bacteria samples were incubated at 37°C for 48 h, while the fungi samples were incubated at 28°C for 7 days. The results were analyzed by counting the number of colonies grown on the surface or in deepness of culture media, the

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result being expressed as CFU (colony-forming units)/mL

B. Color Analysis

The evaluation of color changes was carried out with POCKET SPECT COLOR QA™ by a CIELAB system. The system is based on tristimulus values (X, Y, Z) represented in Cartesian $\cdot 10^{-1}$ or cylindrical coordinates.

The yellowness index is given by the relation:

$$YI = [100 (1.3013 \cdot X - 1.1498 \cdot Z)] / Y$$

where X, Y, and Z are the trichromatic coordinates values.

C. Acidity Analysis

A digital pH-meter WTW-Germania, model PH 526 was used for acidity determination.

D. Plasma Treatment

The three stages of preservation process – decontamination, cleaning and protective coating can be carried out using RF cold plasma treatments [13], [18]. A specialized two-modules cold plasma equipment was developed, designed for treating very friable paper documents.

Module A (Fig. 1), designed for decontamination treatment in RF cold plasma, consists in 1.2MHz RF generator (1), a cylindrical Pyrex-glass reactor (2) and two aluminum plane-parallel electrodes (3). The reactor is placed on stainless steel support (8) with apertures for gas admission, temperature probe, vacuum meter probe, vacuum pump coupling and two vacuum passages for electrodes. The equipment is completed with a needle valve, a vacuum meter, a temperature meter, gas pressure regulator, the gas bomb and the vacuum pump.

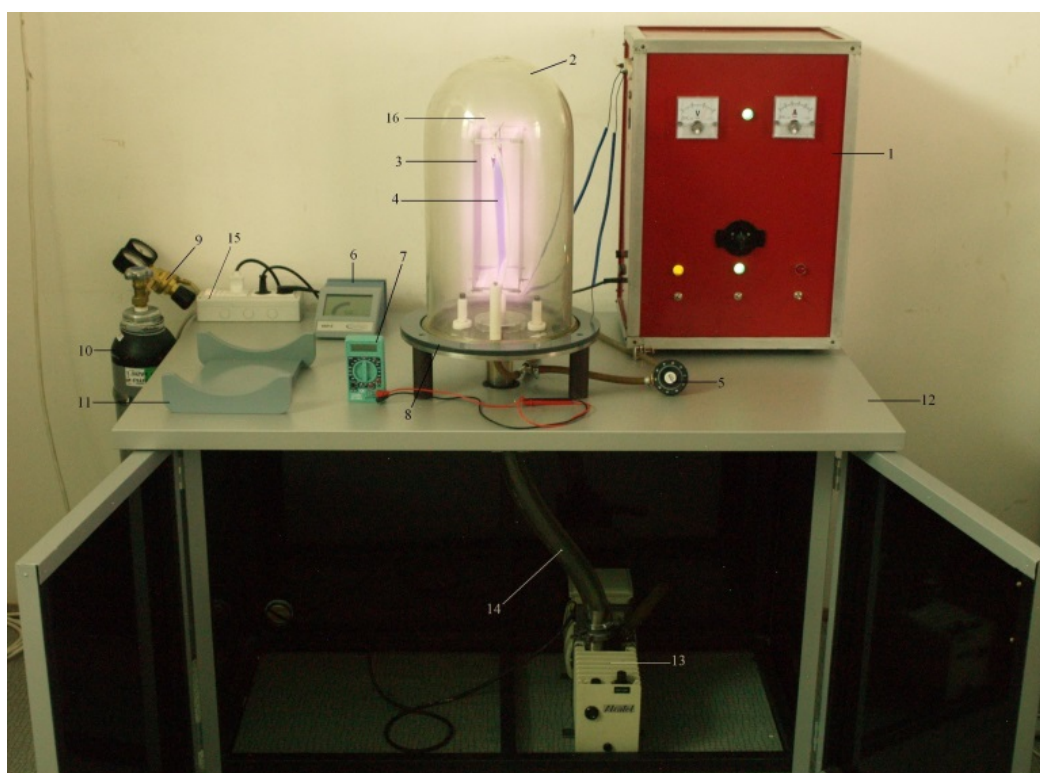


Fig. 1 Module A Legend: 1–RF generator; 2–Pyrex glass reactor; 3– plan -parallel electrodes; 4–paper document; 5–needle valve; 6–vacuum meter; 7–temperature meter; 8–stainless steel support; 9–gas pressure regulator; 10–gas bomb; 11–support for the reactor; 12–working table; 13–vacuum pump; 14–zeolite filter; 15–electric outlet; 16–gas admission

The B module (Fig. 2) consist in DC high voltage generator (17) (8-9 kV), metallic frame (18), mobile aluminum support plate (19), corotron (20), blade (21) for polymer displaying, transfer foil (22) and a displacement system for the document (23).

The module B fulfills two functions:

- electrostatic fastening of the document on acetofan transfer foil
- coating of the friable document with a protective polymer film

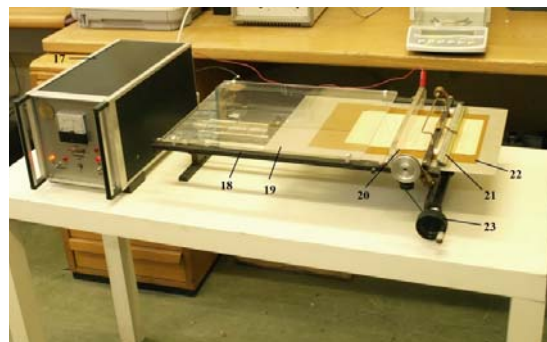


Fig. 2 Module B

1. The Operating Procedure

The document is electrostatically fixed on the transfer foil by sliding under the corotron. The ensemble document-foil is placed on one electrode of module A (Fig. 3 shows it in detail).

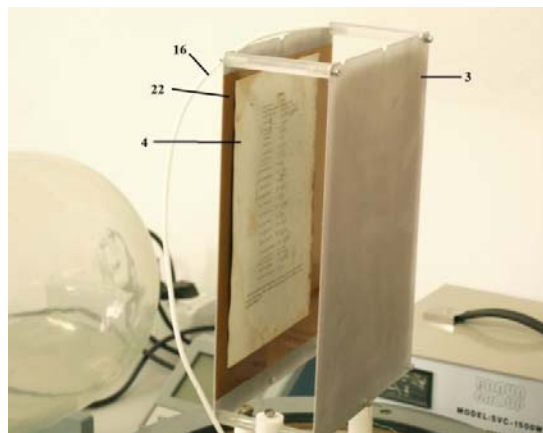


Fig. 3 Document positioning on the electrode for decontamination treatment - detail

After the established duration of plasma treatment the ensemble is placed again on the support plate of the B module for protective coating (Fig. 4).

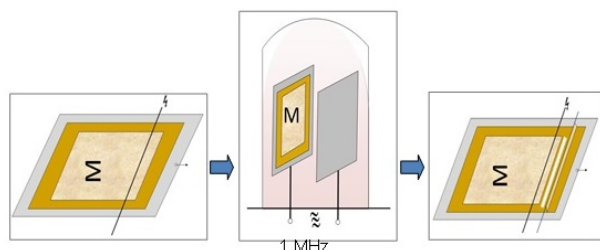


Fig. 4 The operation procedure

An established quantity of polymer is deposited on the transfer foil surface, in an area between the corotron and the displaying blade. The polymer displaying onto the document surface is made manually or electrically, by passing the document under the corotron, connected at 9kV DC, and the displaying blade.

Later studies led to the modification of reactor (1) geometry, so the B module was incorporated in the A module (Fig. 5). Two slides bars (2) are mounted inside the reactor and the mobile electrode (3) (made of duralumin) performs a come and go displacement on these slides, the rectilinear movement being imparted to the electrode by a reversible electric engine. For decontamination and polymer coating the ensemble transfer foil (4) - document (5) is placed on the mobile electrode drawn out the treatment chamber and then is introduced in the reactor. After vacuuming the reactor a discharge is initiated between the mobile electrode and a second electrode (6), fixed at the upper part of the reactor. An established quantity of polymer is deposited on the surface of

transfer foil, between the corotron (7) and the document's border. The ensemble is dragged first under the corotron, connected to the high voltage source, performing the electrostatic fixing of the document, than under the displaying blade (8) of the coating device, for polymer spreading over document's surface.

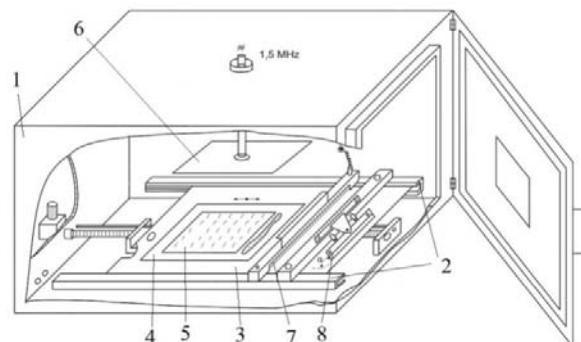


Fig. 5 Multipurpose equipment for the conservation of paper - based documents

TABLE I
RESULTS OF DECONTAMINATION TREATMENT

Duration (min)	Microbiological analysis		Yellowness degree	Surface pH
	Bacteria (CFU/ml)	Fungi (CFU/ml)		
0	7	47	1.17	7.09
4	1	4	2.31	6.85
6	0	0	2.77	6.48
8	0	0	3.04	6.6

III. RESULTS AND DISCUSSION

In order to optimize the equipment treatments in nitrogen plasma have been performed on samples infested with microorganisms, with durations of 4, 6, and 8 min. Plasma parameters:

- pressure: $5 \cdot 10^{-1}$ – $5.5 \cdot 10^{-1}$ mbar;
- operating gas: nitrogen
- maximum temperature: 35° C
- electric field intensity: 50V/cm
- power in the discharge: 40W
- current intensity in the discharge: 100mA
- distance between electrodes: 8cm.

The results (Table I) show that 6 min. of treatment are sufficient for sample decontamination. The colorimetric analysis shows a progressive increase of yellowing degree, while the pH value change is insignificant. In the final stage, a polymer layer for consolidation and protection has been applied on M₂ type paper using B module. The document was coated on one side using 0.62g of methyl cellulose per square meter. In order to verify the effect of the procedure on the paper aspect, as well as the degree of surface coating, yellowness index and ATR-FTIR analysis have been performed

A. Yellowness Degree

The high initial value of yellowness degree is a consequence of oxidative degradation of the lignin content in the raw material from which the paper has been made.

The polymer coating results in an increase of yellowness degree from 73.1 to 77.16.

B. Coating Uniformity:

At least five separate areas on each individual sample were analyzed to determine the chemical homogeneity of the surface-modified sample. It was noticed that all ATR-FTIR spectra (Fig. 6) present the same in intensity and have the same allure, indicating that the coating with methylcellulose is homogeneous. After methylcellulose deposition onto plasma treated paper different changes appears in ATR-FTIR spectrum at 3000-2600 cm^{-1} and 1750-1100 cm^{-1} wavenumber range (see the highlighted regions in Fig. 5) which are associated with $-\text{CH}_3$ stretching on anhydroglucose unit at 2962 cm^{-1} , $-\text{CH}_2-$ stretching on anhydroglucose unit at 2860 cm^{-1} , C=O carbonyl stretching in the anhydroglucose unit of the cellulose at 1643 cm^{-1} , C-OH the in plane bend at 1440 cm^{-1} , CH_3 symmetric bend at 1375 cm^{-1} , C-O stretching from asymmetric oxygen bridge at 1163 cm^{-1} [19].

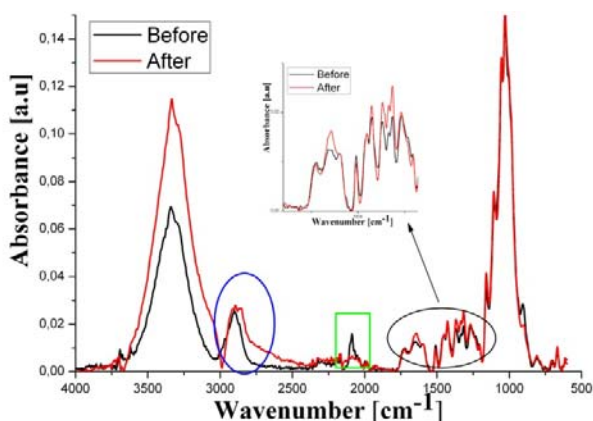


Fig. 6 Samples FTIR spectra

IV. CONCLUSION

The equipment offers the following advantages:

- assures the possibility of performing decontamination, cleaning and protective coating of paper-based documents in successive stages, avoiding the re-contamination with harmful biological agents
- performs an ecological, dry, non-contact procedure
- assures better adherence between the paper document and the protective polymer
- reliable, simple and cheap maintenance

The equipment reduces the risks of additional deterioration of brittle paper document minimizing the manipulation required by the classical conservation-restoration procedures.

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