Revue Roumaine de Chimie, **2007**, *52*(4), 441–447

NEW TENDENCIES IN RESTORATION-CONSERVATION: THE HF PLASMA. II

DECONTAMINATION TREATMENT IN COLD PLASMA

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Received October 31, 2005

This work is focussed on the cold plasma utilization in the restoration and conservation of the inheritance objects (made of natural polymers) in decontamination treatments for destroying or eliminating the microorganism, meant to return them the esthetical aspect and, if possible, their function. The treatments of polymer materials in plasma created by the glow discharge of a air-free gas in a HF current, were materialized by microbiological analyses, scanning electronic microscopy (SEM), thermo-gravimetric and colorimetric analyses, contact angle method and document images.

INTRODUCTION

At the beginning, plasma was studied as the glow discharge phenomenon occurring in a low pressure gas. These studies led the plasma from the laboratory to industry, finding applications in aeronautics, semiconductors and electronic industries. The processes taking place in plasma as result of the interactions between particles and the solid surfaces of certain materials exposed to it permitted plasma utilization for cleaning corrosion and superficial treatment of the most diverse materials, in order to modify their properties or to induce new ones.

This work, part of a more extended study on the plasma treatment used in restoration and conservation,[1,2] presents the HF cold plasma utilization in the process of decontamination of certain pieces belonging to the cultural inheritance being in different states of microbiological contamination. The decontamination is a physical or a chemical process that destroys or eliminates any kind of viable microorganism (fungi, bacteria) and their spores and represents a compulsory preliminary phase in the restoration-conservation process. This process is carried out in a classical way by using toxic substances, damaging for both the object and the restorer, while the HF plasma decontamination represents a non-destructive, non-toxic, ecological and efficient method.

This work has followed the influence of the working conditions (treatment duration and frequency) on the plasma biocidal effect, as well as the effects of this treatment applied to organic or inorganic materials, with the view to reveal possible degradations that they might have suffered.

EXPERIMENTAL

In order to carry out the decontamination treatment, a modular specialized installation was used. The installation, presented in Fig. 1, consists of a reactor (1), a liquid nitrogen trap (3), a vacuum pump (4), the whole set being connected to a command and control block (5). The pressure in the reaction vessel is adjusted by means of a needle valve (6) and is measured with the pressure gauge (7). The reactor from Fig. 1, used for two-dimensional flexible materials, is made of a pyrex-glass vessel endowed with concentric cylindrical electrodes. The piece (9) subjected to treatment is set on a stainless steel grid (10) placed between the electrodes. The reactor from Fig. 1 can be replaced by another reactor presented in Fig. 2, when three-dimensional rigid pieces are to be treated. The second type of reactor (Fig. 2), destined for treating three-dimensional pieces, is endowed with plane-parallel electrodes (8). The piece (9) to be treated is driven in rotation by an electric motor (11).

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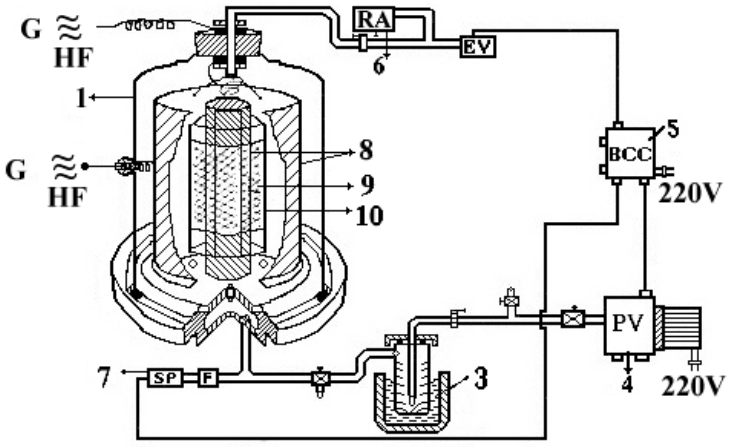


Fig. 1 – Modular installation for plasma decontamination of two-dimensional flexible objects.

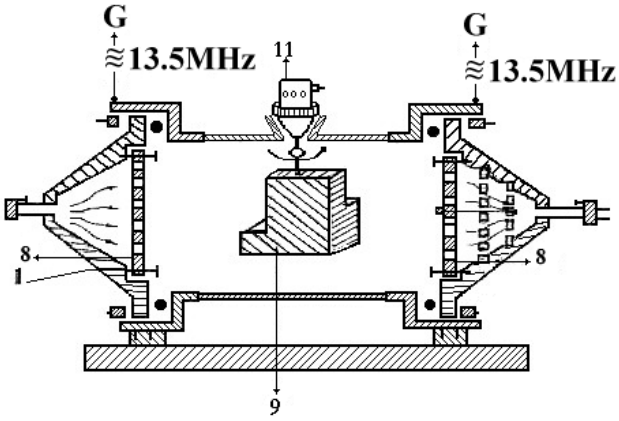


Fig. 2 – Reactor for the decontamination of three-dimensional rigid objects.

The HF discharge in the reaction vessel is ignited and maintained by the generator (G) with the frequency of 1.2–13.5 MHz.. In order to keep constant the HF glow discharge parameters during the treatments, the generator (G) is equipped with a master oscillator with adjustable frequency within the range 1.2–1.5 MHz and a load tuned power amplifier. A control-command block (5) adequately connected to magnet valves, pressure and temperature sensors, permits to establish the gas pressure and flow within the reactor.

The experiments have been carried out under the following working conditions: temperature 40 ÷ 50°C, pressure 3.5 ÷ 7.5· 10^{-1} mbar, frequency 1.2 and 1.35 MHz, electric field intensity 20 ÷ 50 V/cm, glow power 100 W, the utilized gas- air, the treatment duration being 30 and 60 min. respectively. The samples were placed directly in the plasma region.

The studies have been carried out on:

• Witness sample – consisting of glass plates and wool specimens on which a suspension of *Aspergillius niger* fungal spores were deposited.

• Samples consisting of microbiologically infested specimens, taken from inheritance objects made of organic matter (leather).

• Samples consisting of inheritance objects made of inorganic (metals) materials.

The results of decontamination treatments were materialized by microbiological analyses, scanning electronic microscopy (SEM), thermo gravimetric and colorimetric analyses, contact angle method and document images.

The microbiologic analyses consisted of insemination on special culture mediums. The techniques of stria description (after scrapping the material surface) were used. As selective insulation mediums were used gelose for bacteria and Sabouraut medium for fungi. The incubation was performed at 37°C for 24 hours for bacteria, and 7 days at 28°C for fungi.

The electronic microscopy images were obtained with a scanning electronic microscope type TESLA BS 301 with secondary electrodes, for the examination of the samples fixed on aluminium substrates. The samples were gilded by cathode evaporation.

The thermo-gravimetric analyses were performed using a derivatograph type Q_2- 1500 DMOM. The measurements were carried out in air at a heating rate of 10°C/min, from 0°C to 700°C.

The colorimetric measurements were performed using a device type SPECTROFLASH SF- 300 Data color, which measures the color difference, using the CIELAB system.

The contact angle was measured with a laboratory prototype.

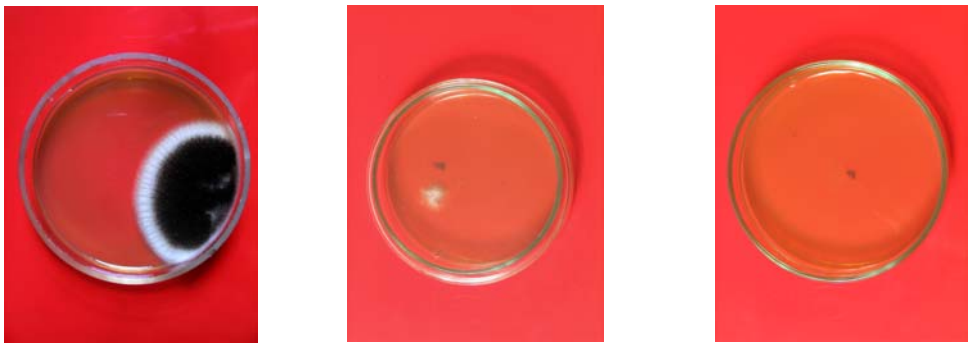
The document images were obtained by taking pictures to the microbial colonies with a digital camera type DSC- P73.

RESULTS AND DISCUSSION

In a first stage, we treated the witness specimens consisting of glass plates on which a suspension of *Aspergillius niger* fungal spores was deposited. The results of the witness specimens determinations were demonstrated using the insemination on culture mediums, and scanning

electron microscopy. Both methods rendered evident the biocidal effect of HF plasma.

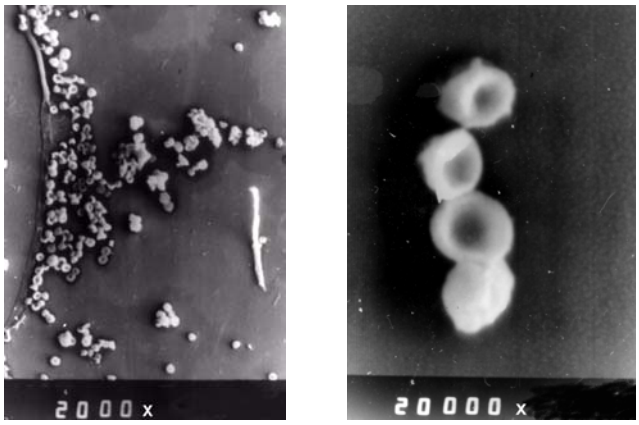
When the untreated witness sample was introduced in the culture medium, it formed colonies with hypha morphology (Fig. 3a). The sample surface turned brown, black micelles being noticed. The witness samples treated in plasma for 30 min and 1 h respectively were not capable of germination when introduced in a favorable medium (Figs. 3b, 3c), which indicates the lack of spores activity.



a) b) c)

Fig. 3 – The aspect of fungal colonies (*Aspergillius niger*) deposited on glass substrate, before and after the plasma treatment: a – witness sample; b – sample treated for 30 min; c – sample treated for 1 h.

The images obtained with the scanning electron microscope for untreated samples and plasma treated samples (30 min and 1 h respectively) are presented in Figs. 4 and 5. The untreated spores which are deposited on the plate surface individually or in groups, show no deterioration, a slight collapse being noticed (Fig. 4b). In the case of plasma treated samples, the mechanism of spores surface erosion was obvious, these being almost completely removed in the case of the samples subjected to a longer treatment of 1 h (Figs. 6b, 6d). In the case of a long treatment of the superficial surfaces, the volatilization of the biologic material occurs, as in the case of synthetic polymers such as polyethylene or polypropylene.

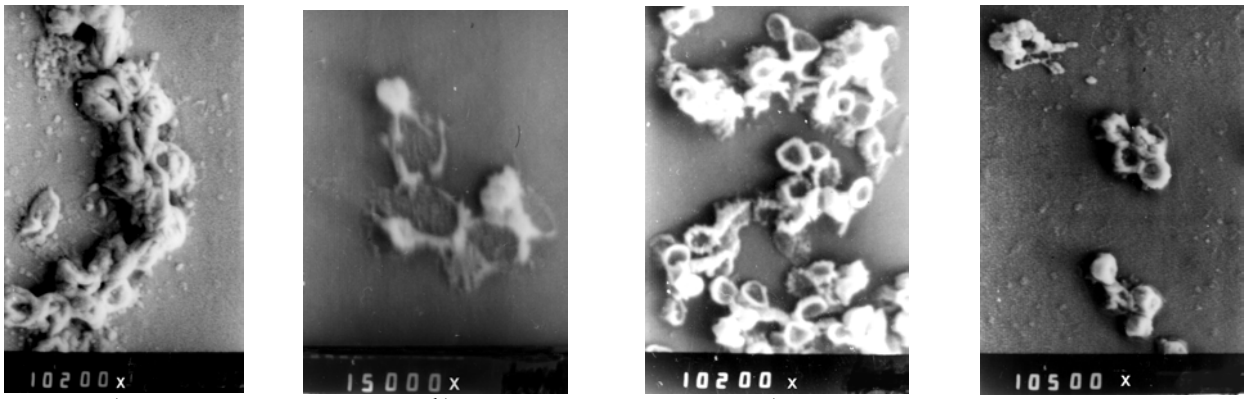


a) b)

Fig. 4 – Electronic microscopy images of fungal spores (*Aspergillius niger*) deposited on glass substrate before plasma treatment: a – global image; b – detail.

At low frequency, the discharge behaves like a d.c. discharge, with limitations concerning the minimum firing frequency. As the frequency increases, the minimum operation (firing) pressure starts to decreases, having a value lower that 1 mtorr at 13.56 MHz. For a given pressure, the discharge impedance decreases with increasing frequency such that through the discharge, a larger current is driven at a given voltage. That is why both the frequency and the electric field intensity

are important in electron motion determination.[7] For this reason, due to additional ionization, the electrons collision becomes an important mechanism. Yet, the reactions within the HF plasma do not depend very much on frequency, and therefore frequencies within the range 1-60 MHz can be used, and mainly 13.56 MHz, a frequency available for the power sources.[8] This aspect was proved by treating the biological material deposited on glass plates at two frequencies: 1.2 MHz- the minimum value of the optimum working frequency interval, and 13.56 MHz the value currently available at the power sources.

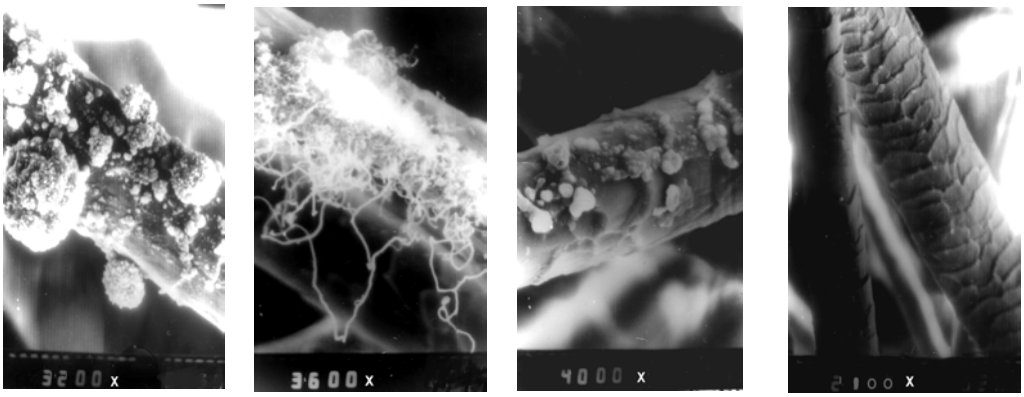


a) b) c) d)

Fig. 5. Electronic microscope images of fungal spores (*Aspergillius niger*) deposited on glass substrate, after the plasma treatment: a – sample treated for 30 min. at a frequencyof 13.5 MHz; b – sample treated for 1 h at 13.5 MHz; c – sample treated for 30 min. at 1.2 MHz; d – sample treated for 1h at the frequency of 1.2 MHz.

For the both treatment intervals, the images obtained with the scanning electron microscope indicate a high degree of erosion destruction (Fig. 5a, b, c, d). The reactions in HF plasma do not depend on frequency to a large extent.[1]

The plasma biocidal effect can be also noticed during the decontamination carried out on wool cloth samples, on which a suspension of *Aspergillius niger* fungal spores was deposited, revealed by the scanning electron microscope images in Fig. 6.



a) b) c) d)

Fig. 6 – Electron microscopy images of the wool cloth samples infested with fungi (*Aspergillius niger*):
a – fibers with untreated spores; b – sample with untreated hypha; c – fiber decontaminated for 30 min.; d – fiber decontaminated for 1 h.

In the images from Figs. 6a and b, which represent the samples non-decontaminated in plasma, fibers can be notices with spores groups and layers (Fig. 6a) and wool fibers on which fungi developed. One can also notice the presence of filaments (hypha), conidiophores and conidia (spores) (Fig. 6b). After the decontamination treatment the disappearance of hypha can be noticed, as well as the disappearance of spores deposits on fibers (Fig. 6c), which is complete after one hour of treatment (Fig. 6d).

The high frequency plasma decontamination was also carried out on samples consisting of microbiologically infested specimens, with Gram positive bacilli and *Aspergillius niger fungi* (Fig. 7a, b, c), taken from inheritance objects made of organic (leather) and inorganic (metals) materials. The biocidal plasma effect was proved by document images taken before and after decontamination treatment (Fig. 7) and scanning electron microscopy – SEM (Fig. 8).

The microbiological analyses carried out on samples taken from decontaminated objects confirm the inactivation of the identified microorganisms. This phenomenon is due to the plasma reactive species (especially the monoatomic oxygen) whose action has deep effects in cells by reacting with different types of macromolecules, components of the cells wall and the genetic material (DNA).[6] The monoatomic oxygen has one of the smallest atomic rays, as compared to any other elements from the periodic table, which permits its fast diffusion through membranes. On the plasma treated specimens no microorganisms colony developed after incubation on specific nutrient mediums (Fig. 7d,e,f). In the case of the metallic ring, one can also notice the presence of a cleaning treatment accompanying the decontamination treatment (Fig. 7f).

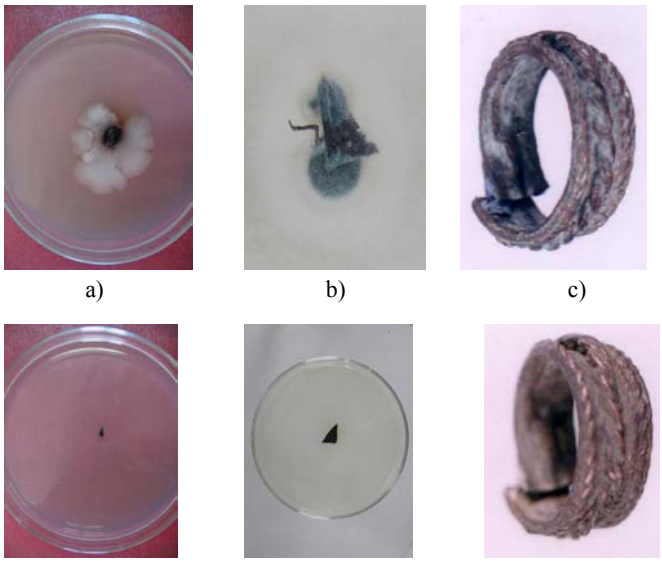
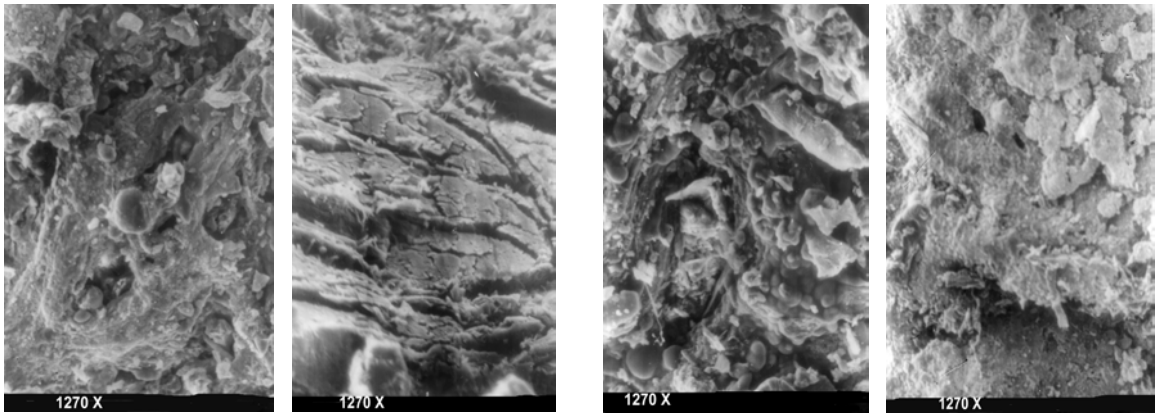


Fig. 7 – The aspect of the microorganisms colonies developed on inheritance objects specimens, untreated and plasma treated respectively: a – leather infested with Gram positive bacilli – untreated; b – leather infested with fungi (*Aspergillius*) untreated; c – metallic ring infested with fungi and bacteria – untreated; d – leather infested with Gram positive bacilli – treated; e – leather infested with fungi (*Aspergillius*) – treated; f – metallic ring infested with fungi and bacteria – treated.

From the scanning electron microscope images one can notice the presence of spores agglomerations on the infested dermal material (Fig. 8 a, c). Both the samples treated for 30 min. in plasma, and those treated for 1h were decontaminated. Individual protein fibers and compact zones can be noticed, but on the SEM inspected surfaces no spores appear. This aspect proves not only the spores inactivity, but also their removal by erosion mechanisms.

It is well known that the plasma treatment of the polymeric materials can produce certain modification of the material superficial characteristics, consisting in modifications of the chemical composition, molecular mass and the superficial layer morphology. The effects of the plasma treatments are restricted to a layer whose size ranges between 50 Å and 10 μm. In order to estimate the effect of the decontamination treatment on the organic materials the inheritance objects are made of, the behavior of the natural polymer (leather, wool) under the influence of the plasma active species has been studied, the results being proved by physical-chemical analyses.

The scanning electron microscopy method proved the preservation of the integrity of treated protein material (Fig. 8a, c), as well as the fibrilary structure specific to collagen fibers persisting even after the treatment (Fig. 8b, d).



a **b** **c** **d**

Fig. 8 – Electron microscope images of the leather specimens: a – spore infested sample- untreated; b – spore infested sample- treated for 30 min; c – spore infested sample- untreated; d – infested sample- treated for 1h.

In the case of the wool cloth, after 1 h of treatment only a volatilization of the biologic material occurs, while no morphological modification of the wool fiber can be noticed (Fig. 6c, d). At the same time, neither the melting nor the re-crystallization zones are destroyed on the leather or wool samples. The microscopic examination shows no major modifications at the supra-molecular structure level of the plasma treated organic material.

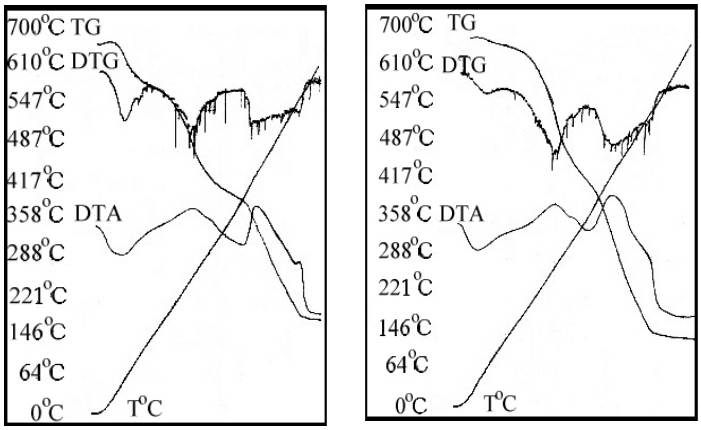


Fig. 9 – Thermographs accomplished on dermal substrate before (a) and after (b) the plasma treatment.

The same result was also confirmed by the thermo gravimetric method (Fig. 9), that does not evidence any modifications in the material inner structure (dermal substrate), as well as by the colorimetric method, the recorded color turnings being insignificant. The color differences between the plasma treated and untreated samples is 2.547 for the leather sample, and 1.673 for the wool cloth. As the result of the superficial chemical modifications, an increase of the wettability can be noticed, proved by the contact angle measurements. While for the leather samples an insignificant wettability modification was found, the contact angle value changing from 28° to 23°, for the plasma treated wool cloth samples the increase is significant, the contact angle value changing from 140° to 85°.

CONCLUSIONS

Cold plasma is an adequate technique for decontamination of inheritance objects The method was applied to a number of categories of organic materials and metals. One can notice that:

The decontaminating effect of the HF cold plasma determined a severe erosion of spores agglomerations.

It does not degrade the natural polymeric fibers by the action of cold plasma.

The superficial chemical modifications do not go deeper.

REFERENCES

1. E. G. Ioanid, A. Ioanid, S. Dunca and I. Neamțu, *Proc. 8thNational Symposium of Restoration – Conservation ,,RESTAURARE 2000"*, Iași. 2000, 69.
2. S. Lerouge, A. C. Fozza, M. R. Wertheimer, R. Marchand and L'H Yahia, *Plasmas Polymers,* **2000**, *5*, 31–46.
3. B. Chapman, "Glow Discharge Processes, A Wiley – Interscience Publication", J. Wiley & sons, New-York, 1980, p. 139.
4. N. Philip, B. Saoudi, J. Barbeau, M. Moisan and J. Pelletier, *13th Int. Coll. Plasma Processes (SFV)* Antibes 2001; *Le vide : Sci. Tech. Appl. Numero special : Actes de Colloque,* 245–247.
5. V.A. Khomich, I. A. Soloshenko, V. V.Tsiolko and I. L. Mikhno. *Proc.12th International Conference on Gas Discharge and their Applications,* 1997, Greifswald, *2*, 740–744.
6. M. Moisan, J. Barbeau, M. – C. Crevier, J. Pelletier, N. Philip and B. Saoudi, *Pure Appl.Chem.,* **2002**, 74, 349–358.
7. L. H.Coopes, K. J.Gifkins, *J. Macromol. Sci. Chem*., **1982**, *A17*, 217–226.
8. J. Pelletier, *Agressologie*, **1993**, *33*, 105.