Energy-Effective Plasma-Chemical Surface Modification of Polymers and Polymeric Materials at Atmospheric Pressure

Peter Dineff, Dilyana Gospodinova*
Technical University of Sofia
8 Kliment Ohridski Blvd, Sofia 1756, Bulgaria
Phone: +0359 2 965 3753, E-mail: dilyana@elap.vmei.acad.bg,
Mailing address: Bulgaria, Sofia 1756, Technical University, Department of Electrical Apparatuses

ABSTRACT: The plasma-chemical surface modification performed at atmospheric pressure through corona or barrier air discharges is characterized by a specific change in the surface density of the active electric power. Two characteristic regions of changes in the surface density are observed: the first one, up to 25 W/m2, is the energy- and technology-effective region of the oxygen-containing technological plasma, and the second one, above 100 W/m2, the energy- and technology-ineffective region of plasma containing mostly nitrogen oxides.

Based on experimental investigations of the plasma-chemical modification of high-porous non-woven textile on the basis of polyethylene terephthalate, it is proposed to use the surface density of active power as a basic parameter of the technological process. Using that parameter permits defining the energy- and technology-effective region of this process.

Keywords: corona discharge, oxygen-containing plasma, plasma surface modification, surface density of active power.

I. INTRODUCTION

It is well known that as a result of plasma-chemical oxidation of the carbon the ozone- and oxygen-containing cold plasma of the barrier discharge is in position to create diverse oxigen-containing functional groups (C-O, C=O, O-C=O, C-O-C, and COOR) onto the polymer surface. These are the so-called active surface centers modifying the lyophobo-lyophilic equilibrium of the surface and determining its chemical actuation [1] – [2].

Concurrently with this, processes of plasma-chemical etching go on as well. They modify the surface micro-relief, increase its area, and also influence the lyophobo-lyophilic equilibrium and wetting of the surface [1]. There have also been noticed processes of cross-linking by oxygen bridges in the polymer surface layer, which are most probably a result of the penetration of excited oxygen molecules into the bulk of the polymer matrix [2].

Paper accepted for presentation at the 3rd Mediterranean Conference and Exhibition on Power Generation, Transmission, Distribution and Energy Conversion MED POWER 2002, jointly organized by National Technical University of Athens, IEE Hellas, Israel and Cyprus, Athens, Greece, November 4-6, 2002

The task of the present work consists in proposing technology-effective and energy-profitable regimes of the barrier discharge, based on an analysis of the elementary processes of ionization and recombination going on in the plasma itself. A correspondence between the type of the volt-ampere characteristic of the discharge and those elementary processes is sought for.

II. STATIC VOLT-AMPERE CHARACTERISTIC

The elementary processes of ionization, ion re-charging and recombination are realized by exchange, i. e. by giving and accepting electrons. The processes of oxidation and reduction as well as those of etching and cross-linking are of the same nature. This permits to connect directly the technological effectiveness with the average value of the electric discharge current I_{moy}, that can be measured experimentally, Fig. 1 [3].

The static no-load volt-ampere characteristic of the barrier discharge between two plane electrodes placed at a distance of 3 mm, i. e. without any material to be treated in the air gap, has the appearance shown in Fig, 2.

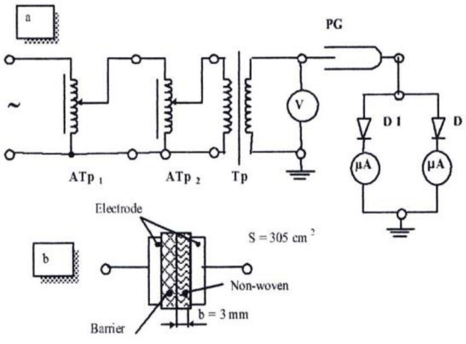

Fig. 1. Electric circuit for measuring the volt-ampere characteristic: the average value of current I_{moy} and. the effective value of voltage U_{eff}.

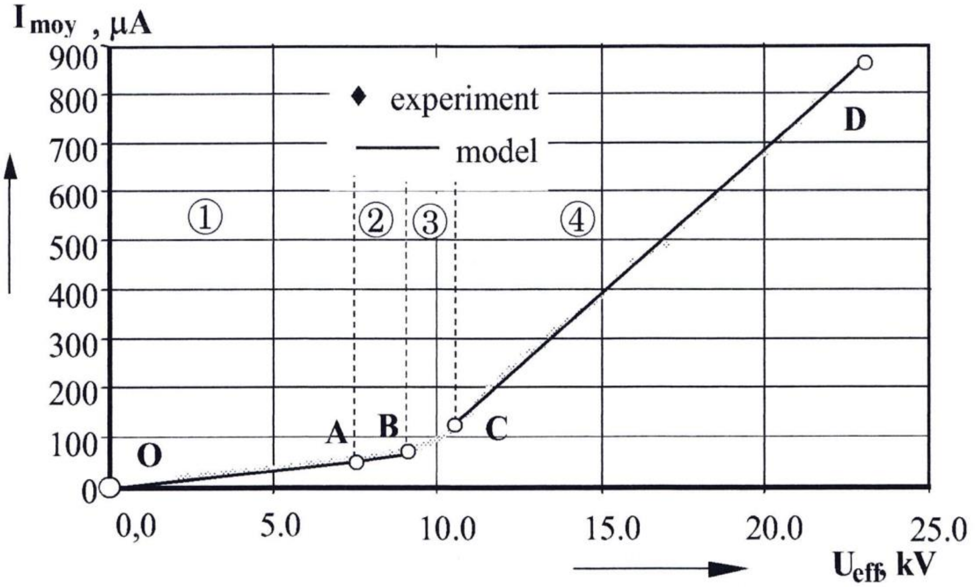

Fig. 2. Static volt-ampere characteristic of barrier discharge: variation of the average value of current I_{moy} with that of applied voltage U_{eff}.

Four characteristic regions of the barrier discharge are clearly distinguished: ◆ region **OA** corresponding to the occurrence of capacity current through the discharge gap and through the dielectric barrier (glass), there is no electric discharge yet; ◆ regions **AD** or **AB**, **BC**, and **CD**, corresponding to the presence of electric current through the air gap in the conditions of electric discharge.

The existence of those three regions **AB**, **BC** и **CD** can mean only one thing: the electric discharge is realized by three different elementary processes of ionization and deionization, going on in the air gap.

Region **OA** can be linearized with a coefficient of linear correlation $r_C = 0.9994$, U_{eff} in V, Fig. 2:

$$(1)\quad I_{moy} = A_I\, U_{eff} + B_I = 75.495\, U_{eff} - 35.971,\ \mu A.$$

Region **AB** is also susceptible to linearization at $r_C = 0.9941$, U_{eff} in V, Fig. 2:

$$(1)\quad I_{moy} = A_O\, U_{eff} + B_O = 94.857\, U_{eff} - 175.676,\ \mu A.$$

Region **CD** is linearized as follows at $r_C = 0.9993$, U_{eff} in V, Fig. 2:

$$(2)\quad I_{moy} = A_N\, U_{eff} + B_N = 584.621\, U_{eff} - 4861.064,\ \mu A.$$

The linear character of the volt-ampere characteristic variation in electric discharge region **AD** means that the voltage drop across discharge gap does not depend on discharge current, i. e. that drop remains constant irrespective of current variation, Fig. 3.

This fact allows the assumption of two different mechanisms of barrier discharge existence in the regions considered, whereas region **BC** is perceived as a transition region between these two mechanisms of the existence of electric discharge. The width of that transition region is relatively small: 500 ÷ 600 V. It cannot be linerized due to the fact that processes of ionization and recombination, which are of different nature, go on concurrently.

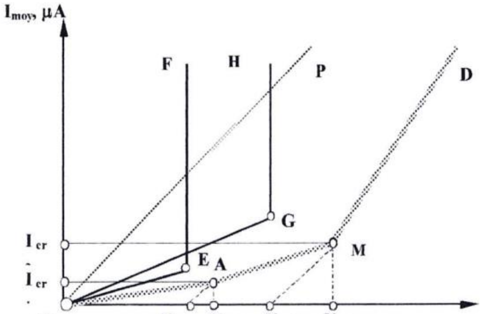

Fig. 3. Idealized volt-ampere characteristic OAMD of the discharge: **MD** – voltage drop across the barrier; **OEF** - voltage drop across the discharge gap; **OGH** - voltage drop across the discharge gap; **OA** – no discharge; **AMD** – discharge in the working gap.

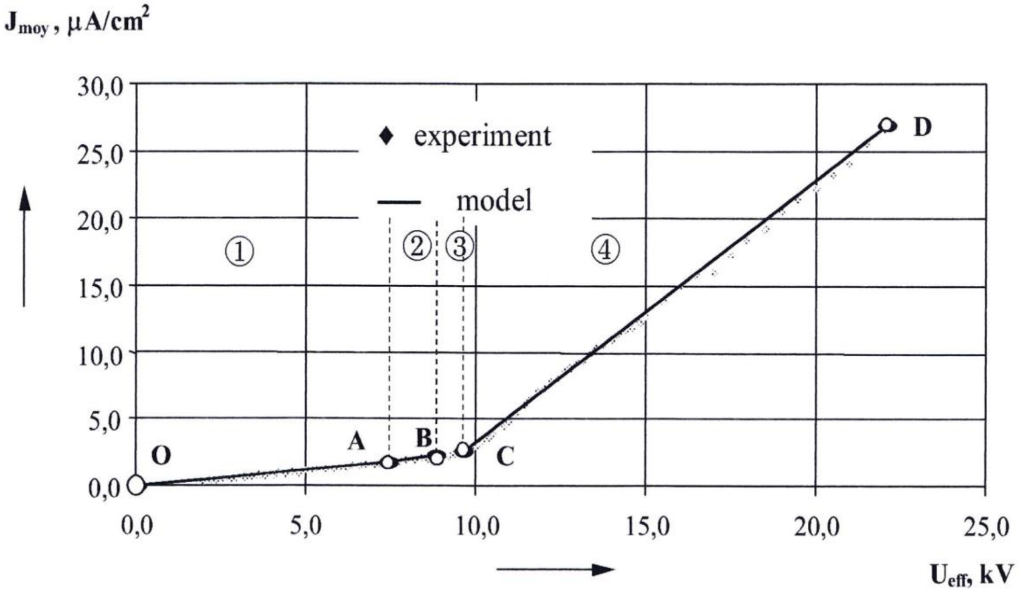

Fig. 4. Relationship between the average value of current density J_{moy} and the effective value of voltage U_{eff}.

This appearance of the characteristic corresponds to three simplified models of the discharge gap for different regions of the characteristic, Fig. 5: for region **OA** – three capacitors connected in series: C_δ - capacitance of the barrier, and C_O, C_N - capacitances of the air gap; for region **AM** – two capacitors connected in series C_δ and C_N, and a source of constant voltage $U_{g,O} = const$; for region **MD** – one capacitor C_δ and two sources of constant voltage $U_{g,N} = const$.

A measure for the intensity of plasma-chemical transformation is the average value of electric current density $J_{moy} = I_{moy}/S$, where S is the active area of electrodes, Fig. 4. It reflects the result of plasma-chemical treatment and serves as a quantitative indicator for the effectiveness of technological process.

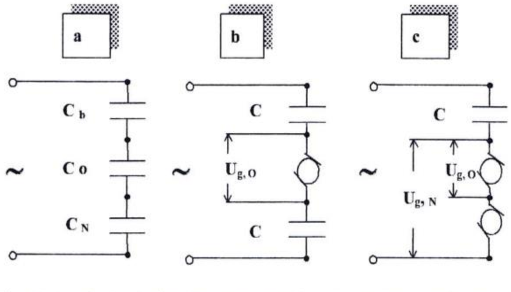

Fig. 5. Equivalent circuits corresponding to various regimes of existence of electric discharge: a – the discharge is not ignited yet; b – the discharge is maintained burning by mechanism I; c - the discharge is maintained burning by mechanism II.

However, the nature of changes is qualitatively different in the treatment region **AB** and region **CD**. This is supported by the experimental technological investigations as well as by the known facts regarding the elementary processes in discharge.

ELEMENTARY PROCESSES

The plasma-chemical treatment is characterized by a multiplicity of elementary process concurrently going on, which strongly impedes the study and control of the whole process. The dissociation and ionization as a source of chemically active particles stand at the beginning of the whole chain of elementary processes. The electric discharge in air exists as a result of the dissociation and ionization of oxygen and nitrogen. The energy of nitrogen dissociation (941.64 kJ/mol) is rather high, meanwhile the ionization energy of molecular nitrogen (15.8 eV) is considerably higher than that of atomic nitrogen (14.5 eV).

Treatment in ozone- and oxygen-containing electric discharge is based on the generation of ozone O_3 and chemically active products of its decomposition.

The energy of oxygen dissociation (493.57 kJ/mol) is considerably lower; the ionization energy of molecular oxygen (12.5 eV) being considerably lower that that of atomic oxygen (13.5 eV).

Several characteristic regions are being formed: from **12.5** to **13.5** eV – ionization of molecular oxygen O_2 and formation of positive O_2^+ and negative molecular ions O_2^-, ionization of water molecules (13.2 eV); from **13.5** to **14.5** eV – ionization of atomic oxygen and formation of positive

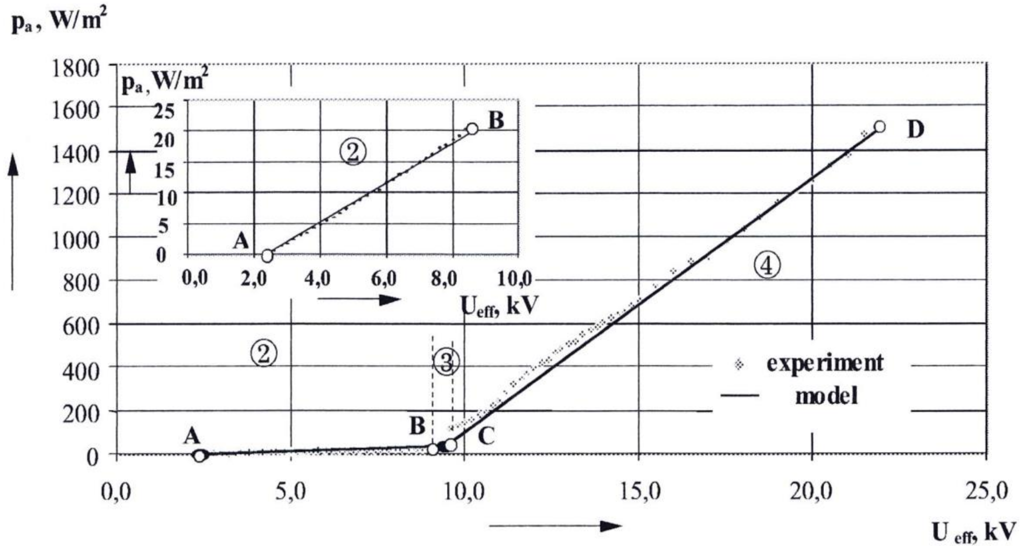

Fig. 6. Relationship between the average value of the surface power density p_a and the the effective value of voltage U_{eff}: DE – region of intensive plasma-chemical surface modification; EF – region of ineffective plasma surface modification of materials.

O^+ and negative O^- atomic ions, ionization of carbon monoxide CO (14.1 eV) and dioxide CO_2 (14.3 eV); from **14.5** to **15.8** eV – ionization of atomic and molecular nitrogen, ionization of molecular hydrogen and of argon.

Ozone generation can occur in accordance with two mechanisms: from positive and negative molecular ions (O_2^+, O_2^-) in a cold discharge region, and from positive and negative atomic ions (O^+, O^-) in a hot discharge region [3]. Regretfully, due to its high chemical activity the ozone decomposes and is absorbed easily in the presence of atomic oxygen O and atomic ion O^-. The generation of nitrogen oxides NO_X also leads to intensive ozone absorption.

Only in the first region of cold electrical discharge (12.5÷13.5 eV) there exist favorable conditions for generating ozone without being absorbed by the gas components. In the rest of the regions the ozone generated takes part in nonproductive gas reactions and contributes very weakly to the plasma surface treatment. This process exhibits itself with maximum intensity after 14.5 eV, where nearly the whole quantity of ozone is consumed for the oxidation of nitrogen oxides.

In such a way three characteristic regions are formed: 12.5 ÷ 13.5 eV – a region of the action of ozone and products of its decomposition upon the polymeric surface; 13.5 ÷ 14.5 eV – a transition region, where the ozone is being absorbed by atomic oxygen O and atomic oxygen ion O^- and to ever higher degree by the newly obtained nitrogen oxides; above 14.5 eV – a region of ever more active generation of nitrogen oxides and ozone absorption.

It is obvious that these three regions of various elementary processes in the discharge correspond to the regions already observed for the volt-ampere characteristic of electric discharge, Fig. 2.

From the viewpoint of technological process namely the first region **AB** is of interest, because the large quantity of ozone and products of its decomposition there ensures a maximum technological effect of chemical surface activation, etching or cross-linking. In transitional region **BC** there begins an ever more intensive decomposition and absorption of ozone by the gaseous products, which has already been prevailing in region **CD**. An intensive ozone generation by positive and negative atomic ions goes on in it but the ozone is intensively absorbed by the gaseous medium and exerts weak influence upon the surface technological processes.

SURFACE DENSITY OF THE ACTIVE POWER AND ENERGY EFFECTIVENESS

The surface power density $p_a = P_a / S$, where P_a is the active power of the discharge, depends proportionally on the current density J_{moy} and at the same time gives a notion about the electric energy transformation into energy of the plasma-chemical transformation of the material:

$$p_a = U_{eff} \left(J_{moy} - J_{cr} \right), \tag{4}$$

where J_{cr} is the critical current density, at which the electric discharge fires up ($J_{cr,1}$) or passes to the region of nitrogen oxide generation ($J_{cr,2}$).

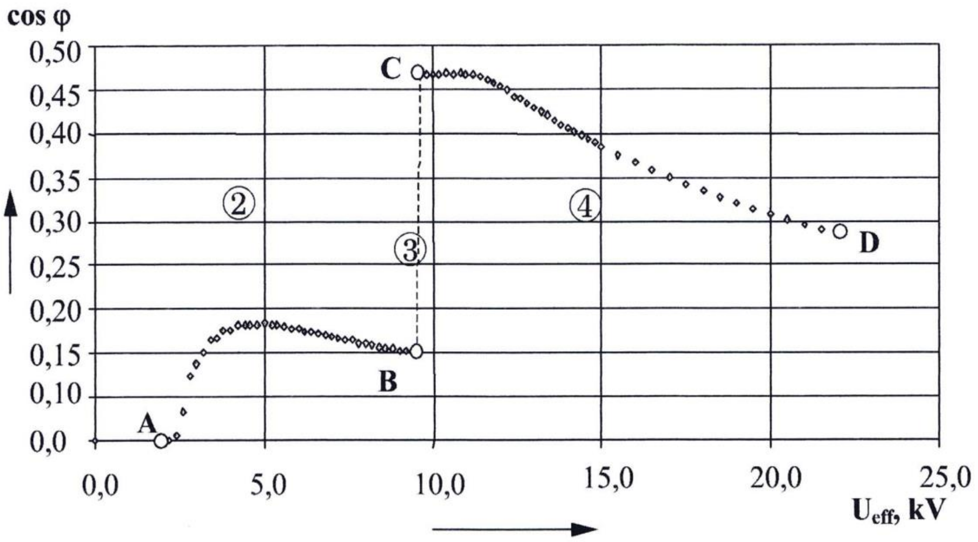

Fig. 7. Dependence of the power factor cos φ on the effective value of voltage U_{eff}: **AB** – region of intensive plasma-chemical surface modification; **CD** – region of ineffective plasma surface modification of materials – generation of nitrogen oxides.

The dependence of the surface density of active power p_a on the burning voltage of electric discharge is characterized by two regions, namely region **AB** of active plasma-chemical surface treatment and region **CD** of active generation of nitrogen oxides and absorption of ozone and products of its decomposition. Values of surface density of the active power up to 25 W/m^2 correspond to effective technological process. The second region that is ineffective from technological point of view corresponds to considerably higher values of surface density p_a, i. e. it is a technology- and energy-ineffective region, Fig. 6.

Irrespective of the better power factor cos φ $(0.25 \div 0.45)$ and substantially higher active powers p_a, region **CD** remains technologically ineffective, which also means ineffectiveness in respect of energy, Fig. 7.

TECHNOLOGICAL EXPERIMENTS

The so-substantiated thesis about a connection between the effectiveness of plasma-chemical modification and the surface density of active power as well as the possibility of determining this process parameter from the experimentally measured volt-ampere characteristic permit that all changes in the surface properties of material be monitored through it.

An experimental investigation on plasma-chemical modification of non-woven high-porous textile material, *Geotextil 500* (produced by *Netakan Tekstil Ltd.*, Bulgaria), on the basis of polyethylene terephthalate (**PET** 500, 500 g/m^2, 15 tex, 32 mm, needle-stuffed) was carried out. Test specimens were placed in the space between electrodes and treated for certain time (30, 300, 600, or 1200 s). The effect of temporal factor upon the process was studied, Fig. 8.

The gravimetric variation of the mass of test specimens was studied, namely the loss ($\Delta G > 0$) or increase ($\Delta G < 0$) of mass after plasma-chemical surface treatment. The loss of mass was most probably due either to ion sputtering, i. e. physical etching, or to plasma-chemical oxidation of carbon atoms on the surface and production of volatile substances, namely chemical etching. The increase in mass was connected with a diffusion of the chemically active excited molecule of oxygen and formation of oxygen bridges, i. e. cross-linking.

During treatment the stability of selected electric regime, $p_a < 25$ W/m^2, was monitored. The electric discharge current I_{moy} was measured, Fig, 1.

Fig. 9 shows the mass variation of test specimens of non-woven textile after a treatment in the conditions of selected effective regime of surface modification. No experimental results are shown for the second region of treatment, as the mass variation is virtually inessential.

The regions of plasma etching of PET (at high values of the surface power density) and those of cross-linking (at low values of the surface power density and large treatment times) are very clearly outlined.

Depending on the pre-set objective, the whole region of effective plasma modification of PET, where $p_a < 25$ W/m^2, can be utilized.

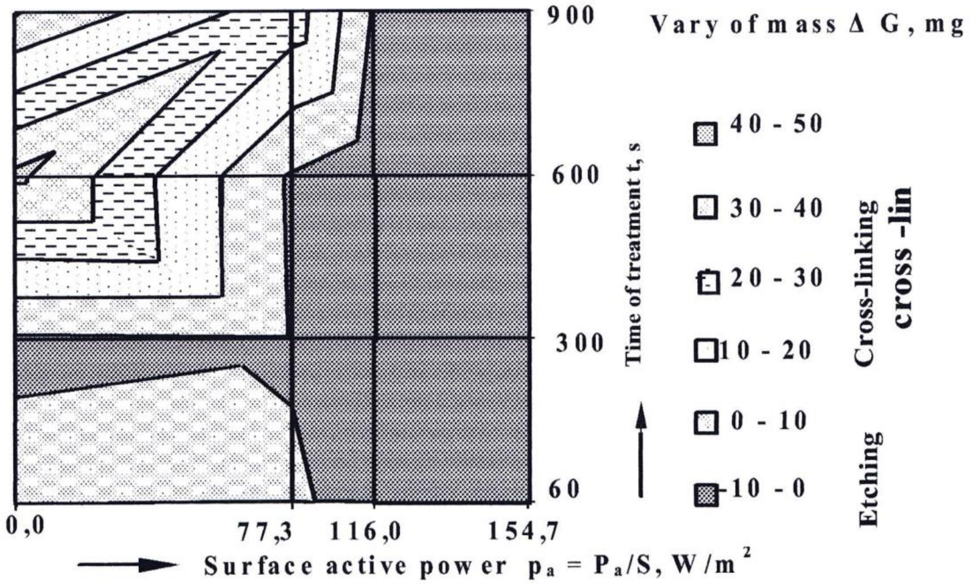

Fig. 8. Variation of mass ΔG of specimens of non-woven high-porous textile materials with the surface density of active power p_a and the duration of plasma treatment t.

The results obtained confirm the analysis performed for the elementary processes going on in the electric discharge.

CONCLUSION

The theoretical and experimental investigations performed justify the acceptance of proposed hypothesis for mutual correspondence between the elementary processes going on in the electrical barrier discharge and its volt-ampere characteristic.

Plasma modification of polymers and polymeric materials in ozone- and oxygene-containing electrical discharge is a result of the generation of ozone and products of its decomposition.

The surface density of the active power can be used as a technological parameter and as a parameter of energy effectiveness for plasma-chemical treatment in an electrical barrier discharge.

III. REFERENCES

[1] Polymer Surface Modification and Characterization (by Chan Chi-Ming). Munich, Germany, Carl Hanser Publisher, 1993, pp. 220-250.

[2] Low Temperature Plasma Technology Applications (by Quellette R., Barbier M., Cheremisinoff P.) Ann Arbor, Ann Arbor Science Publisher, 1980, pp. 185-198.

[3] Electrotechnology: Introduction to Electrotechnology (by Dineff, P. D.). Sofia, Academic Press, 2001, pp. 324-326.

[4] Electric Phenomena in Gases and Vacuum (by Kaptsov, N. A.). Moscow & St Petersburg, Academic Press, 1950, pp. 193-240.

IV. BIOGRAPHIES

Peter D. Dineff, *Ph.D.*, is an Associate Professor with the Department of Electrical Apparatuses at the Technical University of Sofia. He works in the field of the electrotechnology, i. e. in the applied-research field of electrotechnological processes and apparatuses. In recent years his works exhibit an emphasized interest in the plasma and plasma-chemical technologies and their industrial implementation.

Dilyana N. Gospodinova, *M.E.,* is a full-time Ph.D. student with the Department of Electrical Apparatuses at the Technical University of Sofia from the year 2000. She works in the field of applying the electric corona and capacity discharges at atmospheric pressure in air plasma surface technologies.