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(54) METHOD AND DEVICE FOR SURFACE TREATMENT WITH A PLASMA AT ATMOSPHERIC PRESSURE

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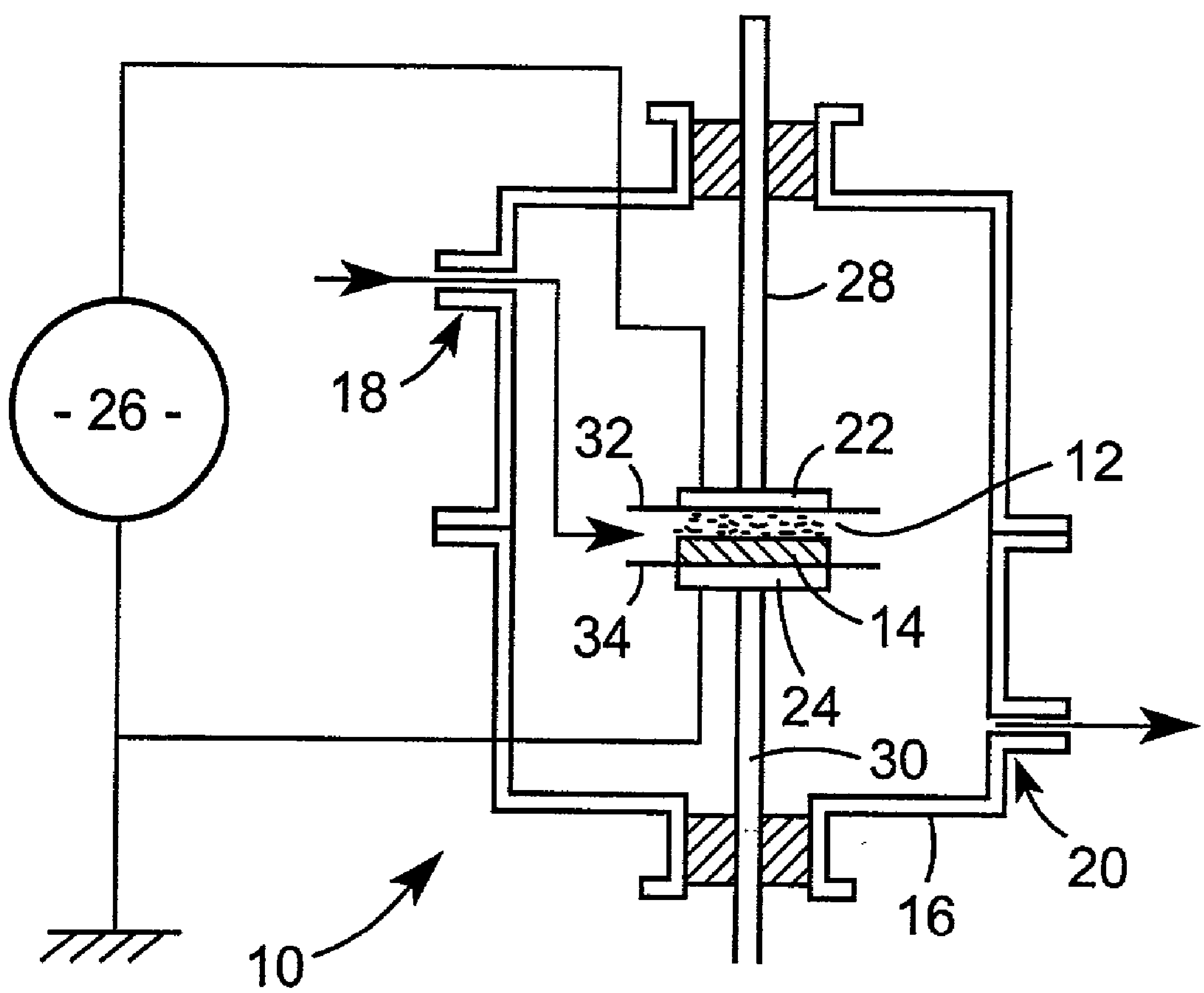
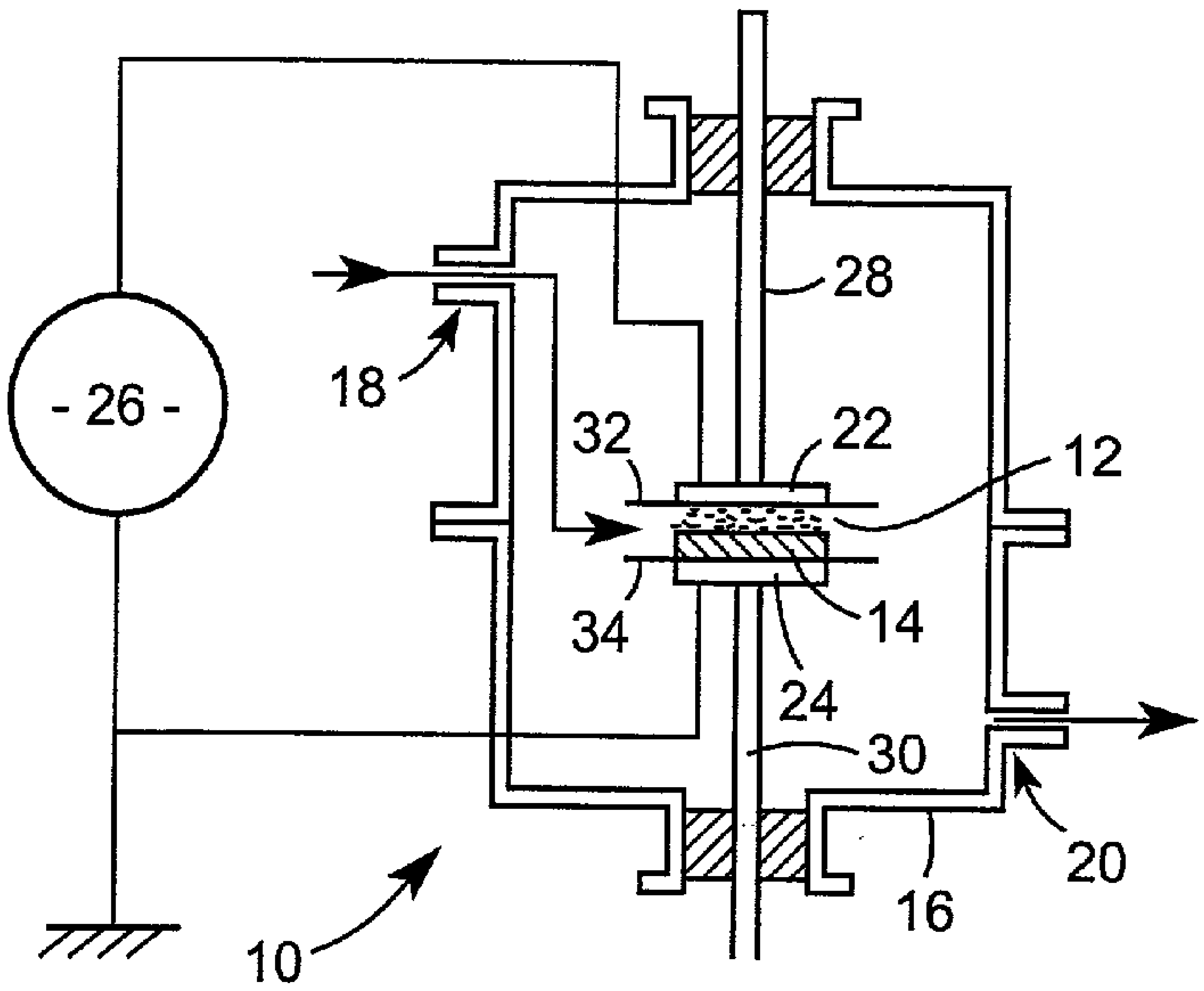
(57) **ABSTRACT**

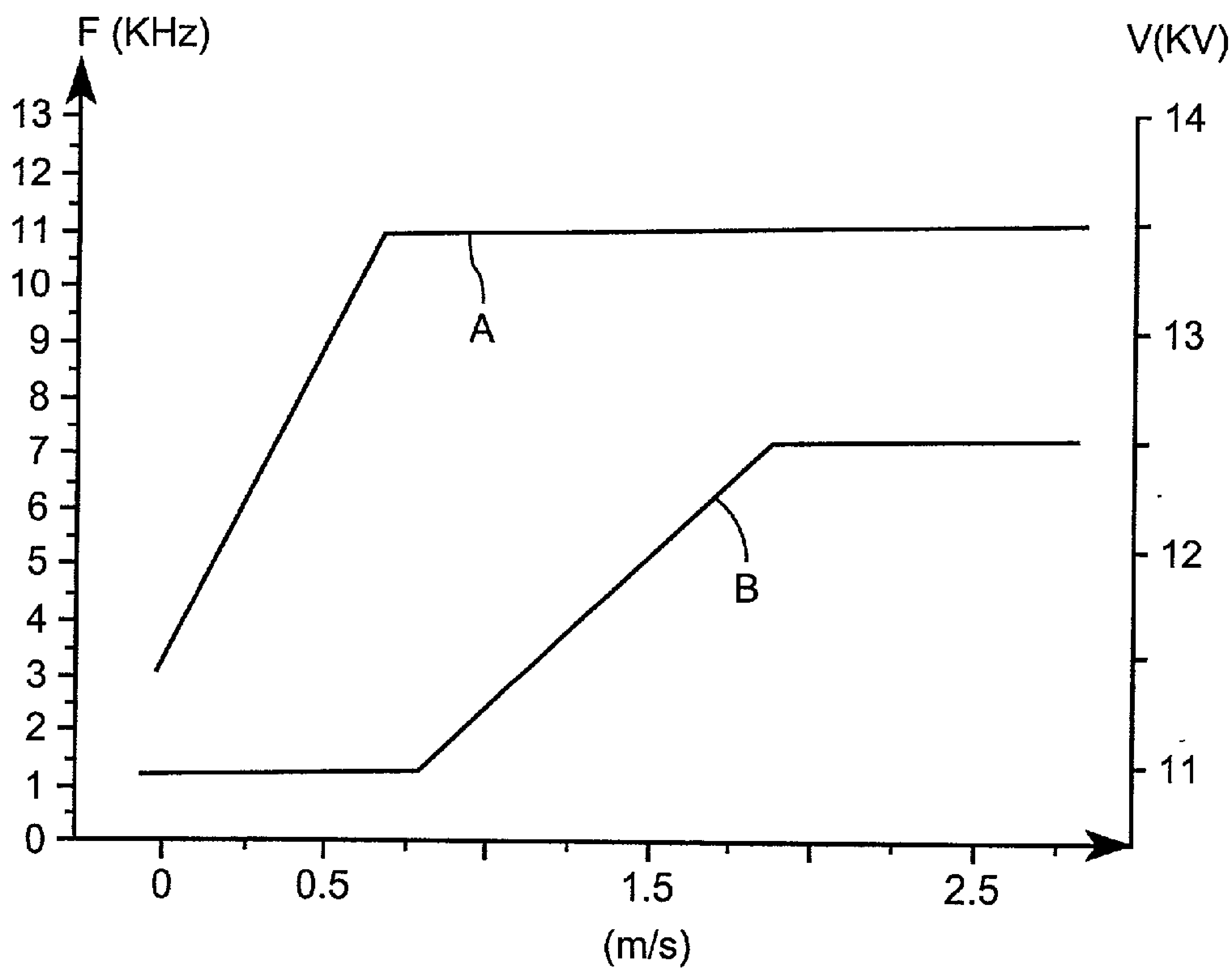
This method for surface treatment with a plasma at atmospheric pressure comprises the step of introducing a treatment gas into a treatment reactor (**16**), in which a surface (**14**) to be treated is placed between two exciting electrodes (**22, 24**), and applying a supply voltage to the two electrodes so as to cause the appearance of a discharge (**12**) in the treatment gas. The supply voltage is an AC voltage whose amplitude and frequency are adapted in order to maintain at least some of the components of the treatment gas in the excited state, and/or the presence of electrons, between two successive half-cycles of the supply voltage.





- 26 -
18
28
32
22
12
34
14
24
30
20
16
10

FIG. 1



F (KHz)
V(KV)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
14
13
12
11
A
B
0
0.5
1.5
2.5
(m/s)

FIG. 2

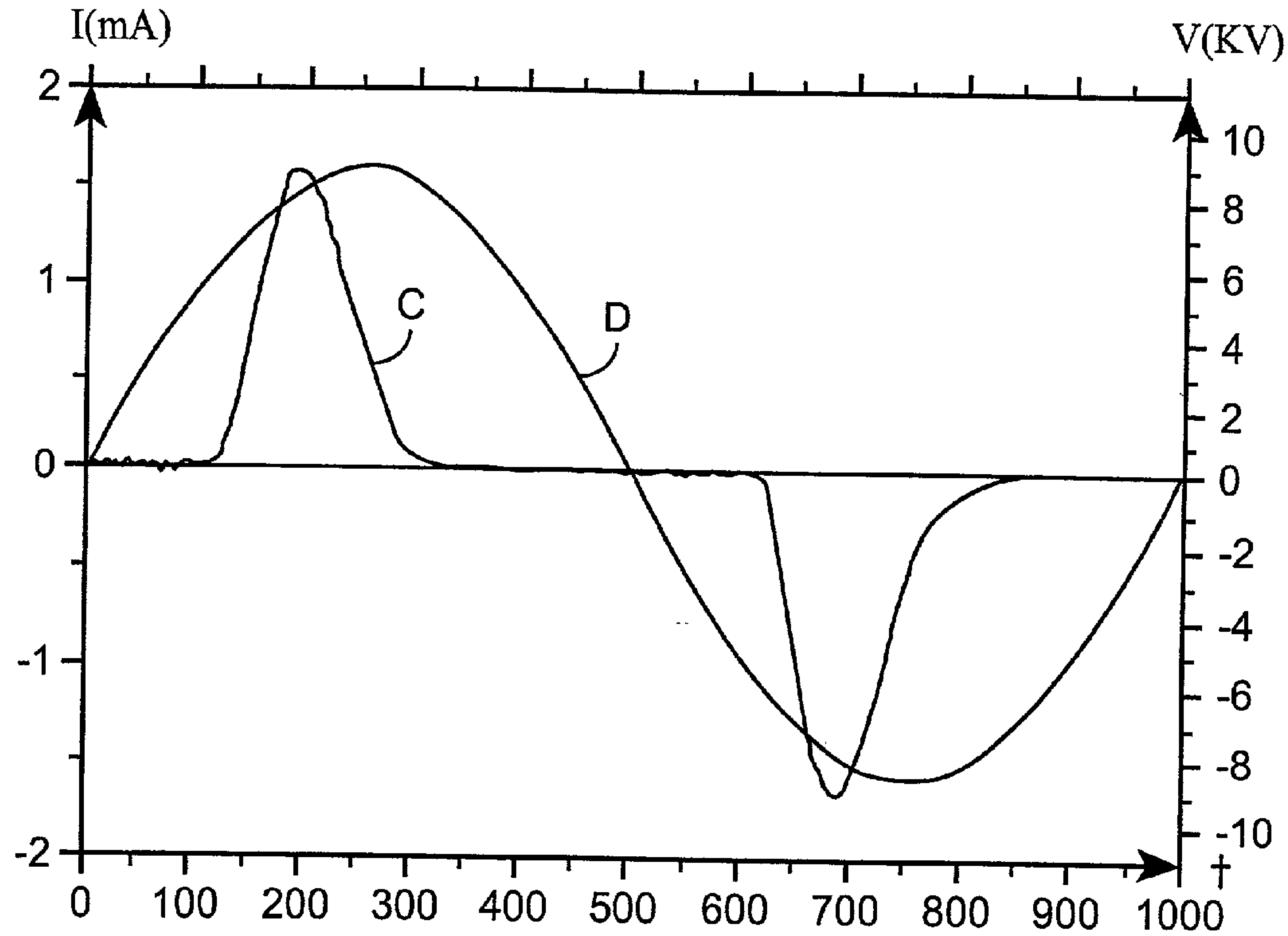

I(mA)
V(KV)
2
1
0
-1
-2
10
8
6
4
2
0
-2
-4
-6
-8
-10
C
D
0
100
200
300
400
500
600
700
800
900
1000
t

FIG. 3

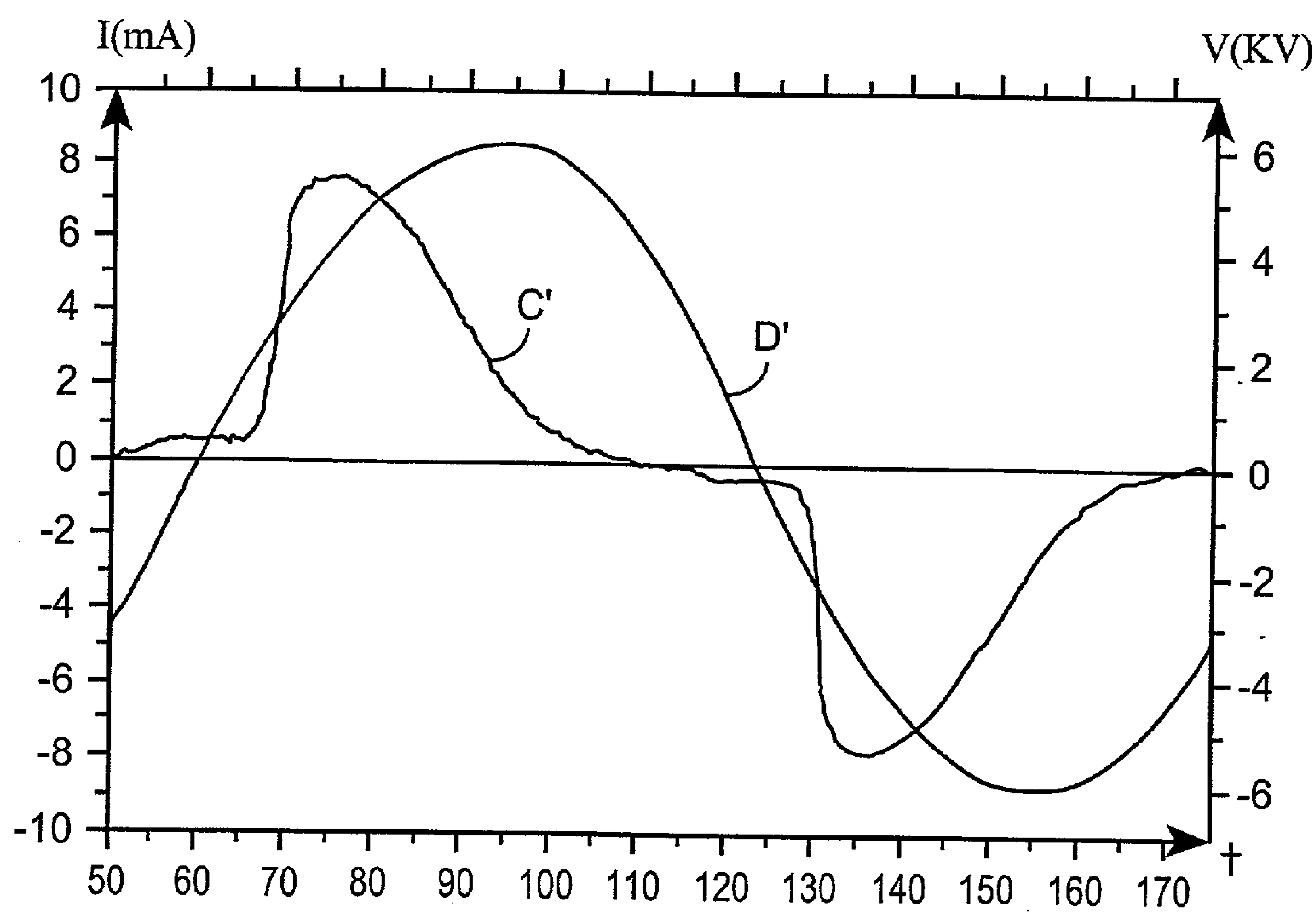

I(mA)
V(KV)
10
8
6
4
2
0
-2
-4
-6
-8
-10
6
4
2
0
-2
-4
-6
C'
D'
50
60
70
80
90
100
110
120
130
140
150
160
170
t

FIG. 4

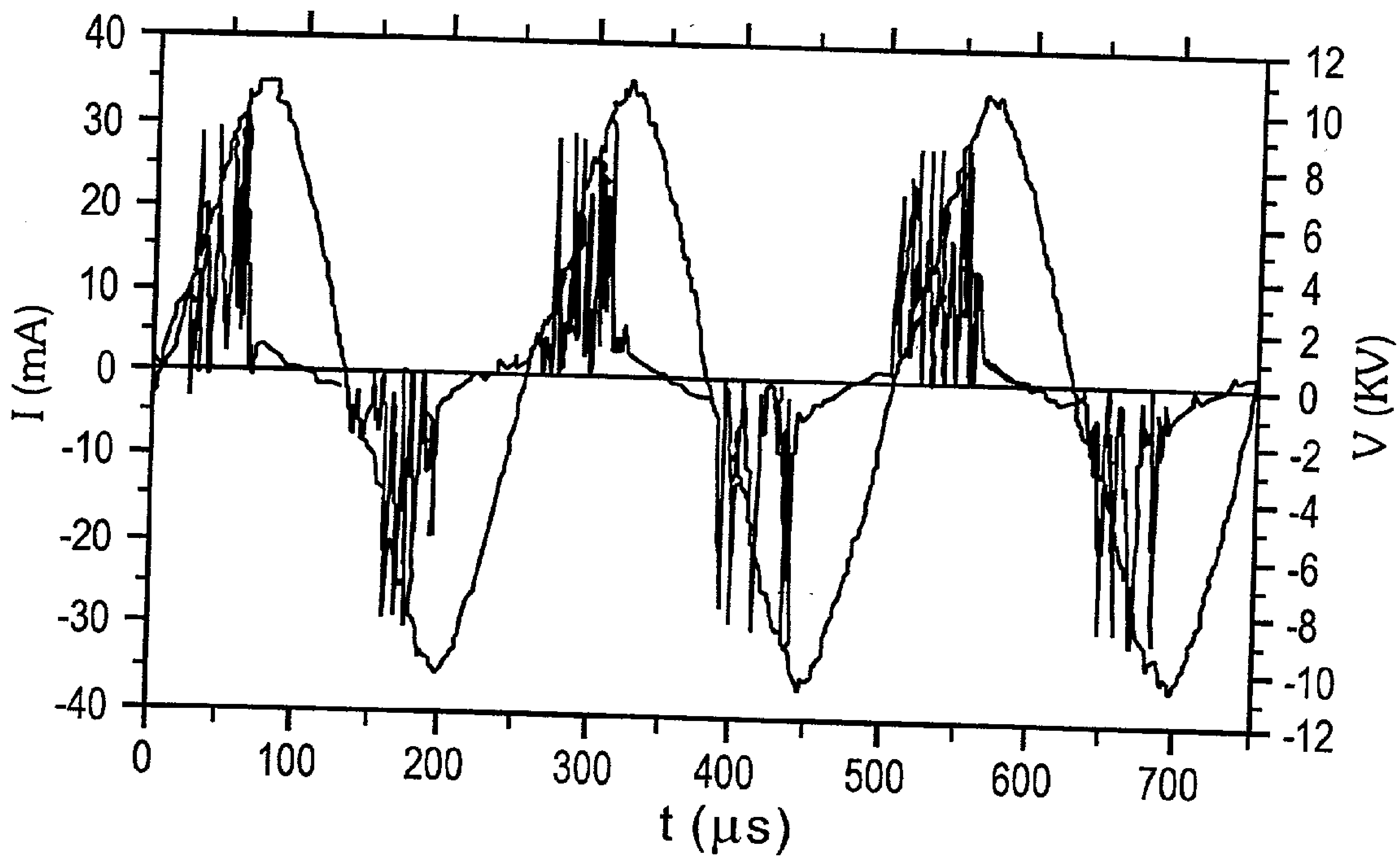

40
30
20
10
0
-10
-20
-30
-40
I (mA)
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
V (KV)
0
100
200
300
400
500
600
700
t (μs)

FIG. 5

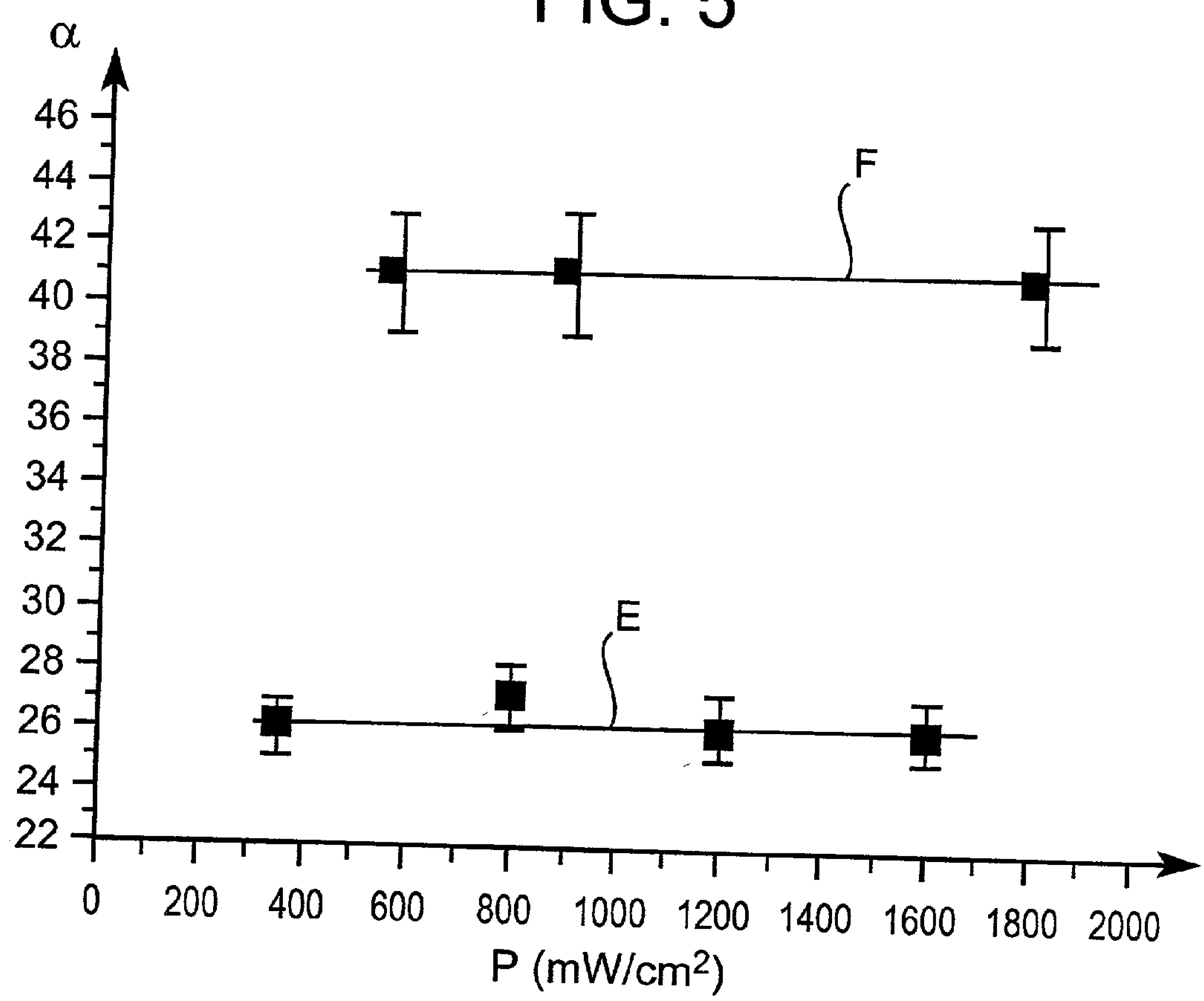

α
46
44
42
40
38
36
34
32
30
28
26
24
22
F
E
0
200
400
600
800
1000
1200
1400
1600
1800
2000
P (mW/cm2)

FIG. 6

METHOD AND DEVICE FOR SURFACE TREATMENT WITH A PLASMA AT ATMOSPHERIC PRESSURE

[0001] The present invention relates to a method and to a device for creating a uniform discharge at atmospheric pressure (non-filamentary) in a gas, in particular in nitrogen or in a gas mixture based on nitrogen, and to its application in particular to surface treatment using a plasma at atmospheric pressure or alternatively to the breakdown of effluents.

[0002] One of the applications relates more particularly to treatments for modifying the surface characteristics of a polymer film with a view, for example, to modifying its wettability or forming chemical bonds capable of improving the adhesion of a future coating.

[0003] In methods for surface treatment using a plasma, the surface to be treated is traditionally brought into contact with a plasma created by ionizing a treatment gas so as to create excited chemical species and electrons, which in particular can collide with third species (in particular neutral ones).

[0004] These collisions can cause energy to be transferred to the species so as to form new chemically active species, in particular so-called "metastable" species, atomic species, radicals, ions and electrons. Chemically active species with a long lifetime can in turn collide with third species, which can thus create other active species and electrons.

[0005] The active species can interact with the surface of an article in contact with the gas, which makes it possible to modify the surface characteristics of this article, on the one hand creating new molecular structures capable of interacting with the molecules of a coating deposited later, and on the other hand modifying the morphology of the material and, in particular, the mobility of chains or chain segments in the case of polymers.

[0006] It is known that electric discharges at atmospheric pressure have the advantages, on the one hand, of not requiring the use of bulky and expensive devices for creating a powerful vacuum in the treatment reactor in which the discharge is formed and, on the other hand, of permitting continuous treatments which are compatible with productivity requirements.

[0007] The electric discharges employed at atmospheric pressure, such as "corona" discharges, are generally referred to as "filamentary" since they are generated in the form of sorts of current microchannels, typically some hundred microns in diameter, which develop randomly in space and time between the two electrodes.

[0008] However, it has been found that such a "filamentary" discharge technique is not efficient enough at the microscopic level because it has a number of drawbacks at the microscopic level. Specifically, the discharge created in this way is microscopically nonuniform since, firstly, between two filaments, the surface has untreated regions and furthermore, even at the individual filaments, the treated surface is liable to be degraded by an excessive number of polymer chain breaks or even local heating.

[0009] Attempts have been made to overcome this drawback by subjecting the surface to be treated to a uniform discharge, that is to say a discharge in which the excited chemical species are regularly distributed over the surface to be treated, while of course maintaining atmospheric pressure conditions (specifically, attempts could have been made to make the discharge uniform by reducing the pressure).

[0010] It is thus known to produce a uniform discharge at atmospheric pressure in a neutral gas, essentially helium (reference may for example be made to documents U.S. Pat. No. 5,456,972 and EP-A-346 055). However, for treating surfaces with such a plasma created in a gas based on nitrogen, at least one electrode in the form of a grill is still used.

[0011] However, work carried out by the Applicant Company has shown that such electrodes do not make it possible for the uniformity of the discharge created to be improved satisfactorily at the microscopic level.

[0012] The object of the invention is to overcome this drawback and to provide a method for creating a uniform electric discharge in nitrogen, or a gas containing nitrogen, making it possible in particular to improve the conditions of surface treatment with a plasma at atmospheric pressure.

[0013] It therefore relates to a method for creating an electric discharge in an initial gas which is at atmospheric pressure and lies between two exciting electrodes, by applying a supply voltage to the two electrodes, which is characterized in that the supply voltage is an AC voltage whose amplitude and frequency are adapted in order to maintain at least a portion of the components of the gas in the excited state, and/or the presence of electrons, between two successive half-cycles of the supply voltage.

[0014] As will be illustrated in more detail further on in the present application, the method according to the invention avoids the conditions of strong field and breakdown voltage typically characteristic of the filamentary mode, by making it possible to create and maintain, between two discharges (i.e. between two half-cycles), sufficient quantities of metastable species and electrons for each discharge to start with a low electric field value (the metastable species relax, for example, on contact with a third species to create an electron and an ion of this third species itself or of the metastable species). The electrons lead to avalanches which produce ions, accelerated toward the cathode, which cause secondary emission of electrons at the cathode, etc.

[0015] The method for creating a discharge according to the invention may further have one or more of the following characteristics, taken individually or in any technically feasible combinations:

[0016] the supply voltage lies between about 5 kV and 30 kV, with a more preferential embodiment in the range of from 10 kV to 25 kV, and the frequency of the voltage lies between about 200 Hz and 35 kHz, with a preferential range of less than or equal to 15 kHz;

[0017] the initial gas is introduced into the inter-electrode space with a gas velocity of between 0 m/s and 10 m/s, with a preferential range of less than or equal to 5 m/s.

[0018] the initial gas includes one or more of the gases in the group formed by nitrogen, silicon precursor gases, oxygen and gases capable of releasing oxygen such as N_2O, CO_2, NO_2, H_2O . . . ;

[0019] the thickness of the gas space between the exciting electrodes is between about 0.5 and 5 mm;

[0020] at least one of the electrodes is covered with a dielectric or semiconductor material (such as alumina, glass, polymer, etc.), the thickness of which advantageously lies in the range of from a few tens of microns to 1 cm, and preferably in the range of from 500 microns to 2 mm.

[0021] The invention also relates to a device for creating an electric discharge in a gas at atmospheric pressure, for implementing a method as defined above, including two exciting electrodes, a source for supplying the inter-electrode space with an initial gas and a voltage supply source which is connected to the exciting electrodes, and which is characterized in that the voltage supply source is capable of delivering an AC voltage whose amplitude and frequency are adapted in order to maintain at least a portion of the components of the gas in the excited state, and/or the presence of electrons, between two successive half-cycles of the voltage.

[0022] The invention also relates to a method for surface treatment with a plasma at atmospheric pressure, including the step of introducing a treatment gas into a treatment reactor, in which a surface to be treated is arranged between two exciting electrodes and applying a supply voltage to the two electrodes so as to cause the appearance of an electric discharge in the treatment gas, and which is characterized in that the supply voltage is an AC voltage whose amplitude and frequency are adapted in order to maintain at least a portion of the components of the treatment gas in the excited state, and/or the presence of electrons, between two successive half-cycles of the supply voltage.

[0023] The method for surface treatment according to the invention may furthermore have one or more of the following characteristics, taken individually or in any technically feasible combinations:

[0024] the surface to be treated being capable of generating species liable to de-excite (relax) the active (excited or unstable) components in the gas which are needed for obtaining a uniform discharge, the proportion of said species liable to de-excite the gas is limited by implementing one or more of the following measures:

[0025] i) the treatment gas includes at least one component capable of interacting with said species liable to cause de-excitation to negate their detrimental effect;

[0026] j) the power of the discharge is controlled, the rate at which said species liable to cause de-excitation are generated being thus controlled;

[0027] k) the rate at which the treatment gas is replenished in the inter-electrode space is controlled.

[0028] the supply voltage lies between about 5 kV and 30 kV, with a more preferential embodiment in the range of from 10 kV to 25 kV, and the frequency of the voltage lies between about 200 Hz and 35 KHz, with a preferential range of less than or equal to 15 kHz;

[0029] the treatment gas is introduced into the inter-electrode space with a gas velocity of between 0 m/s and 10 m/s, with a preferential range of less than or equal to 5 m/s;

[0030] the treatment gas includes one or more of the gases in the group formed by nitrogen, silicon precursor gases, oxygen and gases capable of releasing oxygen such as N_2O, CO_2, NO_2, H_2O . . . ;

[0031] the thickness of the gas space between the exciting electrodes is between about 0.5 and 5 mm;

[0032] at least one of the electrodes is covered with a dielectric or semiconductor material, the thickness of which advantageously lies in the range of from a few tens of microns to 1 cm, and preferably in the range of from 500 microns to 2 mm.

[0033] The invention also relates to a device for surface treatment with a plasma at atmospheric pressure, for implementing a method for surface treatment as defined above, having a treatment reactor including two exciting electrodes, between which an article to be treated is arranged, a source for supplying the reactor with a treatment gas at atmospheric pressure and a voltage supply source which is connected to the exciting electrodes and can deliver a supply voltage to them, the device being characterized in that the voltage supply source is capable of delivering to the electrodes an AC voltage which is adapted in order to cause the appearance of a discharge in the treatment gas and whose amplitude and frequency are capable of maintaining at least a portion of the components of the treatment gas in the excited state between two successive half-cycles of the supply voltage.

[0034] As seen above, the aim of the invention is to create, control and use uniform discharges, in particular in atmospheres based on nitrogen, and to do this at atmospheric pressure. It will, of course, be understood that it is possible to work at pressures lying a few tens of millibars, or even a few hundreds of millibars, either side of atmospheric pressure without departing from the scope of the present invention.

[0035] Other characteristics and advantages will become apparent from the following description, which is given solely by way of example and made with reference to the appended drawings, in which:

[0036] **FIG. 1** is a schematic sectional view of a device for surface treatment according to the invention;

[0037] **FIG. 2** illustrates the variation of the maximum frequency and voltage to be supplied, as a function of the velocity of the treatment gas, in order to obtain a uniform discharge;

[0038] **FIG. 3** (according to the invention) shows the variation, as a function of time, in the current and the supply voltage of the exciting electrodes, for a zero value of the velocity of the gas treatment (no replenishment of the atmosphere);

[0039] **FIG. 4** (according to the invention) shows the variation, as a functional time, in the current and the supply voltage of the exciting electrodes, for a gas velocity equal to 1.5 m/s (and furthermore with a gas space of 1 mm, an excitation frequency of 8 kHz and an amplitude of 12 kV);

[0040] **FIG. 5** (comparative) shows the variation, as a function of time, in the current and the supply voltage of the exciting electrodes, in the case of a filamentary discharge (comparative example, obtained for a gas velocity equal to 0 m/s, a gas space thickness of 3 mm, an excitation frequency of 4 kHz and an amplitude of 20.5 kV);

[0041] **FIG. 6** shows curves illustrating the variation, as a function of the average power consumed in the discharge, in the angle formed by a water drop in contact with a surface treated under nitrogen, on the one hand, using a method according to the invention and, on the other hand, using a filamentary discharge.

[0042] **FIG. 1** schematically represents a device for surface treatment with a plasma at atmospheric pressure, denoted by the overall numerical reference **10**.

[0043] It is intended to generate a uniform discharge **12** by exciting a treatment gas, with a view to modifying the surface properties of an article **14** to be treated.

[0044] In the rest of the description, it will be assumed that the article **14** to be treated consists of a film of polymer, for example of polypropylene, but the invention also applies, of course, to the treatment of articles consisting of different materials.

[0045] As can be seen in **FIG. 1**, the reactor **16** is provided with a first orifice/injection system **18** in communication with a source (not shown) for supplying treatment gas, as well as a discharge orifice **20**.

[0046] The treatment gas consists, for example, of nitrogen.

[0047] The injection **18** and discharge **20** orifices are each provided with suitable means, of the conventional type, for controlling the gas flow rate inside the reactor **16**.

[0048] Two exciting electrodes, **22** and **24** respectively, between which the article to be treated is arranged extend parallel inside the reactor **16**.

[0049] They each consist, for example, of a metal disc and are each connected to a source **26** for supplying AC voltage, the applied voltage and excitation frequency of which can be adjusted in a predetermined range.

[0050] They are also each supported by an adjustment bar, **28** and **30** respectively, which is accessible from outside the reactor **16** so as to adjust the inter-electrode gas space in a range lying, for example, between about 0.5 and 5 mm.

[0051] Each electrode **22** and **24** is also covered with a layer, **32** and **34**, of a dielectric or semiconducting material suitable for the use in question, for example alumina.

[0052] As can be seen in this **FIG. 1**, the article **14** to be treated is, in the case of the embodiment represented, placed on one of the exciting electrodes, (i.e. on the material covering one of the electrodes).

[0053] As mentioned above, the discharge **12** is obtained by exciting the electrodes **22** and **24** using the supply source **26**.

[0054] In order to do this, and with a view to obtaining a uniform discharge **12**, the supply voltage is fixed at a value lying between about 5 kV and 30 kV, considered peak to peak, and the frequency of the excitation voltage supplied between the electrodes **22** and **24** lies between about 200 Hz and 35 kHz, this being as a function of the thickness of the inter-electrode gas space, the flow of the treatment gas as well as the composition of the treatment gas.

[0055] In the case of nitrogen, for an inter-electrode distance close to 1 mm, the peak-to-peak value adopted for the supply voltage is thus advantageously close to 11 kV, and is advantageously equal to 24 kV when the inter-electrode distance is, for example, equal to 3 mm.

[0056] Similarly, as can be seen in **FIG. 2**, in the case illustrated the maximum value of the voltage V and of the excitation frequency F is defined as a function of the velocity of the treatment gas. In these figures, which correspond to a thickness equal to about 1 mm for the inter-electrode gas space, the portion lying above the curves corresponds to operation under filamentary discharge conditions, while the part below each curve corresponds to operating conditions with uniform discharge. Curve A corresponds to the variation in the maximum frequency F as a function of the gas velocity, and curve B corresponds to the variation in the maximum supply voltage V as a function of the gas velocity.

[0057] It can thus be seen in this **FIG. 2** that, for an inter-electrode distance equal to about 1 mm, and for a zero flow rate of the treatment gas (atmosphere introduced but not replenished), the maximum value of the excitation frequency F is fixed at about 3 kHz.

[0058] In this case (distance close to 1 mm), the supply voltage is close to 11 kV.

[0059] Similarly, with values higher than 2 m/s for the gas velocity, the maximum value of the excitation frequency is close to 11 kHz, while the supply voltage is close to 12.5 kV, still considered peak-to-peak.

[0060] As can be seen in **FIGS. 3 and 4**, which represent the variation, as a function of time, in the discharge current I (curves C and C') and of the supply voltage V (curves D and D') respectively for a zero gas velocity (without replenishment of the gas, **FIG. 3**) and for a gas velocity of 1.5 m/s (**FIG. 4**), the maximum value of the frequency of the supply voltage is advantageously adopted in such a way as to maintain at least a portion of the components of the gas in the excited state, and/or the presence of electrons, between two successive half-cycles of the supply voltage.

[0061] These figures do actually show that, for each half-period of the supply voltage, the curve for the current as a function of time has a single peak, representing the fact that there is a single event in which electrons and ions are transferred from one electrode to the other. Following the peak, the value of the current is very low but not zero, representing the fact that at least a portion of the components of the gas are maintained in the excited state. A new excitation, taking place under the effect of the following half-cycle, occurs before all the excited species contained in the gas have been fully de-excited.

[0062] A sufficient number of excited species in the discharge, as well as electrons, is therefore maintained between two half-cycles of the supply voltage, which makes it possible to obtain ionization of the particles in the gas with a low electric field, and a discharge which is self-sustained by emission of electrons at the cathode.

[0063] These figures give a better illustration of the phenomena explained further above in the present description (explanations which, as will be understood, have been given by way of illustration without any limiting nature being attributable to them in view of the complexity of the mechanisms involved and the time which would be needed to verify them), according to which explanations sufficient quantities of metastable species and electrons are created and maintained between two discharges (i.e. between two half-cycles of the voltage) for each discharge to be initiated with a small value of the electric field, i.e. an electric field less than the breakdown electric field of the gas at rest. The metastable species relax, for example, on contact with a third species to create an electron and an ion of this same third species or of the metastable species, and the electrons give rise to avalanches which produce ions which are accelerated towards the cathode, thus causing secondary emission of electrons at the cathode, etc.

[0064] Let us now return to the case, already mentioned above, of surfaces to be treated which are capable of generating species liable to de-excite (relax) the active (excited or unstable) components of the gas which are needed for obtaining a uniform discharge in the gas: let us take the case of treating certain polymers, such as polypropylene, which tend to generate hydrogen under the effect of the discharge. The hydrogen generated in this way moreover tends to de-excite the excited species in the gas, in particular the metastable species of nitrogen. A treatment gas composition will then advantageously be adopted, according to the invention, which contains an element capable of interacting with the hydrogen particles (to negate their detrimental effect) so as to maintain the desired discharge conditions.

[0065] Thus, in the case of using a treatment gas containing nitrogen, of which it is desirable to keep the metastable species created in the discharge, a treatment gas will advantageously be used which further contains an oxidizing element, such as oxygen, or another element capable of releasing oxygen, such as N_2O, H_2O, CO_2, NO_2, etc., the list just made being given solely by way of illustration, and without implying any limitation.

[0066] It will be noted, however, that since atomic oxygen is itself liable to relax the metastable species of nitrogen (albeit to a lesser extent than hydrogen does), the level of oxidizing gas in the treatment gas will have to be adjusted and controlled in reasonable compromise proportions.

[0067] With **FIGS. 3 and 4** having shown the spectacular result obtained according to the invention, namely of a uniform discharge characterized by a single peak demonstrating the fact that there is a single event in which electrons and ions are transferred from one electrode to the other, it is satisfying to see that, in comparison, **FIG. 5** (comparative example) which was obtained under filamentary discharge conditions unequivocally has a current profile corresponding to discharge microchannels measuring some one hundred microns in diameter which develop randomly in space and time between the electrodes.

[0068] It will therefore have been gathered, from reading the description above, that the device and the treatment method which have just been described make it possible to obtain a uniform discharge.

[0069] Nevertheless, the Applicant Company has also demonstrated that a polypropylene film treated using this technique has improved wettability characteristics.

[0070] In this regard, **FIG. 6** represents the variation, as a function of the average power P consumed in the discharge, in the contact angle α of a water drop with the treated surface, characterizing the surface tension. Let us recall that the lower the contact angle α is, the more the water drop spreads over the surface, and the higher is the surface tension (small angles are therefore desired in general).

[0071] This **FIG. 6** therefore clearly shows that a film treated using uniform discharge in nitrogen according to the invention (curve E) has a smaller contact angle than a film treated using filamentary discharge (curve F).

[0072] In the description which has just been given, examples were illustrated in which the treatment gas consists of nitrogen, optionally mixed with an oxidizing element.

[0073] According to other advantageous embodiments of the invention, it is also possible to use a treatment gas comprising nitrogen, or another carrier gas, and a silicon precursor gas, for example monosilane (SiH_4), so as to create chemical bonds on the surface of the article which are suitable for the deposition of future coatings, in particular groups such as Si_xO_y or $Si_xO_yH_t$.

[0074] Such a treatment gas, containing a silicon precursor gas, could also of course advantageously contain an oxidizing element so as not only to reduce the de-excitation of the excited species in the gas, as mentioned above, but also to provide the oxygen needed for forming Si_xO_y or indeed $Si_xO_yH_t$ compounds containing oxygen atoms.

[0075] The method for surface treatment according to the invention can therefore have the aim of making a deposit of a silicon-based material on the surface to be treated (a deposit which may moreover be continuous or discontinuous), the treatment gas then containing a carrier gas, such as nitrogen or argon, a silicon precursor gas, and oxygen or a gas capable of releasing oxygen.

[0076] Quite logically, the work carried out by the Applicant Company in comparing deposits made on a polymer surface (polypropylene) according to the invention with deposits made under filamentary discharge, show structures and therefore properties which are very different.

[0077] Thus, by way of illustration, taking the example of the surface roughness of the deposit, after a treatment time of 90 seconds in a discharge set up according to the invention in a nitrogen/monosilane mixture with 90 ppm silane, the surface roughness observed for the deposits is almost 10 times less than for deposits formed with a filamentary discharge using the same treatment time.

1. Method for creating an electric discharge in an initial gas which is at atmospheric pressure and lies between two exciting electrodes, by applying a supply voltage to the two electrodes, characterized in that the supply voltage is an AC voltage whose amplitude and frequency are adapted in order to maintain at least a portion of the components of the gas in the excited state, and/or the presence of electrons, between two successive half-cycles of the supply voltage.

2. Method for creating an electric discharge according to claim 1, characterized in that the supply voltage lies between about 5 kV and 30 kV, and its frequency lies between about 200 Hz and 35 kHz.

3. Method for creating an electric discharge according to claim 2, characterized in that the frequency of the voltage is less than or equal to 15 kHz.

4. Method for creating an electric discharge according to one of claims 1 to 3, characterized in that the initial gas is introduced into the inter-electrode space with a gas velocity of between 0 m/s and 10 m/s.

5. Method for creating an electric discharge according to one of claims 1 to 4, characterized in that the initial gas includes one or more of the gases in the group formed by nitrogen, argon, silicon precursor gases, oxygen and gases capable of releasing oxygen.

6. Method for creating an electric discharge according to one of claims 1 to 5, characterized in that the thickness of the gas space between the exciting electrodes is between about 0.5 and 5 mm.

7. Method for creating an electric discharge according to one of the preceding claims, characterized in that at least one of the electrodes is covered with a dielectric or semiconductor material, the thickness of which advantageously lies in the range of from a few tens of microns to 1 cm, and preferably in the range of from 500 microns to 2 mm.

8. Device for creating an electric discharge in a gas at atmospheric pressure, including two exciting electrodes, at least one of the electrodes being covered with a dielectric or semiconductor material, a source for supplying the inter-electrode space with an initial gas and a voltage supply source which is connected to the exciting electrodes, characterized in that the voltage supply source is capable of delivering an AC voltage whose amplitude and frequency are adapted in order to maintain at least a portion of the components of the gas in the excited state, and/or the presence of electrons, between two successive half-cycles of the voltage.

9. Device for creating an electric discharge according to claim 8, characterized in that the thickness of said dielectric or semiconductor material lies in the range of from a few tens of microns to 1 cm, and preferably in the range of from 500 microns to 2 mm.

10. Method for surface treatment with a plasma at atmospheric pressure, including the step of introducing a treatment gas into a treatment reactor, in which a surface **(14)** to be treated is arranged between two exciting electrodes **(22, 24)**, and applying a supply voltage to the two electrodes so as to cause the appearance of a discharge **(12)** in the treatment gas, characterized in that the supply voltage is an AC voltage whose amplitude and frequency are adapted in order to maintain at least a portion of the components of the gas in the excited state, and/or the presence of electrons, in the region in which the discharge is established, between two successive half-cycles of the supply voltage.

11. Method for surface treatment according to claim 10, characterized in that, the surface to be treated being capable of generating species liable to de-excite the excited or unstable species in the gas, the proportion of said species liable to de-excite the gas, in the region in which the discharge is established, is limited by implementing one or more of the following measures:

i) the treatment gas includes at least one component capable of interacting with said species liable to cause de-excitation;

j) the power of the discharge is controlled, in order thus to control the rate at which said species liable to cause de-excitation are generated;

k) the rate at which the treatment gas is replenished in the inter-electrode space is controlled.

12. Method for surface treatment according to one of claims **10** and **11**, characterized in that the supply voltage has an amplitude which lies between about 5 kV and 30 kV, and its frequency lies between about 200 Hz and 35 kHz.

13. Method for surface treatment according to claim 12, characterized in that the frequency of the voltage is less than or equal to 15 kHz.

14. Method for surface treatment according to one of claims 10 to 13, characterized in that the treatment gas is introduced into the inter-electrode space with a gas velocity of between 0 m/s and 10 m/s, with a preferential range of less than or equal to 5 m/s.

15. Method for surface treatment according to one of claims 10 to 14, characterized in that the treatment gas includes one or more of the gases in the group formed by nitrogen, argon, silicon precursor gases, oxygen and gases capable of releasing oxygen.

16. Method for surface treatment according to one of claims 10 to 15, characterized in that the thickness of the inter-electrode gas space is between about 0.5 and 5 mm.

17. Method for surface treatment according to one of claims 10 to 16, characterized in that the aim of the treatment is to deposit a silicon-based material on said surface, and in that the treatment gas includes a carrier gas, a silicon precursor gas, and oxygen or a gas capable of releasing oxygen.

18. Device for surface treatment with a plasma at atmospheric pressure, comprising a treatment reactor **(16)** including two exciting electrodes **(22, 24)**, between which an article **(14)** to be treated is arranged, a source for supplying the reactor with a treatment gas and a voltage supply source **(26)** which is connected to the exciting electrodes **(22, 24)**, characterized in that the voltage supply source **(26)** is capable of delivering to the electrodes a supply voltage which is adapted in order to cause the appearance of a discharge **(12)** in the treatment gas and whose amplitude and frequency are capable of maintaining at least some of the components of the treatment gas in the excited state, and/or the presence of electrons, between two successive half-cycles of the supply voltage.

19. Device for surface treatment with a plasma according to claim 18, characterized in that at least one of the electrodes is covered with a dielectric or semiconductor material, the thickness of which advantageously lies in the range of from a few tens of microns to 1 cm, and preferably lies in the range of from 500 microns to 2 mm.

20. Product with a silicon-based deposit, characterized in that this deposit is obtained in accordance with the method according to claim **17**.

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