

The present invention concerns a device for forming excited or unstable gaseous molecules, of the type comprising a tubular gas passage having an axis, formed between a first electrode and a dielectric coaxial with the first electrode and associated with a second electrode, the electrodes being connected to a high-voltage, high-frequency source.

A discharge device of this type is known from the document EP-A-0 160 964, which describes an ozonizer with axial circulation of the gas to be excited in the gas passage.

The object of the present invention is to propose a novel device, compact in configuration, offering significantly improved performance and increased reliability and which is suitable for numerous uses.

For this purpose, according to one characteristic of the invention, the first electrode surrounds the dielectric and has an elongate gas inlet and outlet, parallel to the axis and substantially diametrically opposite, the second electrode being applied to the internal wall of the dielectric.

According to more particular characteristics of the invention:

- the second electrode is formed by metallisation of the internal wall of the dielectric, the external wall of which is covered with a layer of enamel;
- the gas inlet and outlet of the first electrode have a height not exceeding the radial thickness of the gas passage, which does not exceed 2.5 mm;
- electrical field limiting means are provided close to the axial ends of the second electrode in order to prevent the formation of micro-discharges on the surface of the dielectric at its ends.

With such an arrangement of the dielectric barrier discharge type, it is possible to produce, in an extremely compact volume, a "cold" electric discharge, also known, according to the authors, as corona discharge or "Silent Discharge" or "Atmospheric Pressure Glow Discharge", of several kW, functioning at a pressure of between  $0.3 \times 10^5$  Pa and  $3 \times 10^5$  Pa, for example at atmospheric pressure, and offering an improved production yield of excited species (ratio of power stored in the gas in the form of excited species of vibrational quanta to the total power provided by the device), in excess of 50%, without significant heating of the outgoing gas, and suited to multifarious uses with different gases.

Another object of the present invention is the use of such a device for the production of ozone, to supply a CO<sub>2</sub> mixing laser, for the production of metal nitriding atmospheres or for the production of reducing atmospheres for descaling.

Other characteristics and advantages of the present invention will emerge from the following description of embodiments, which is given for purposes of illustration but is in no way limitative, given in conjunction with the accompanying drawings, in which:

- Figure 1 is a schematic view in cross section of a device according to the invention;
- Figure 2 is a view in longitudinal section of a preferred embodiment of the invention; and
- Figure 3 is a detail, to a larger scale, of an embodiment of one end of the dielectric according to the invention.

In the description that follows and in the drawings, identical or analogous elements bear the same reference numerals, with a prime where appropriate.

As shown in Figure 1, the device according to the invention comprises a first tubular electrode 1, formed for example by an internal face of a metal block 2, and in which is disposed, concentrically, an assembly consisting of a tube made from dielectric material 3, for example ceramic, on the internal face of which is disposed, by metallisation, a second electrode 4 (shown exaggeratedly thick in Figure 1 for purposes of clarity). The assembly consisting of the dielectric 3 and the second electrode 4 thus defines, externally with the first electrode 1, a tubular gas passage 5 and, internally, an internal volume 6 in which a refrigerant is circulated, advantageously a Freon® for its electronegative character. The internal gas passage 5 has an axial length of less than 1 metre, typically less than 50 cm, and its radial thickness  $e$  does not exceed 3 mm and is typically less than 2.5 mm.

The block 2 has, diametrically opposite one another, two longitudinal slots 7 and 8, forming respectively the inlet for the gas to be excited in the passage 5 and the outlet for the gas flow including excited or unstable molecules. The slots 7 and 8 extend over the entire axial length of the cavity 5 and have a height that does not exceed the thickness  $e$  and which is typically substantially identical to the latter. The body 2 is advantageously formed, on the periphery of the first electrode 1, with a multiplicity of pipes 60 through which a refrigerant can pass, water for example. The gas inlet 7 communicates with a homogenisation chamber or plenum 9 formed in a box 10 attached to the block 2 and having a duct 11 for feeding gas at a pressure of between  $0.3 \times 10^5$  Pa and  $3 \times 10^5$  Pa, from a gas source 12. The electrodes 1 and 4 are connected to a high-voltage, high-frequency electrical generator 13 functioning at a frequency greater than 15 kHz, the current technological limits being 60 kHz for a power of approximately 10 kW. The gas flow containing the excited species available at the outlet 8 is directed to a user station 14, as will be seen later.

In the embodiment shown in Figure 2, the dielectric tube 3 can be seen, with a thickness of approximately 2 mm with its internal metallisation 4 forming the second electrode, the first electrode 1 here consisting of a metal tube having diametrically opposite slots forming the inlet 7 and outlet 8. The first electrode 1 and the dielectric tube 3 are assembled so as to form an airtight coaxial assembly by means of a first insulating end-piece 15 and a second insulating end-piece 16, the assembly being inserted so as to slide airtight in a bore 17 in a parallelepipedal body 20 having an elongate inlet opening 18 into which the inlet 7 opens out, and an elongate outlet opening 19 into which the outlet 8 of the first electrode opens out.

Though the ceramic materials used to produce the dielectric tube 3 have excellent electrical properties suitable for the production of capacitors, they generally have grainy faces, even when they are polished, which give rise to inferior behaviour under corona charges. To remedy this, according to one aspect of the invention, the external surface of the dielectric is covered with a fine layer of enamel 21, of less than 100 microns, and typically of approximately 20 microns. In addition, even though close contact between the internal electrode and the dielectric 3 enables the formation of micro-discharges along the latter to be prevented, even in cases where very large specific powers permitted by the dielectric 3/ enamel 21 pair are used, problems of high local reinforcement of the electrical field arise at the ends of the internal electrode 4. To remedy this, according to the embodiment shown in Figure 2, the internal electrode 4 is fed by a central tubular conductor 22 connected to the opposite ends of the electrode 4 by flexible metal contacts with evolute profiles 23 whose profile allows a slow, continuous change in the equipotential formed by the electrode 4 whilst avoiding discharge in the cooling liquid, the risk of discharge being further considerably reduced by using as a refrigerant a chlorofluorocarbon because of its highly

electronegative character. In fact, according to one aspect of the invention, the tubular conductor 22 passes through the second insulating nozzle 16 while being closed off by a metal block 24 forming a connector for connection to the source 13, the nozzle 16 having a radial passage 25 opening out into the conductor 22 and a second radial passage 26 opening out into the inner chamber 6 in order to produce in the latter a circulation of cooling oil. As a variant, electrical field peak limiting means at the ends of the high-voltage electrode 4 may be produced by means of a thickening, advantageously progressive, towards the interior of the end of the dielectric tube 3 or by the addition, between the end of the dielectric 3 and the end facing the first electrode 1, of a dielectric ring whose annular faces are enamelled at the same time as the dielectric tube 3 and whose periphery is advantageously metallised.

Another variant of these peak electrical field limiting means is shown in Figure 3, in the form of metal guard rings 27 disposed in line with the end of the high-voltage electrode 4 and covered, along with the end of the electrode 4, with an internal layer of enamel 28 of the same nature as the external layer of enamel 21.

As mentioned above, the device according to the invention may be used to create excited species of different gases.

If the gas introduced into the device contains a majority of nitrogen, typically with a content greater than 78% in a mixture typically containing oxygen, this device essentially creates vibrationally excited nitrogen, but also atomic nitrogen and molecular nitrogen excited on the level  $A^3 \Sigma g^+$ . The vibrationally excited nitrogen finds two major applications, namely  $CO_2$  mixing power lasers, where the excited nitrogen is mixed rapidly with  $CO_2$ , to which it transfers its energy, thus creating the population inversion necessary for the laser effect, and nitriding of metal

surfaces with limited heating of the metal. The nitrogen content plays an important role. The  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$  and above all  $\text{H}_2\text{O}$  impurities, which de-excite the vibrational nitrogen, must be limited. When there is oxygen present in the nitrogen, the production yield falls more or less in proportion to the concentration of oxygen. For nitriding treatments, nitrogen containing 5% oxygen, advantageously obtained by permeation or adsorption, is a good compromise, since the price of the gas is considerably reduced compared to that of pure nitrogen, without the production yield of excited species being significantly reduced.

The device according to the invention may advantageously be used for the production of ozone from dry air or from pure oxygen. In the case of oxygen, the device provides ozone, singlet oxygen and atomic oxygen. The respective quantities of these species produced are dependent on numerous parameters, in particular the temperature of the gas (depending on the flow of gas for a given power) and the frequency of the electrical generator. The temperature of the gas in fact determines the eventual destruction rate of the ozone, and therefore the evolution of the atomic oxygen, and the frequency influences the energy of the electrons and therefore the excitation and dissociation of the molecular oxygen. Besides the applications of pollution control and sterilisation, the products thus generated are used to modify the surface properties of polymers, in particular their properties of adhesion and wettability.

By supplying the device with hydrogen or a hydrogen-based mixture (hydrogen/argon, for example), excited or atomic species having a high reducing power are created, which are used, for example, for descaling.

Although the present invention has been described in relation to particular embodiments, it is not for all that limited

thereby, but on the contrary is open to any modifications and variants which may be apparent to experts.



## CLAIMS

1. Device for forming excited or unstable gaseous molecules, comprising a tubular gas passage (5) having an axis, formed between a first electrode (1) and a dielectric (3), coaxial with the first electrode and associated with a second electrode (4), the electrodes being connected to a high-voltage, high-frequency source (13), characterised in that the first electrode (1) surrounds the dielectric (3) and has an elongate gas inlet (7) and outlet (8), parallel to the axis and substantially diametrically opposite, the second electrode (4) being applied to the internal wall of the dielectric (3).
2. Device according to Claim 1, characterised in that the second electrode (4) is formed by metallisation of the internal wall of the dielectric (3).
3. Device according to Claim 1 or Claim 2, characterised in that the gas inlet (7) and outlet (8) have a height not exceeding the radial thickness (e) of the gas passage (5).
4. Device according to one of the preceding claims, characterised in that the external wall of the dielectric is covered with a fine layer of enamel (21).
5. Device according to one of the preceding claims, characterised in that it includes electrical field limiting means (23; 27) close to the axial ends of the second electrode (4) in order to prevent the formation of micro-discharges at the ends of the dielectric (3).
6. Device according to Claim 5, characterised in that the field limiting means comprise profiled contacts (23) between the second electrode (4) and a central conductor (22).



7. Device according to Claim 5 or Claim 6, characterised in that the field limiting means comprise guard rings (27) formed on the dielectric (3) axially in line with the second electrode (4).

8. Device according to one of the preceding claims, characterised in that it includes means (6; 25, 22, 26) for circulating a refrigerant in the unit consisting of the dielectric (3) and the second electrode (4).

9. Device according to one of the preceding claims, characterised in that the electrodes (1; 4) and the dielectric (3) are produced in the form of a cylindrical subassembly which can be inserted in a body (20) having elongate gas inlet and outlet passages (18, 19).

10. Device according to one of the preceding claims, characterised in that the radial thickness (e) of the gas passage (5) does not exceed 2.5 mm.

11. Device according to Claim 9, characterised in that it comprises a homogenisation chamber (9) between the inlet passage (18, 7) and a gas feed pipe (11).

12. Device according to one of Claims 1 to 11, characterised in that the gas inlet (7) is connected to a source of gas (12) which is air.

13. Device according to Claim 11, characterised in that the gas inlet (7) is connected to a source of gas (12) which is oxygen.

14. Device according to Claim 11, characterised in that the gas inlet (7) is connected to a source of gas (12) which is nitrogen.



15. Device according to Claim 11, characterised in that the gas inlet (7) is connected to a source of gas (12) which is hydrogen.
16. Use of the device according to Claim 12 or Claim 13, for the production of ozone.
17. Use of the device according to Claim 12 or Claim 14 for supplying a CO<sub>2</sub> mixture laser.
18. Use of the device according to Claim 14 for producing metal nitriding atmospheres.
19. Use of the device according to Claim 15 for producing reducing atmospheres.