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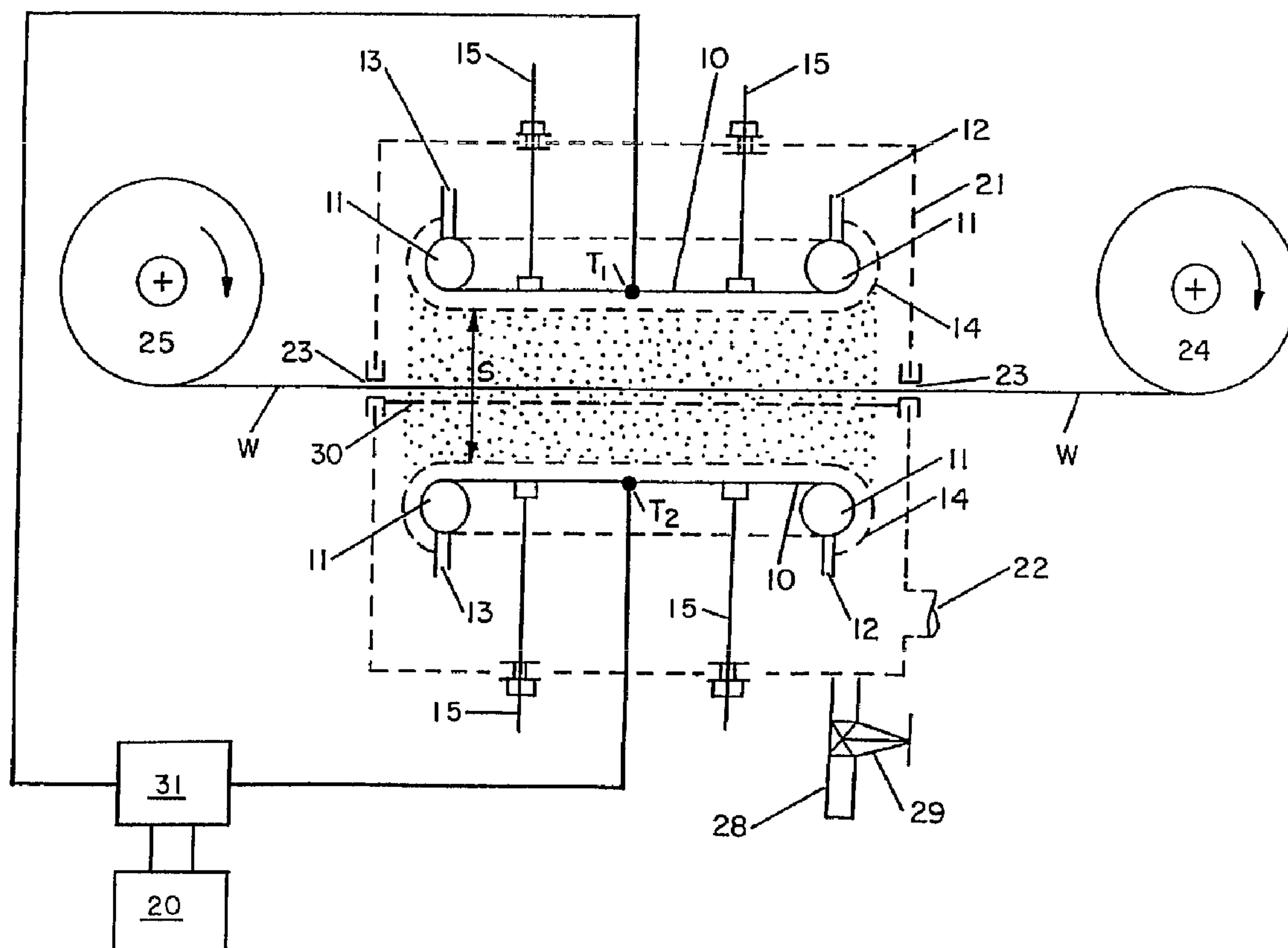
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(54) Title: METHOD AND APPARATUS FOR GLOW DISCHARGE PLASMA TREATMENT OF POLYMER MATERIALS
AT ATMOSPHERIC PRESSURE



(57) Abrégé/Abstract:

A steady-state glow discharge plasma is generated at one atmosphere of pressure within the volume (S) between a pair of insulated metal plate electrodes (14) spaced up to 5 cm apart and rf energized with an rms potential of 1-5kV at 1-100kHz (20).

(57) **Abrégé(suite)/Abstract(continued):**

Space between the electrodes is occupied by air, nitrous oxide, and a noble gas such as helium, neon, argon, etc., or mixtures thereof. The electrodes are charged by an impedance matching network (31) adjusted to produce the most stable, uniform glow discharge. Also, a method for treating a meltblown polymer web, using the aforementioned plasma device, is included.

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(57) Abstract

A steady-state glow discharge plasma is generated at one atmosphere of pressure within the volume (S) between a pair of insulated metal plate electrodes (14) spaced up to 5 cm apart and rf energized with an rms potential of 1-5kV at 1-100kHz (20). Space between the electrodes is occupied by air, nitrous oxide, and a noble gas such as helium, neon, argon, etc., or mixtures thereof. The electrodes are charged by an impedance matching network (31) adjusted to produce the most stable, uniform glow discharge. Also, a method for treating a meltblown polymer web, using the aforementioned plasma device, is included.

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METHOD AND APPARATUS FOR GLOW DISCHARGE PLASMA TREATMENT
OF POLYMER MATERIALS AT ATMOSPHERIC PRESSURE

BACKGROUND OF THE INVENTION

The present invention relates to a method and
5 apparatus for modifying the surface properties of organic
and inorganic polymer materials such as film and fabric,
woven and non-woven.

One of the many utilities for meltblown polymer
web is as a wet cell battery plate separator. The base
10 polymer compound is impervious to the electrolyte. The
meltblown, non-woven fabric structure is ion permeable if
the surface thereof is thoroughly wetted by the
electrolyte. Unfortunately, this latter requirement of
wettability is not an inherent characteristic of most
15 commercial polymers such as nylon, polypropylene,
polyethylene and poly(ethylene terephthalate).

Although meltblown webs of these polymers are
currently used as battery plate separators, wettability is
achieved chemically by means of surfactants. This process
20 not only generates hazardous industrial waste but produces
a product of limited utility life.

Wettability is also a desirable property for
tissue and cloth used to wipe or clean the body, for
surgical sponges, wound dressings, feminine hygiene
25 products and reusable woven knit fabrics. Similarly,
wettability is an important material surface property for
printing and laminating.

Some success has been recently achieved by a glow
discharge plasma treatment of polymer webs. The term
30 "plasma" usually describes a partially ionized gas composed
of ions, electrons and neutral species. This state of
matter may be produced by the action of either very high
temperatures, or strong direct current (DC) or radio
frequency (RF) electric fields. High temperature or "hot"

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plasmas are represented by celestial light bodies, nuclear explosions and electric arcs. Glow discharge plasmas are produced by free electrons which are energized by an imposed DC or RF electric field and then collide with
5 neutral molecules. These neutral molecule collisions transfer energy to the molecules and form a variety of active species which may include photons, metastables, individual atoms, free radicals, molecular fragments, monomers, electrons and ions. These active species are
10 chemically active and/or capable of physically modifying the surface and may therefore serve as the basis of new surface properties of chemical compounds and property modifications of existing compounds.

Low power plasmas known as dark discharge coronas
15 have been widely used in the surface treatment of thermally sensitive materials such as paper, wool and synthetic polymers such as polyethylene, polypropylene, polyolefin, nylon and poly(ethylene terephthalate). Because of their relatively low energy content, corona discharge plasmas can
20 alter the properties of a material surface without damaging the surface.

Glow discharge plasmas represent another type of relatively low power density plasma useful for non-destructive material surface modification. These glow
25 discharge plasmas can produce useful amounts of visible ultraviolet radiation. Glow discharge plasmas have the additional advantage therefore of producing visible and UV radiation in the simultaneous presence of active species. However, glow discharge plasmas have heretofore been
30 successfully generated typically in low pressure or partial vacuum environments below 10 torr which may necessitate batch processing and the use of expensive vacuum systems. Several polymer species exposed to low pressure glow discharge plasmas respond with enhanced surface wettability
35 characteristics. However, the chemical/physical mechanisms

are not understood and the characteristic is lost upon drying. Rewettability remains elusive.

The generation of low power density plasmas at one atmosphere is not new. Filamentary discharges between parallel
5 plates in air at one atmosphere have been used in Europe to generate ozone in large quantities for the treatment of public water supplies since the late 19th century. Such filamentary discharges, while useful for ozone production, are of limited utility for the surface treatment of materials, since the
10 plasma filaments tend to puncture or treat the surface unevenly.

It is an object of an aspect of the present invention, therefore, to provide a non-byproduct producing process for enhancing the wettability of meltblown polymer webs and other
15 types of polymeric substrates.

Another object of an aspect of the invention is to teach a glow discharge plasma process for treating polymer web or film that provides a stable, rewettable product.

Another object of an aspect of the invention is to
20 provide a method and apparatus for continuously processing a polymer web or film of indefinite length through a glow discharge plasma at atmospheric pressure and standard temperature.

A still further object of an aspect of the present
25 invention to teach the construction and operating parameters of a glow discharge plasma having operability in an environmental pressure of about one atmosphere or slightly greater.

INVENTION SUMMARY

30 The present invention provides as a product an improved web, preferably a meltblown polymer web, having a surface enhanced by exposure to a sustained atmospheric, glow discharge plasma. The invention also includes a process specially adapted for the manufacture of said web product, and
35 apparatus specifically designed for carrying out said process.

The above and other objects of the invention to be subsequently explained or made apparent are accomplished with an apparatus based upon a pair of electrically insulated metallic plate electrodes which may or may not have a median plate or screen between them. These plates are mounted in face-to-face parallel or uniformly spaced alignment with means for reciprocatory position adjustment up to about 5 cm of separation. Preferably, the plates are water cooled and covered with a dielectric insulation.

To broaden the range of operating frequency and other parameters over which the desirable uniform (as opposed to filamentary) glow discharge is observed, an impedance matching network is added to the circuit for charging the electrodes. The parameters of such a matching network are adjusted for the most stable, uniform operation of the glow discharge. This condition can occur when the reactive power of the plasma reactor is minimized.

A radio frequency power amplifier connected to both plates delivers at least 180 watts of reactive and plasma power at a working voltage of 1 to at least 5 kV rms and at 1 to 100 kHz.

To assist the starting of the plasma, the electrical discharge from a standard commercial Tesla coil may be briefly applied to the volume between the R.F. energized plates. An electric field established between the metallic plate electrodes must be strong enough to electrically break down the gas used, and is much lower for helium and argon than for atmospheric air. The RF frequency must be in the right range, discussed below, since if it is too low, the discharge will not initiate, and if it is too high, the plasma forms filamentary discharges between the plates. Only in a relatively limited frequency band will the atmospheric glow discharge plasma reactor form a uniform plasma without filamentary discharges.

An electric field established between the metallic plate electrodes must be strong enough to electrically break down the gas used, and is much lower for helium and argon than for atmospheric air. The RF frequency must be in the right range, discussed below, since if it is too low, the discharge will not initiate, and if it is too high, the plasma forms filamentary discharges between the plates. Only in a relatively limited frequency band will the atmospheric glow discharge plasma reactor form a uniform plasma without filamentary discharges.

At least in the volume between the plates wherein the plasma is established, a one atmosphere charge of air, helium or argon is established and maintained for processing material such as polymer film and web to produce desired surface characteristics such as wettability and re-wettability.

Accordingly, in one aspect of the present invention there is provided a method comprising generating a glow discharge plasma with a plasma-sustaining gas at atmospheric pressure in a volumetric space between a pair of electrically insulated electrodes by energizing the electrodes using a radio frequency (RF) amplifier having an impedance matching network, the RF amplifier operating at a potential of at least 1kV rms and at a frequency of 1 to 100 kHz.

In accordance with another aspect of the present invention there is provided an apparatus comprising:

a pair of electrically insulated electrodes;

an RF amplifier having an impedance matching network, the RF amplifier adapted to energize the electrodes at a potential of at least 1kV rms and at a frequency of 1 to 100 kHz;

means for controlling the potential and the frequency of RF amplifier to generate a glow discharge plasma with a plasma-sustaining gas at atmospheric pressure in a volumetric space between the electrodes;

means for placing a workpiece in the volumetric space to subject the workpiece to the glow discharge plasma, wherein the workpiece is a web; and

means for generating a pressure differential between two opposing surfaces of the web such that active species in the glow

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discharge plasma pass through the web due to the pressure differential.

In accordance with yet another aspect of the present invention there is provided a method comprising:

5 generating a glow discharge plasma with a plasma-sustaining gas at atmospheric pressure in a volumetric space between a pair of electrically insulated electrodes by energizing the electrodes using a radio frequency (RF) amplifier having an impedance matching network, the RF amplifier operating at a potential of at
10 least 1kV rms and at a frequency of 1 to 100 kHz;

 placing a workpiece in the volumetric space to subject the workpiece to the glow discharge plasma, wherein the workpiece is a web; and

 generating a pressure differential between two opposing
15 surfaces of the web such that active species in the glow discharge plasma pass through the web due to the pressure differential.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Relative to the drawings wherein like reference characters designate like or similar elements throughout the several figures of the drawings:

 Figure 1 is a schematic of the present invention component assembly.

25 Figure 2 is an impedance matching network distinctively suitable for powering the present invention.

 Figures 3, 4 and 5 are representative alternative power supply output stage circuits.

 Figure 6 schematically represents an alternative embodiment
30 of the invention.

 Figure 7 schematically represents the upper chamber of a one atmosphere glow discharge plasma reactor having a median grid plate.

 Figure 8 represents a graph of voltage, current and power
35 waveforms for a uniform glow discharge plasma.

 Figure 9 represents a graph of voltage, current and power waveforms for a filamentary discharge plasma.

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Figure 10 is a log-log graph of total and plasma power density in milliwatts per cubic centimeter, as functions of RMS voltage applied to the electrodes.

Figure 11 is a log-log graph of total and plasma power density in milliwatts per cubic centimeter, as functions of R.F. frequency.

Figure 12 is a graph of amplifier frequency and corresponding breakdown current phase angles respective to a particular operating example of the invention.

Figure 13 is a graph of amplifier frequency and corresponding power consumption respective to a particular operating example of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the invention schematic illustrated by Figure 1, the electrodes 10 are fabricated of copper plate having a representative square plan dimension of 21.6 cm x 21.6 cm. Silver soldered to the plates 10 are closed loops 11 of 0.95 cm copper tubing having hose nipples 12 and 13 connected therewith on opposite sides of the closed tubing loop. The edges of the electrode plates should have a radius of curvature comparable to the separation between the electrode plates and median plate to discourage electrical breakdown at the edge of the electrodes. Not shown are fluid flow conduits connected to the inlet nipples 12 for delivering coolant fluid to the loop 11 and to the outlet nipples 13 for recovering such coolant fluid.

The integral metallic units comprising plates 10 and tubing 11 are covered with a high dielectric insulation material 14 on all sides to discourage electrical arcing from the edges or back side of the electrode plates.

Preferably, some mechanism should be provided for adjusting the distance s between plates 10 up to about 5 cm separation while maintaining relative parallelism. Such a mechanism is represented schematically in Figure 1 by the rod adjusters 15 secured to the upper and lower plates 10.

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This arrangement anticipates a positionally fixed median plate 30.

Although parallelism is used in the context of parallel planes, it should be understood that the terms
5 also comprises non-planar surfaces that are substantially equidistant. Also included are the geometry characteristics of a cylinder having an axis parallel to another cylinder or to a plate.

Energizing the plates 10 is a low impedance, high
10 voltage, R.F. power amplifier 20 having independently variable voltage and frequency capacities over the respective ranges of 1 to at least 5 kV and 1 to 100 kHz. Between the RF power supply 20 and the plates 10 may be an impedance matching network 31, described in greater detail
15 relative to Figure 2.

Surrounding the plate assembly is an environmental isolation barrier 21 such as a structural enclosure suitable for maintaining a controlled gas atmosphere in the projected plan volume between the plates
20 10. Inlet port 22 is provided to receive an appropriate gas such as air, helium or argon, mixtures of helium or argon with oxygen or air or a mixture of argon with helium. In any case, gas pressure within the isolation barrier 21 is substantially ambient thereby obviating or reducing the
25 need for gas tight seals. Normally, it is sufficient to maintain a low flow rate of the modified atmospheric pressure gas through the inlet port 22 that is sufficient to equal the leakage rate. Since the pressure within the isolation barrier 21 is essentially the same as that
30 outside the barrier, no great pressure differential drives the leakage rate. A vent conduit 28 controlled by valve 29 is provided as an air escape channel during initial flushing of the enclosure. Thereafter, the valve 29 may be closed for normal operation.

35 Narrow material flow slits 23 are provided in the isolation barrier 21 to accommodate passage of a material

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web W between the plates 10 as drawn from a supply reel 24 onto a rewind reel 25. Drive for the reels 24 and 25 is controlled to provide a predetermined residence time between the plates 10 and within the plasma for any given web element.

To broaden the range of operating frequency and other parameters over which the desirable uniform (as opposed to filamentary) glow discharge occurs, an impedance matching network, one embodiment of which is illustrated schematically by Figure 2, is added to the power circuit for charging the electrodes 10. The parameters of this matching network are adjusted for the most stable, uniform operation of the glow discharge. This condition can occur when the reactive power of the plasma reactor is minimized.

Figures 3 through 5 represent alternative power supply options having respective attractions. Figure 3 corresponds to a configuration wherein the bottom electrode terminal T_1 is connected to ground potential and the top terminal T_2 is charged at the full working potential. Figures 4 and 5 are electrical equivalents wherein the T_1 and T_2 voltages are 180° out of phase but at only half the maximum potential. Figure 4 represents a grounded center tap transformer whereas Figure 5 represents a solid state power circuit embodiment.

Shown in Figure 6 are two optional embodiments, the functions of which are to drive a reciprocating gas flow containing active species from the plasma back and forth through the web W. This can be accomplished either by a bellows 35 actuated by a reciprocating shaft 33, or by a piston 36 activated by a reciprocating shaft 32. The change in volume of the upper chamber will give rise to a periodic reversal of the pressure differential across the web W, hence, a periodic reversal of the gas flow. As an alternative embodiment, a passageway from behind the piston can be connected to the lower chamber as shown in the dashed line piping 34.

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The Figure 6 embodiment of the invention provides an electrically grounded screen 30 to support the web W as it is drawn between the opposite material flow slits 23. This configuration attenuates an accumulated electrical charge on the web and also structurally supports the traveling fabric web as a pressure differential membrane between an upper, gas inlet chamber and a lower, vent chamber. This swept flow differential assures an internal saturation of the web W by the gas containing active species from the plasma.

Electric fields employed in a one atmosphere, uniform glow discharge plasma reactor are only a few kilovolts per centimeter, values which, if D.C., would usually be too low to electrically break down the background gas. Gases such as helium and air will break down under such low electric fields, however, if the positive ion population is trapped between the two parallel or uniformly spaced electrodes, this greatly increasing their lifetime in the plasma, while at the same time the electrons are free to travel to the insulated electrode plates where they recombine or build up a surface charge. The most desirable uniform one atmosphere glow discharge plasma is therefore created when the applied frequency of the RF electric field is high enough to trap the ions between the median screen and an electrode plate, but not so high that the electrons are also trapped during a half cycle of the R.F. voltage. The electrons may be trapped by bipolar electrostatic forces.

If the RF frequency is so low that both the ions and the electrons can reach the boundaries and recombine, the particle lifetimes will be short and the plasma will either not initiate or form a few coarse filamentary discharges between the plates. If the applied frequency is in a narrow band in which the ions oscillate between the median screen and an electrode plate, they do not have time to reach either boundary during a half period of

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oscillation and be carried for long times. If the more mobile electrons are still able to leave the plasma volume and impinge on the boundary surfaces, then the desirable uniform plasma is produced. If the applied RF frequency is still higher so that both electrons and ions are trapped in the discharge, then the discharge forms a filamentary plasma.

Without limiting our invention to any particular theory, we are disposed to a relationship between the electrode spacing, the RMS electrode voltage, and the applied frequency which results in trapping ions but not electrons between the two plates, and produces the desired uniform one atmosphere glow discharge plasma. On Figure 7 is a schematic of the upper chamber of the one atmosphere glow discharge plasma reactor. The lower boundary of this space is the midplane screen or base, the floating potential of which should remain near ground if the RF power supply output is connected as a push-pull circuit to the two electrodes with a grounded center tap. In the data reported herein, the median screen was grounded through an inductive current choke. In the configuration of Figure 7, a Cartesian coordinate system is applied as shown, with the applied electric field in the x-direction. The maximum amplitude of the electric field between the grounded median screen and the upper electrode is E_0 , and the separation of the screen from the electrodes is the distance d . The median screen, with an exposed sample on it, is assumed not to allow ions through the median plane from the upper chamber to the lower, or vice-versa.

The electric field between the electrodes shown on Figure 7 is given by

$$E=(E_0\sin\omega t, 0, 0). \quad (1)$$

It is assumed that the one atmosphere glow discharge operates in a magnetic field free plasma. The equation of motion for the ions or electrons between the two plates is

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given by a Lorentzian model, in which the electrons and ions collide only with the neutral background gas and, on each collision, give up all the energy they acquired from the RF electric field since the last collision to the neutral gas. The equation of motion for the ions or electrons in the Lorentzian model is given by

$$F=ma=-mv_c v - eE, \quad (2)$$

where the first term on the right hand side is the Lorentzian collision term, according to which the momentum mv is lost with each collision that occurs with a collision frequency v_c . The x component of Eq. 2 is given by

$$m \frac{d^2 X}{dt^2} + mv_c \frac{dX}{dt} = eE_0 \sin \omega t, \quad (3)$$

where the electric field E from Eq. 1 has been substituted into the right hand side of Eq. 2. The general solution to Eq. 3 is

$$x = C_1 \sin \omega t = C_2 \cos \omega t, \quad (4)$$

where the constants C_1 and C_2 are given by

$$C_1 = -\frac{eE_0}{m} \frac{1}{(\omega^2 + v_c^2)}, \quad (5)$$

15 and

$$C_2 = -\frac{v_c eE_0}{\omega m} \frac{1}{(\omega^2 + v_c^2)} \quad (6)$$

The one atmosphere helium glow discharge is operated at frequencies between $\omega/2\pi = 1$ and 30 kHz, where, for helium at one atmosphere,

$$v_{ci} \approx 6.8 \times 10^9 \text{ ion collisions/sec.}, \quad (7a)$$

and

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$$v_{ce} \approx 1.8 \times 10^{12} \text{ electron coll./sec.} \quad (7b)$$

The collision frequency for ions and electrons given by Eqs. 7a and 7b is much greater than the RF frequency, $V_c \gg \omega$. The relation $v_c \gg \omega$ for ions and electrons, implies that C_2 is much greater than the constant C_1 , or

$$C_2 \approx \frac{eE_0}{m\omega V_c} \gg C_1 \quad (8)$$

- 5 The time dependent position of an ion or an electron in the electric field between the plates is given by substituting Eq. 8 into Eq. 4, to obtain

$$x(t) \approx -\frac{eE_0}{m\omega V_c} \cos \omega t. \quad (9)$$

The RMS displacement of the ion or electron during a half cycle is given by

$$x_{rms} = \frac{2}{\pi} \frac{eE_0}{m\omega V_c} \text{ meters.} \quad (10)$$

- 10 If V_0 is the driving frequency, in Hertz, then the radian RF frequency is given by

$$\omega = 2\pi V_0, \quad (11)$$

and the maximum electric field between the plates can be approximated by the maximum voltage V_0 appearing between them,

$$E_0 = \frac{V_0}{d} = \frac{\pi V_{rms}}{2d}. \quad (12)$$

- 15 If the charge in question moves across the discharge width from the median plane to one of the electrode plates during one full cycle, then we may write

$$x_{rms} \leq \frac{d}{2}. \quad (13)$$

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Equation 13 states that the RMS displacement of the particle has to be less than half the clear spacing in order to have a buildup of charge between the plates. In the geometry shown in Figure 7, the distance d is identified with the distance between the grounded median screen and the energized electrode. Substituting Eqs. 11 to 13 into Eq. 10 yields the relationship

$$\frac{d}{2} \approx \frac{eV_{rms}}{2\pi m v_o v_c d} \quad (14)$$

If we now solve for the critical frequency v_o above which charge buildup should occur in the plasma volume, we have

$$v_o \approx \frac{eV_{rms}}{\pi m v_c d^2} \text{ Hz.} \quad (15)$$

10 In Eq. 15, the collision frequency v_c is approximately given by Eqs. 7a or 7b for ions or electrons, respectively, at one atmosphere, and the RMS voltage is that which bounds the upper and lower limit of the uniform discharge regime.

The range of parameters over which we have operated a one atmosphere, uniform glow discharge plasma reactor is given in Table 1. The nominal pressure at which this discharge has been operated is one atmosphere. The variation of several torr shown in Table 1 is not intended to represent the day-to-day fluctuations of barometric pressure, but the pressure differential across the midplane screen which is intended to drive active species from the upper plasma through the fabric being exposed. The RMS power shown in Table 1 is the net power delivered to the plasma, less the reactive power which does not appear in the plasma. The total volume of plasma between the two electrode plates is given by

$$S=0.93 d(\text{cm}) \text{ liters}, \quad (16)$$

where d is the separation of a plate from the median screen in centimeters.

The power densities shown in Table 1 are far below those of electrical arcs or plasma torches, but also are several orders of magnitude higher than the power densities associated with some other forms of plasma treatment such as corona discharges. The power densities of the one atmosphere glow discharge plasma are generally low enough not to damage exposed fabrics, but are also enough higher than coronal plasmas used for surface treatment that they should provide far more active species than the latter. The plasma parameters, such as electron kinetic temperature and number density are somewhat speculative at this early stage in the development of our invention. A few results from probing the plasma midplane with a floating Langmuir probe indicates that the plasma, without grounding the midplane screen, will float to positive potentials of several hundred volts. The ion kinetic temperatures are very likely close to that of the room temperature atoms with which they frequently collide at these high pressures; the electrons apparently remain numerous and energetic enough to excite the neutral background atoms, hence making this a glow discharge. The existence of excited states which emit visible photons implies that the electron population has a kinetic temperature of at least an electron volt. The diagnostic difficulties of measuring plasma parameters at this high pressure are very severe, since ordinary Langmuir probing technique cannot be applied due to the short mean free paths of the electrons compared to a Debye distance. Electron number densities, however, may be measured by microwave interferometric techniques.

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TABLE 1OPERATING CHARACTERISTICS OF THE ONE
ATMOSPHERE GLOW DISCHARGE PLASMA REACTOR

- 5 working gas = He, He + 1-7% O₂, Ar, Ar + He, Ar + 1-7% O₂,
and atmospheric air
frequency = 1 kHz to 100 kHz
voltage = 1.5 - 9.5 kV_{rms} plate to plate
electrode gap d = 0.8 - 3.2 cm
- 10 pressure = 760 +15, -5 torr
RMS power = 10 watts to 150 watts
power density = 4 - 120 mW/cm³
plasma volume = 0.7 - 3.1 liters
-
- 15 On Figures 8 and 9 are shown two waveforms of
voltage and current taken in helium at the same electrode
separation and gas flow conditions, but at two different
frequencies. Figure 8 was taken in the uniform glow
discharge regime at a frequency of 2.0 kHz, and Figure 9
20 was taken in the filamentary discharge regime at a
frequency above the uniform plasma operating band at 8.0
kHz. The high output impedance of our RF power supply
results in a voltage waveform (trace B) that is very close
to sinusoidal. The reactive current waveform (trace C) is
25 interrupted by a breakdown of the plasma twice each cycle,
once when the voltage is positive, and once when the
voltage is negative. Trace A shows the reactive current
waveform at the same voltage and operating conditions, but
in air, rather than helium. There was no perceptible
30 plasma present in air under these conditions, and the power
is completely reactive. This purely reactive current of
trace A was subtracted from the total plasma current in
trace C, to yield trace D. The instantaneous power
deposited in the plasma (trace E) is found by multiplying
35 the excess plasma current above the reactive current (trace

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D) by the voltage at that point (trace B). The average power is found by integrating over the duration of the pulses shown, and dividing by this duration. It is in this manner that the power and power density into the plasma were calculated for these highly nonsinusoidal current waveforms. Figures 8 for the uniform discharge and 9 for the filamentary discharge show characteristically different power waveforms in trace E; this is a method of distinguishing the uniform from the filamentary discharge.

10 The plasma power is of interest because it is proportional to the production rate of active species in the plasma; the reactive power is significant because it determines the required power handling rating of the plasma power supply and associated equipment. The total power is the sum of plasma and reactive power. On Figure 10 is shown a log-log plot of the plasma and total power density in milliwatts per cubic centimeter, as functions of the RMS voltage applied to the parallel plates. The active plasma volume in Figure 10 was 1.63 liters, with a separation between the median screen and each plate of $d = 1.75$ centimeters in a plasma of helium gas. On Figure 11 is a similar presentation of the power density plotted on log-log coordinates as a function of the frequency. The approximate bound of the uniform plasma discharge regime is shown by the arrow. These data were taken in helium gas for the same plasma volume and electrode separation as Figure 10.

EXAMPLE 1

30 In a first operational example of the invention, the Figure 1 described physical apparatus sustained a glow discharge plasma in one atmosphere of helium at standard temperature with a separation distance s of 3.0 cm between plates 10. The plates were energized with a 4.4 kV rms working potential. Holding these parameters constant, R.F. frequency was increased as an independent variable. As the dependent variable, Figure 12 charts the corresponding

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breakdown current phase angle as determined relative to the voltage waveform node. Similarly, Figure 13 charts the total power, including reactive and plasma input power required to sustain the plasma at the respective R.F. frequencies.

EXAMPLE 2

In a second operational example of the invention, the Figure 1 described physical apparatus is used to sustain a glow discharge plasma in one atmosphere of helium at standard temperature with a separation distance s of 1.0 cm between plates 10. In this example, the R.F. frequency was held constant at 30 kHz while plate potential was manipulated as the independent variable and current breakdown phase angle, θ , (Table 2) and total power, P , (Table 3) measured as dependent variables.

Table 2

V(kV)	1	1.5	2	2.5	3	3.5
θ (deg)	28	40	61	46	65	76.5

Table 3

V(kV)	1	1.5	2	2.5	3	3.5
P(W)	7	13	22	57	50	44.9

EXAMPLE 3

A third operational example of the invention included a one atmosphere environment of helium between a 1 cm separation distance s between plate electrodes 10 charged at 1.5 kV rms potential. The R.F. frequency was manipulated as the independent variable. As a measured dependent variable, Table 4 reports the corresponding phase angle θ of breakdown current. The measured dependent variable of Table 5 reports the corresponding total power consumption data.

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Table 4

f(kHz)	10	20	30	40	50	60	70	80	90	100
Θ (deg)	43	32	43	52	54	61	60	56	45	22.5

Table 5

5	f(kHz)	10	20	30	40	50	60	70	80	90	100
	P(W)	5	8	11	19	35	43	47	57	89	124

EXAMPLE 4

The largest volume helium plasma of 3.1 liters was achieved with the above described apparatus at a 3.2 cm plate separation having a 5 kV rms potential at an R.F. frequency of 4 kHz.

Meltblown webs formed from nylon, poly(ethylene terephthalate), polypropylene and polyethylene have been processed by exposure to the glow discharge plasma described herein to produce desired material characteristics, increased wettability and re-wettability.

Wettability of a material is objectively measured by either or both of two tests including (a) the angle of a water bead supported on the material surface and (b) the time required to wick along a predetermined material length.

By such tests, it was determined that polypropylene, nylon, polyester and polyethylene film experienced a significant wettability and re-wettability improvement after a 2.5 minute plasma exposure as evidenced by a greatly reduced bead angle.

A poly(ethylene terephthalate) web, after 2.5 minutes of glow discharge plasma exposure to a 5kV, 4kHz across a 4.5 cm plate separation, experienced a 0° surface bead angle and a 37.37 second wicking rate determined by the INDA standard absorption test. Prior to plasma exposure, the web had a large surface bead angle and no wicking capacity.

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Similarly, after only 60 seconds of exposure to the same plasma, a nylon web, having a high surface bead angle and no wicking capacity enjoyed a 0° surface bead angle and a 16.61 second wicking rate (INDA standard test) upon wetting and re-wetting.

In another test set, two different meltblown webs poly(ethylene terephthalate) and polypropylene (PET and PP), were treated by the one atmosphere glow discharge plasma with helium or helium plus active gases as the working gas for a treating time period of from one-half minute to two minutes. The power supply voltage was from 1,000 V_{rms} to 4,000 V_{rms} and the frequency was from 1 kHz to 100 kHz. The webs had a fiber size of 2 to 2.5 microns, a pore size of 20-25 microns, and a porosity of 90%. Table 6 lists some initial results from these treatments.

Wettability was justified by contact angle, wickability, and wetout of the liquid through web thickness and on the web surface. Wickability was measured according to INDA standard (1st 10.1-92), in which time was measured for the liquid (double D's water) to rise 2.4 cm high. Physical fiber surface change was analyzed by photomicrographs taken using the ETEC Auto Scan electron microscope for a magnification of 2,000x to 4,000x.

TABLE 6

25	<u>Treating Conditions</u>				<u>Wettability</u>			
	<u>Sample</u>	<u>Time(s)</u>	<u>gases</u>	<u>kV_{rms}</u>	<u>Contact Angle</u>	<u>Wicking Rate(s)</u>	<u>Thickness</u>	<u>Surface</u>
	<u>Wettability</u>							
30	PP 0.35 oz	60	He, O ₂	3.5	reduced	not sig.	90%	good
	PP 0.35 oz	60	He, O ₂	3.0	unchanged	no	75%	
	increased							
	PET 1 oz	90	He	2.3	0	31.74	good	good

Although expansive data is not presently available, it is to be noted that a uniform glow discharge plasma has been sustained by the Figure 1 apparatus with a one atmosphere ambient air environment and an 8 kV/cm electric field.

What is claimed is:

1. A method comprising:

generating a glow discharge plasma with a plasma-sustaining gas at atmospheric pressure in a volumetric space between a pair of electrically insulated electrodes by energizing the electrodes using a radio frequency (RF) amplifier having an impedance matching network, the RF amplifier operating at a potential of at least 1kV rms and at a frequency of 1 to 100 kHz;

placing a workpiece in the volumetric space to subject the workpiece to the glow discharge plasma, wherein the workpiece is a web; and

generating a pressure differential between two opposing surfaces of the web such that active species in the glow discharge plasma pass through the web due to the pressure differential.

2. The method of claim 1, wherein the RF amplifier is operated at a potential of between 1kV and 5kV rms.

3. The method of claim 1, wherein the RF amplifier is operated at a frequency of 1 to 30 kHz.

4. The method of claim 1, wherein the frequency of the RF amplifier is selected such that positive ions of the plasma are trapped between the electrodes during each half cycle of the RF amplifier, while electrons of the plasma are not trapped during said each half cycle of the RF amplifier.

5. The method of claim 1, wherein the plasma-sustaining gas is air.

6. The method of claim 1, wherein the plasma-sustaining gas is a noble gas.

7. The method of claim 1, wherein the plasma-sustaining gas comprises at least one of helium, argon, and air.

8. The method of claim 1, wherein the electrodes are in equidistant opposition.

9. The method of claim 8, wherein the electrodes are parallel-plate electrodes.

10. The method of claim 8, wherein the distance between the electrodes is 5 cm or less.

11. The method of claim 1, further comprising adjusting position of one of the electrodes relative to the other electrode to control the generation of the glow discharge plasma.

12. The method of claim 1, wherein the glow discharge plasma is a uniform glow discharge plasma.

13. The method of claim 1, wherein the web is a meltblown polymer web.

14. The method of claim 13, wherein the meltblown polymer web is formed from polypropylene.

15. The method of claim 1, wherein the workpiece is drawn between the electrodes to subject different parts of the workpiece to the glow discharge plasma over time.

16. The method of claim 15, wherein the workpiece is drawn between the electrodes at a substantially uniform rate to subject the different parts of the workpiece to the glow discharge plasma for a substantially equal duration.

17. The method of claim 1, wherein the workpiece is subjected to the glow discharge plasma in order to alter one or more surface characteristics of the workpiece.

18. The method of claim 17, wherein one surface

characteristic is wettability.

19. The method of claim 17, wherein one surface characteristic is re-wettability.

20. The method of claim 1, further comprising the step of fluid-cooling the electrodes.

21. The method of claim 20, wherein the electrodes are fluid-cooled by passing a cooling fluid through conduits that are bonded to the electrodes to extract heat from the electrodes.

22. The method of claim 1, further comprising the step of charging the volumetric space with a substantially continuous flow of the plasma-sustaining gas.

23. The method of claim 22, wherein the volumetric space is enclosed by an isolation barrier.

24. The method of claim 1, wherein:

the RF amplifier is operated at a potential of between 1kV and 5kV rms and at a frequency of 1 to 30 kHz;

the plasma-sustaining gas is air; and

the glow discharge plasma is a uniform glow discharge plasma.

25. The method of claim 24, wherein the electrodes are parallel-plate electrodes; and comprising:

charging the volumetric space with a substantially continuous flow of the plasma-sustaining gas, wherein the volumetric space is enclosed by an isolation barrier;

drawing the web through the volumetric space between the electrodes at a substantially uniform rate to subject different parts of the web to the glow discharge plasma for a substantially equal duration; and

generating the pressure differential between two opposing surfaces of the web such that active species in the glow

discharge plasma pass through the web due to the pressure differential, wherein the web is subjected to the glow discharge plasma in order to alter one or more surface characteristics of the web.

26. Apparatus comprising:

a pair of electrically insulated electrodes;

an RF amplifier having an impedance matching network, the RF amplifier adapted to energize the electrodes at a potential of at least 1kV rms and at a frequency of 1 to 100 kHz;

means for controlling the potential and the frequency of RF amplifier to generate a glow discharge plasma with a plasma-sustaining gas at atmospheric pressure in a volumetric space between the electrodes;

means for placing a workpiece in the volumetric space to subject the workpiece to the glow discharge plasma, wherein the workpiece is a web; and

means for generating a pressure differential between two opposing surfaces of the web such that active species in the glow discharge plasma pass through the web due to the pressure differential.

27. The apparatus of claim 26, wherein:

the RF amplifier is operated at a potential of between 1kV and 5kV rms and at a frequency of 1 to 30 kHz;

the plasma-sustaining gas is air; and

the glow discharge plasma is a uniform glow discharge plasma.

28. The apparatus of claim 27, wherein the electrodes are parallel-plate electrodes; and comprising:

means for charging the volumetric space with a substantially continuous flow of the plasma-sustaining gas, wherein the volumetric space is enclosed by an isolation barrier;

means for drawing the web through the volumetric space between the electrodes at a substantially uniform rate to subject different parts of the web to the glow discharge

plasma for a substantially equal duration; and

means for generating the pressure differential between two opposing surfaces of the web such that active species in the glow discharge plasma pass through the web due to the pressure differential, wherein the web is subjected to the glow discharge plasma in order to alter one or more surface characteristics of the web.

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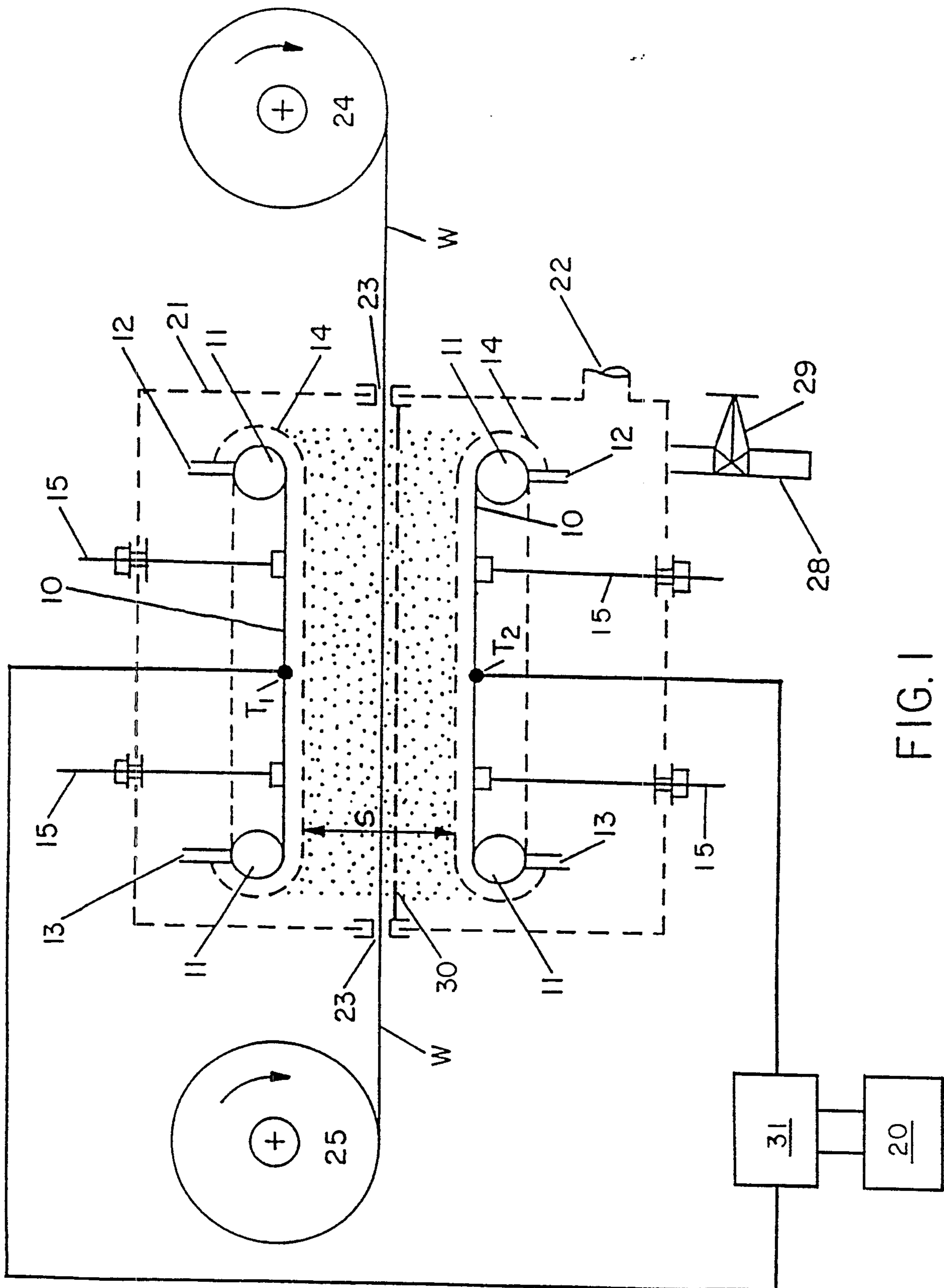
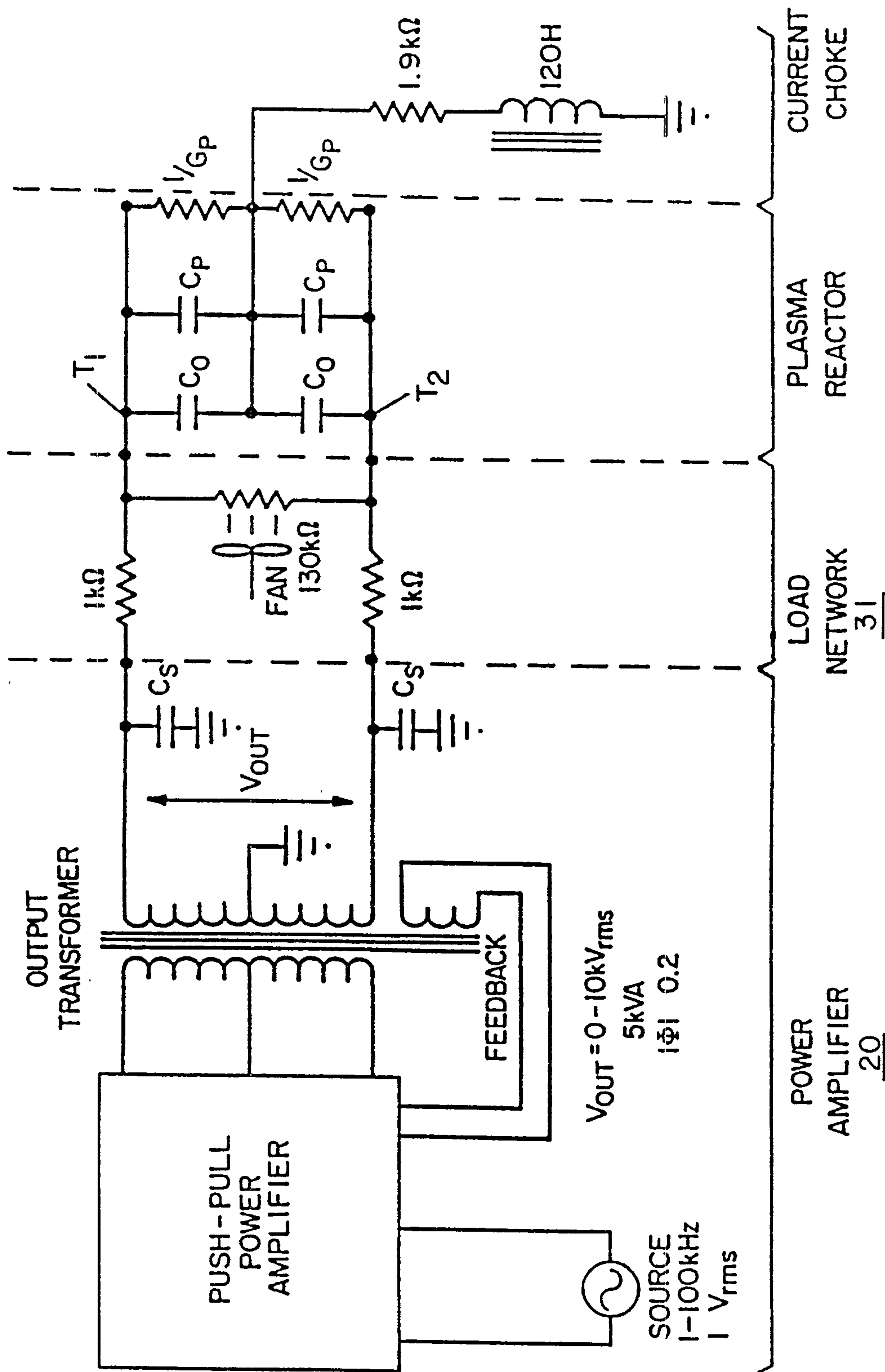


FIG. 1

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FIG. 3

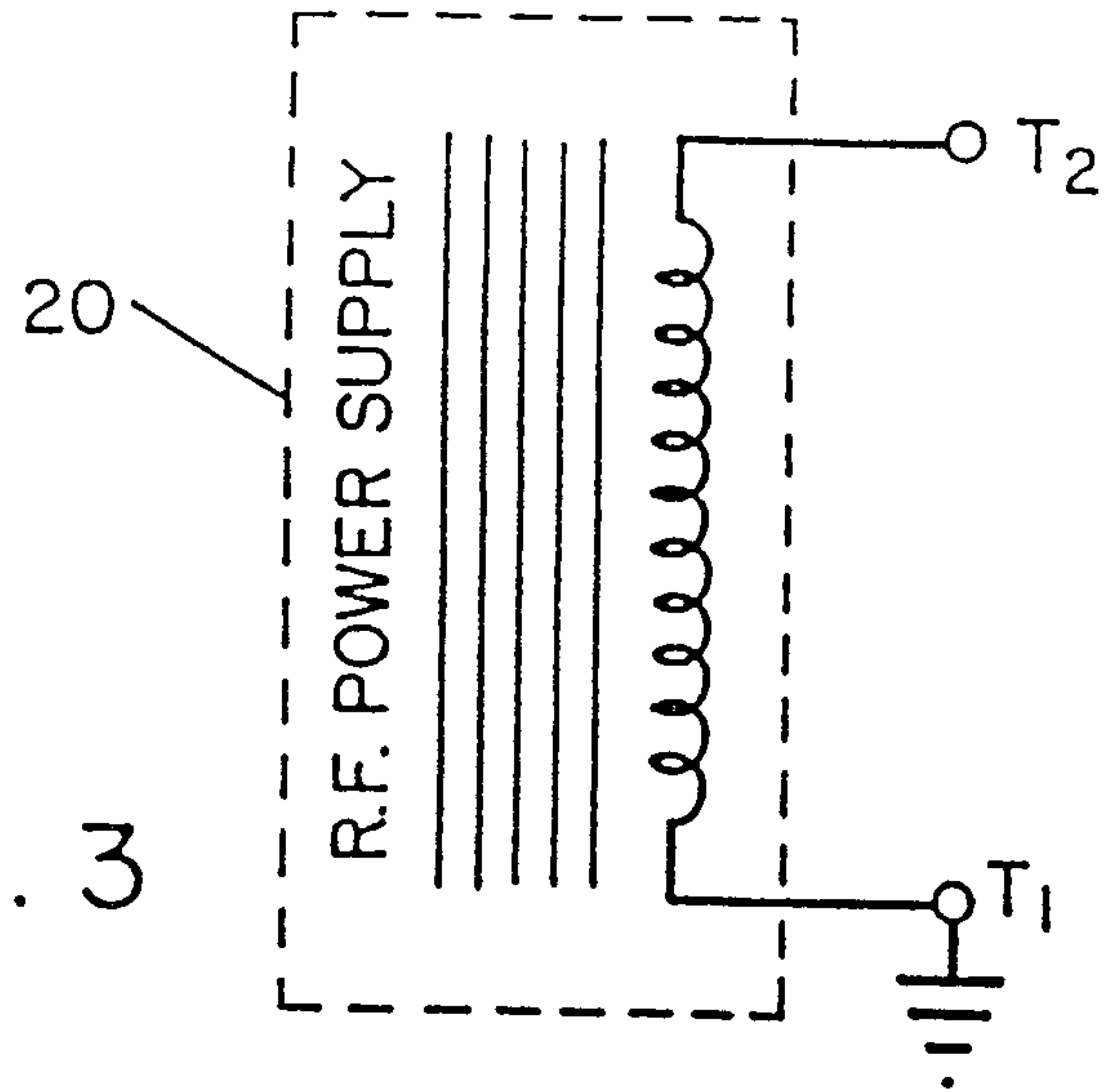


FIG. 4

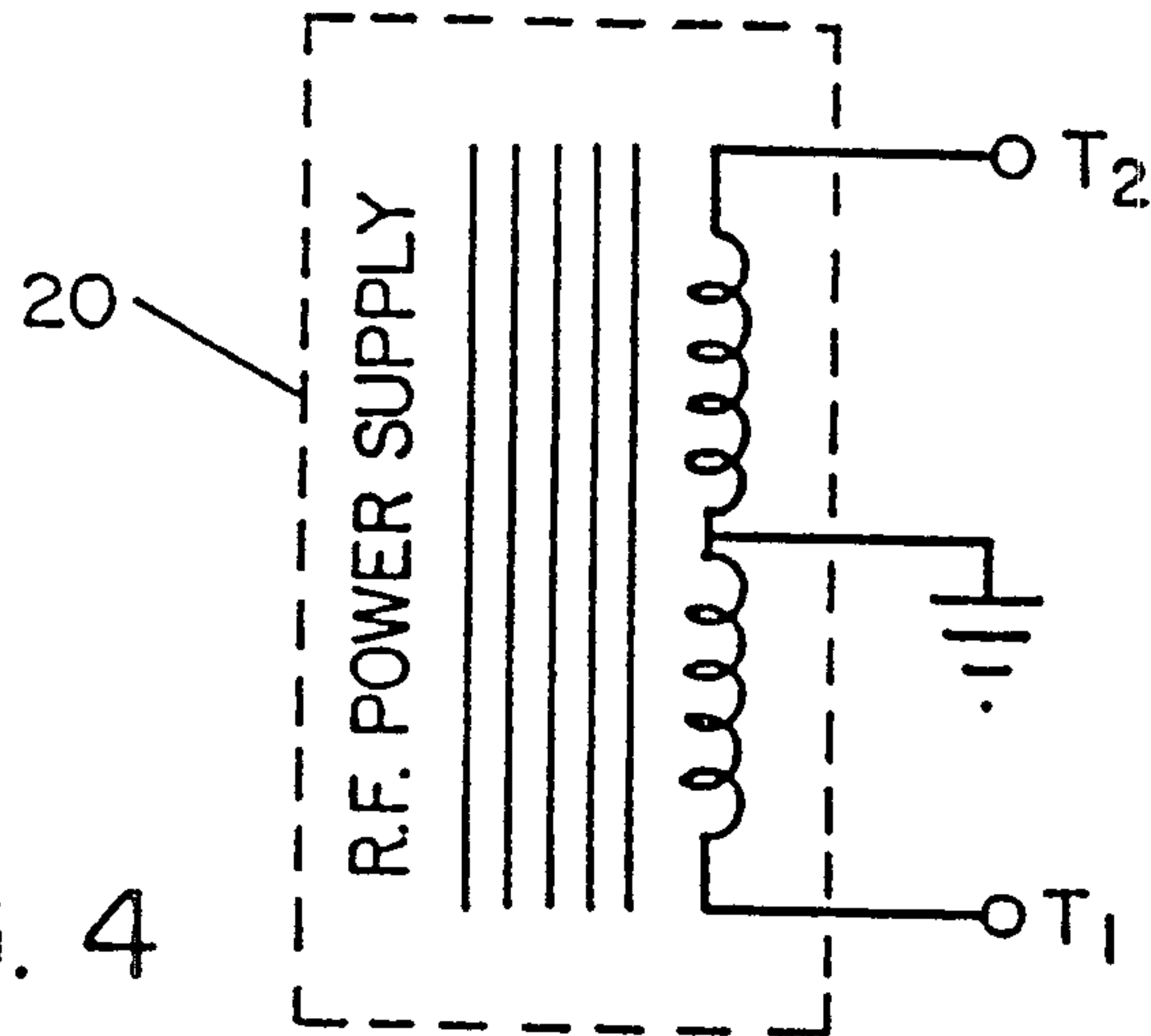
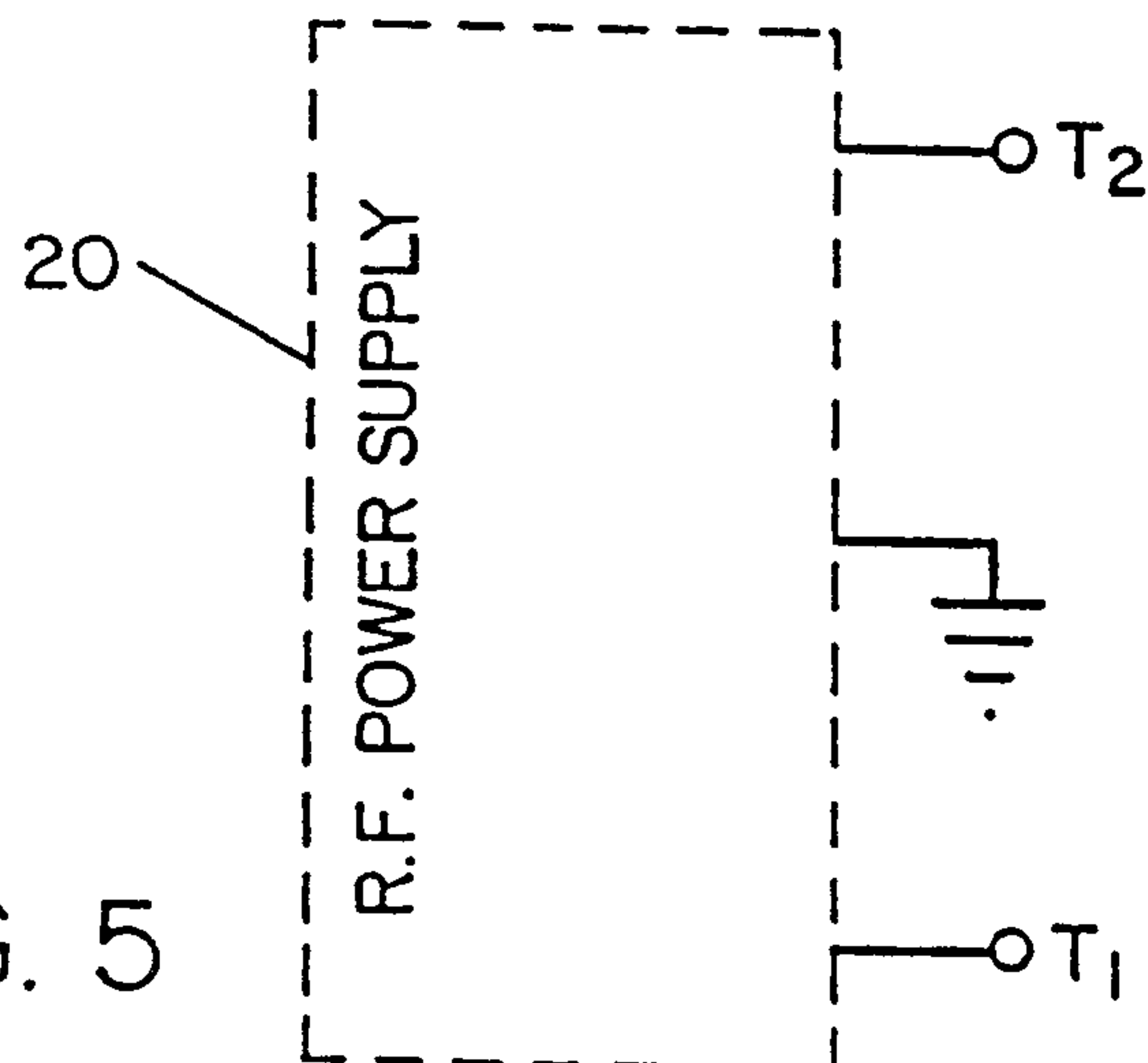


FIG. 5



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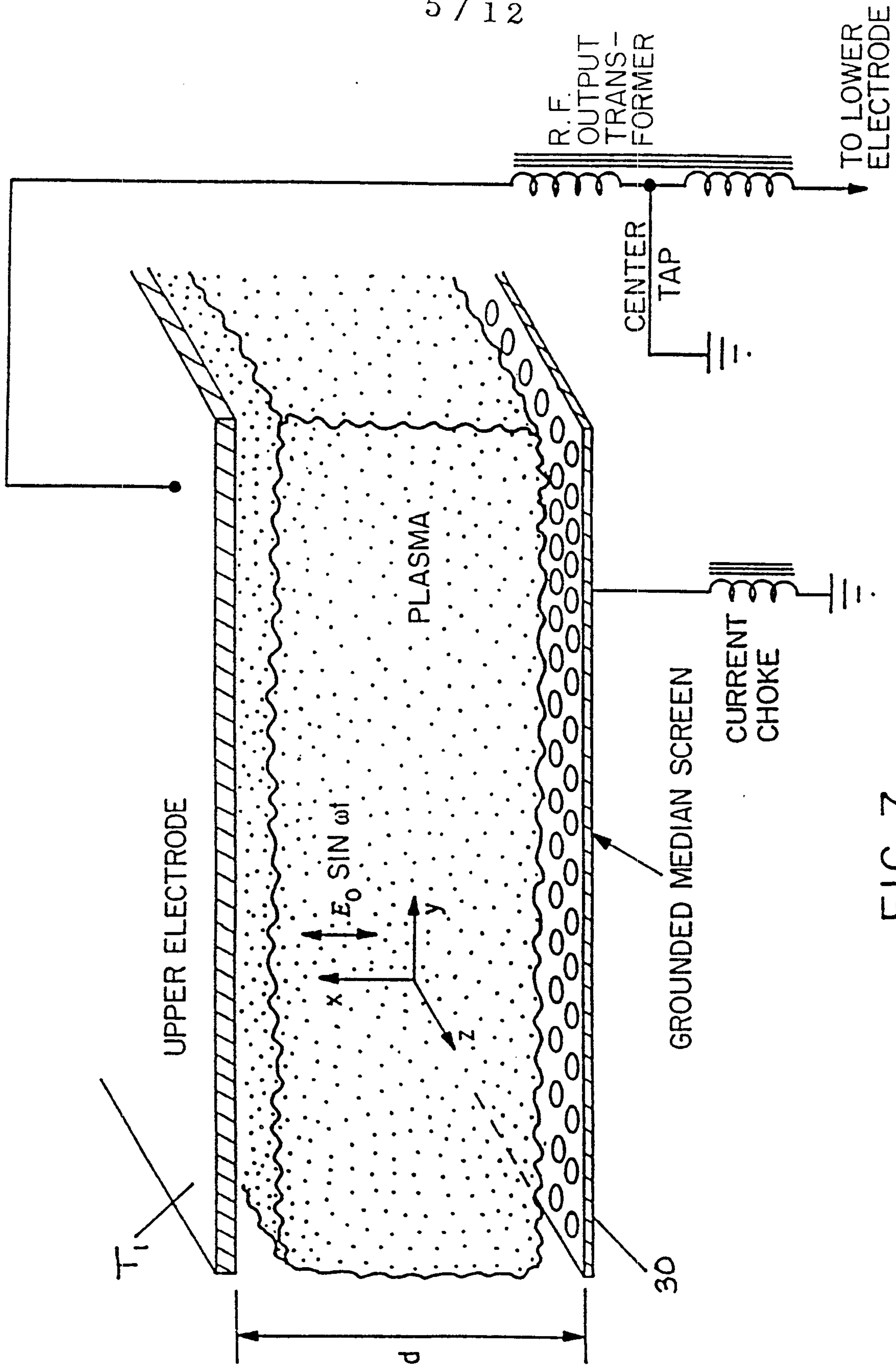


FIG. 7

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FIG. 8A

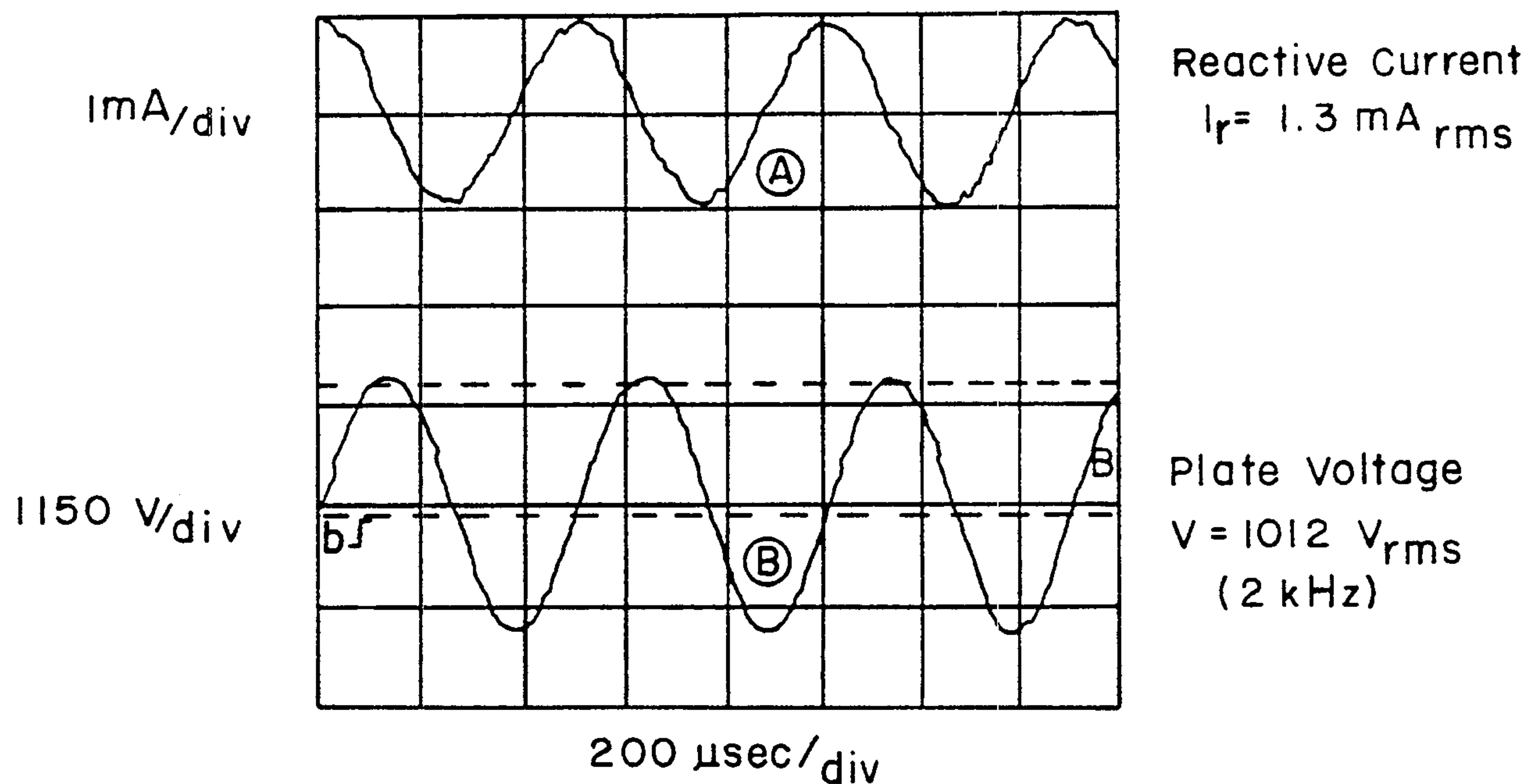
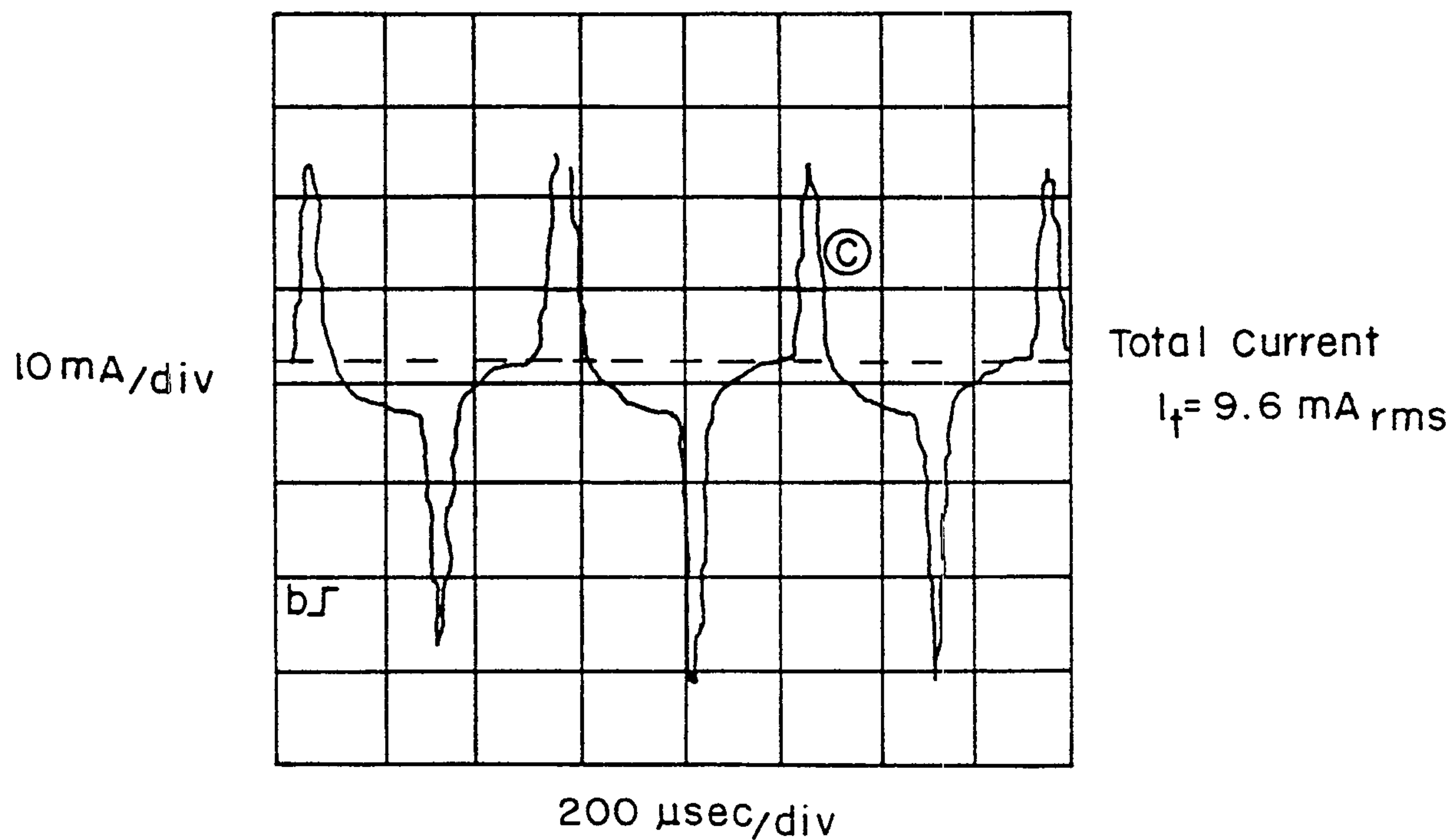


FIG. 8B



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FIG. 8C

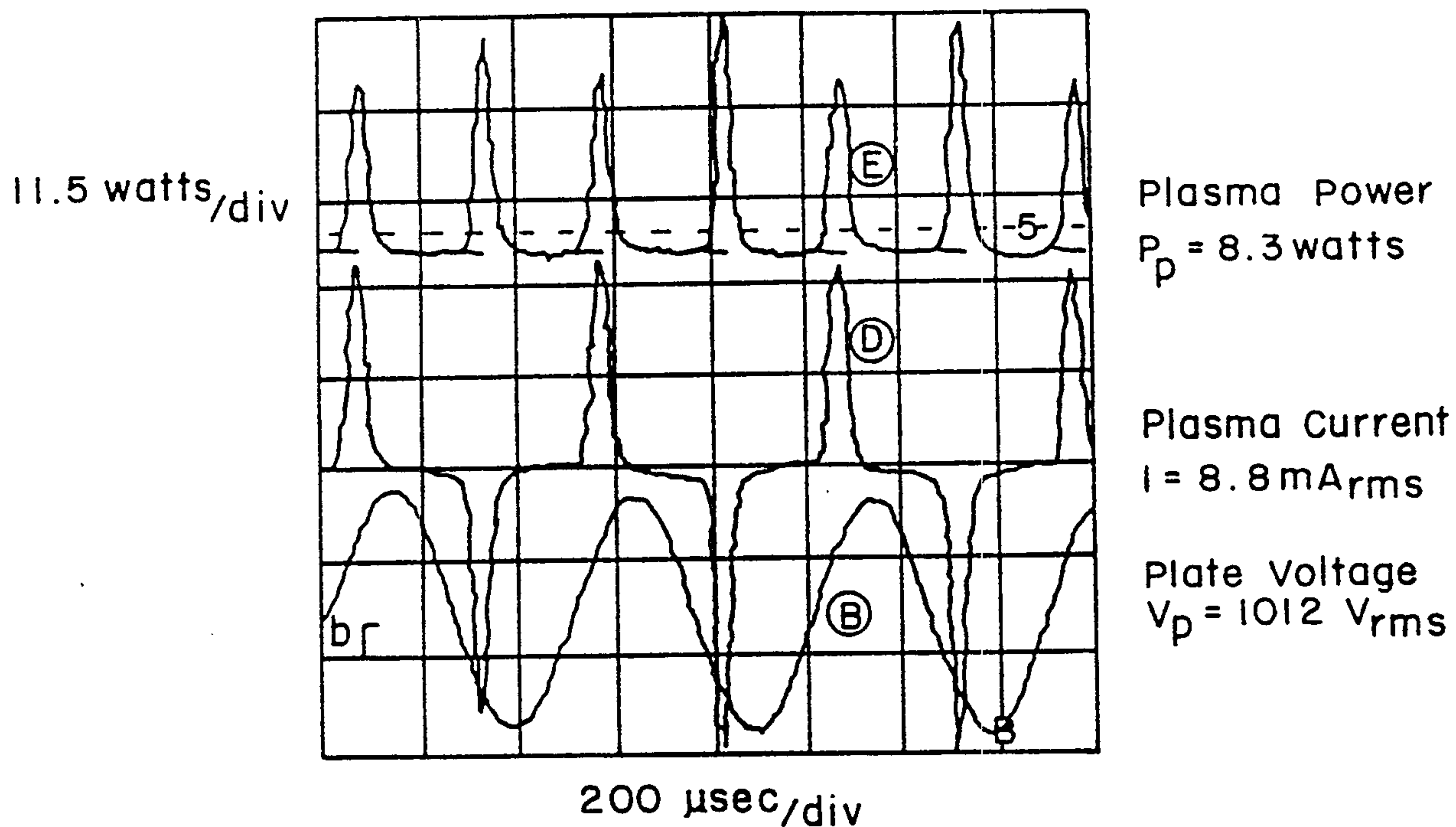
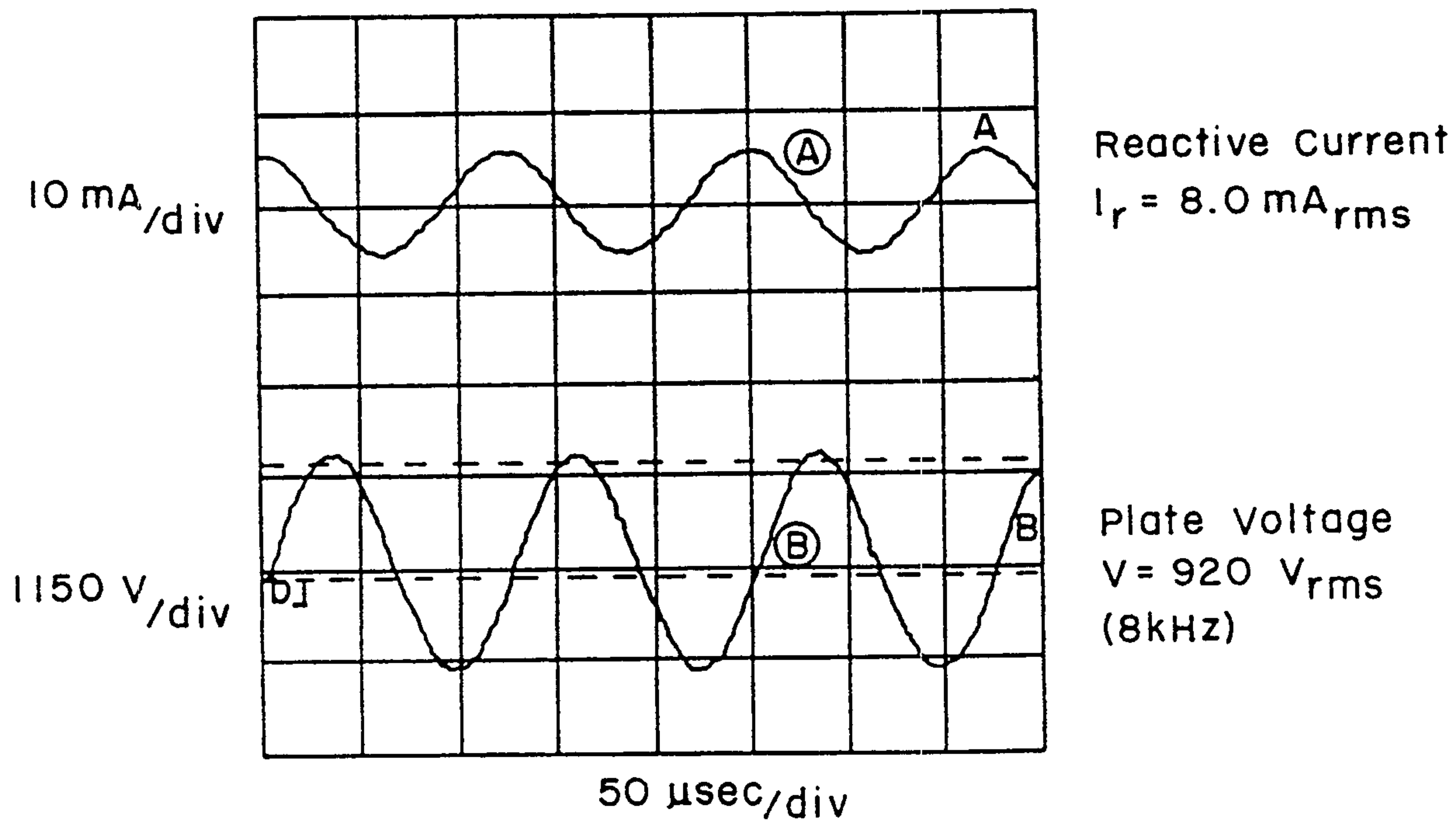


FIG. 9A



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FIG. 9B

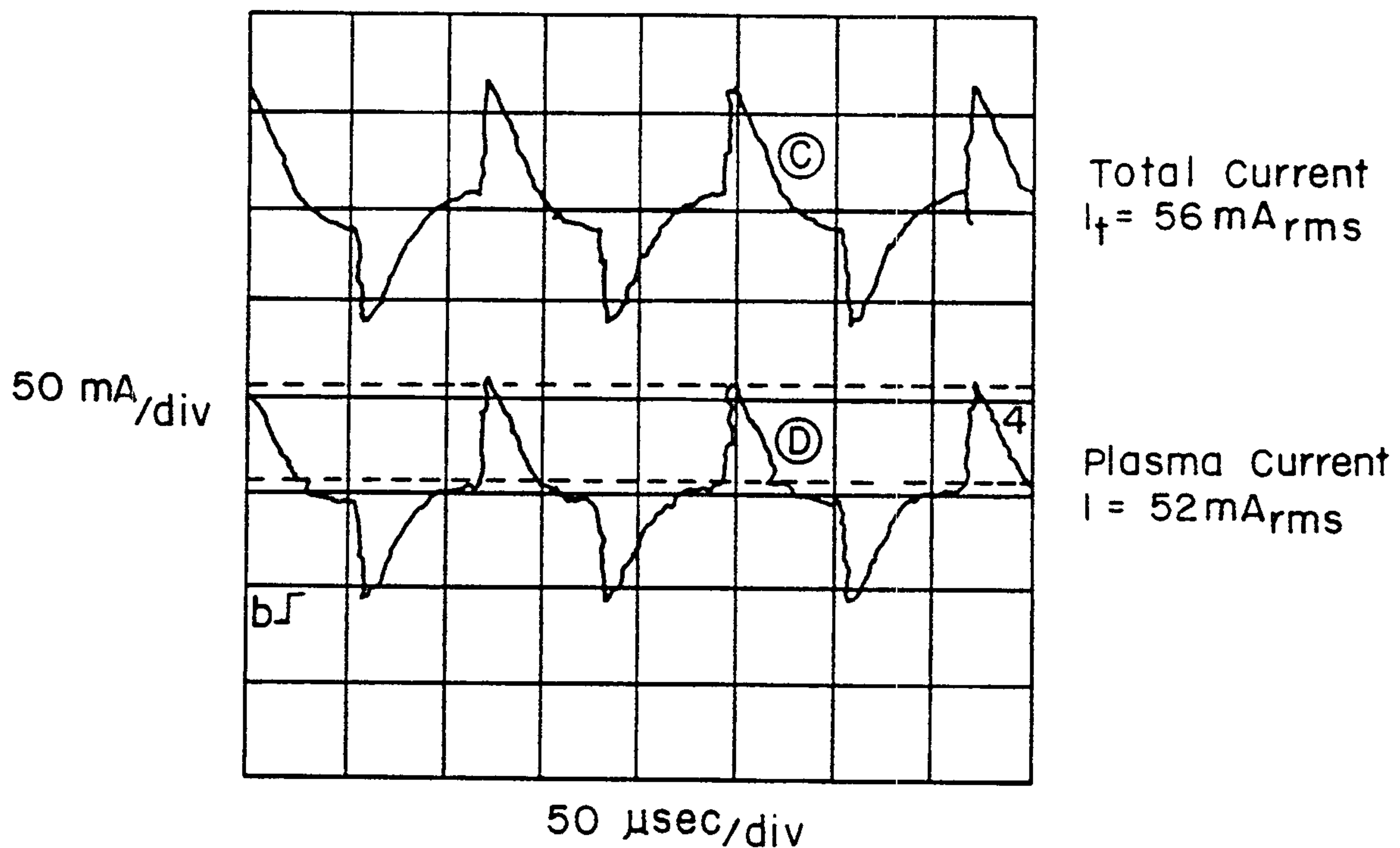
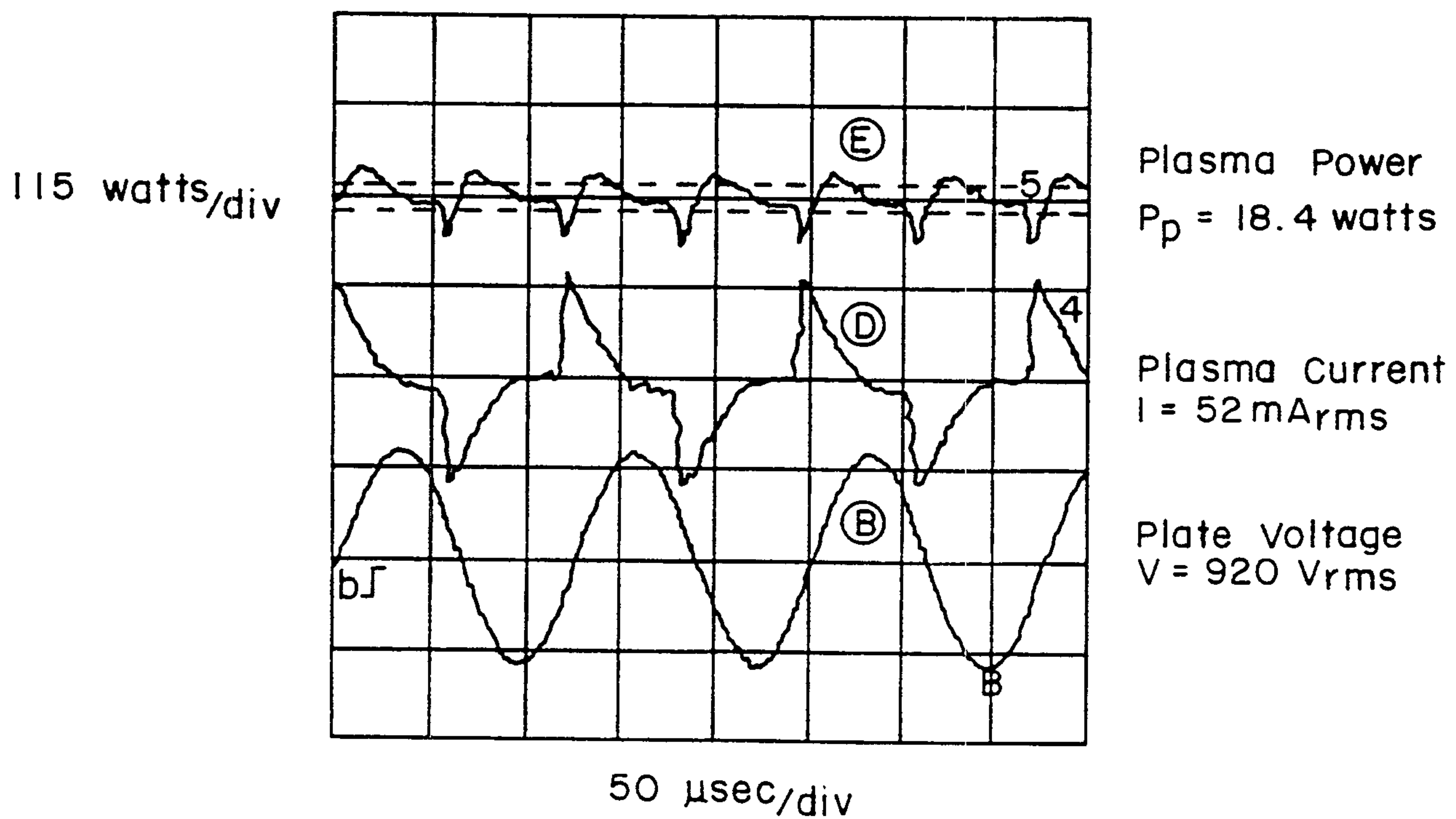


FIG. 9C



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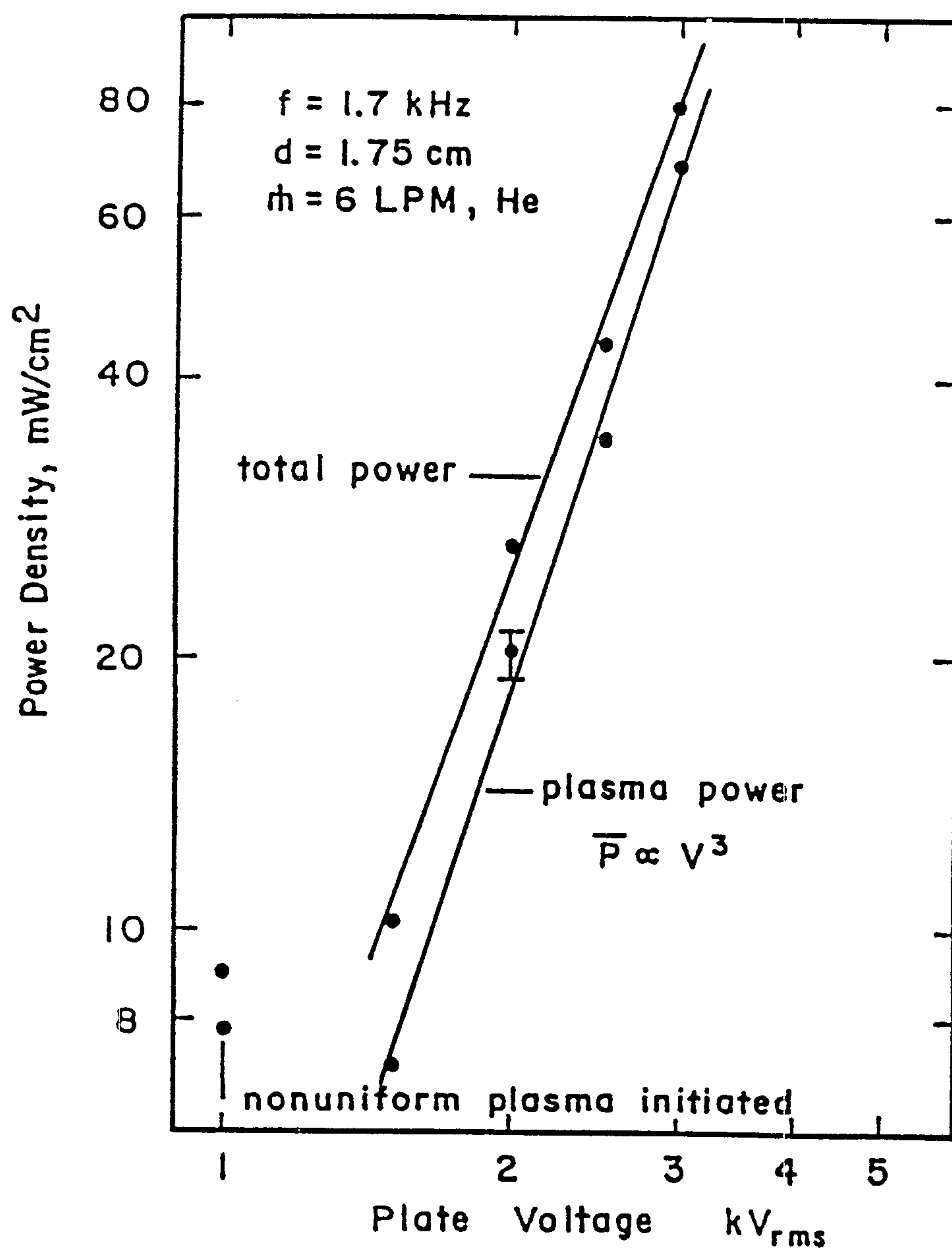


FIG. 10

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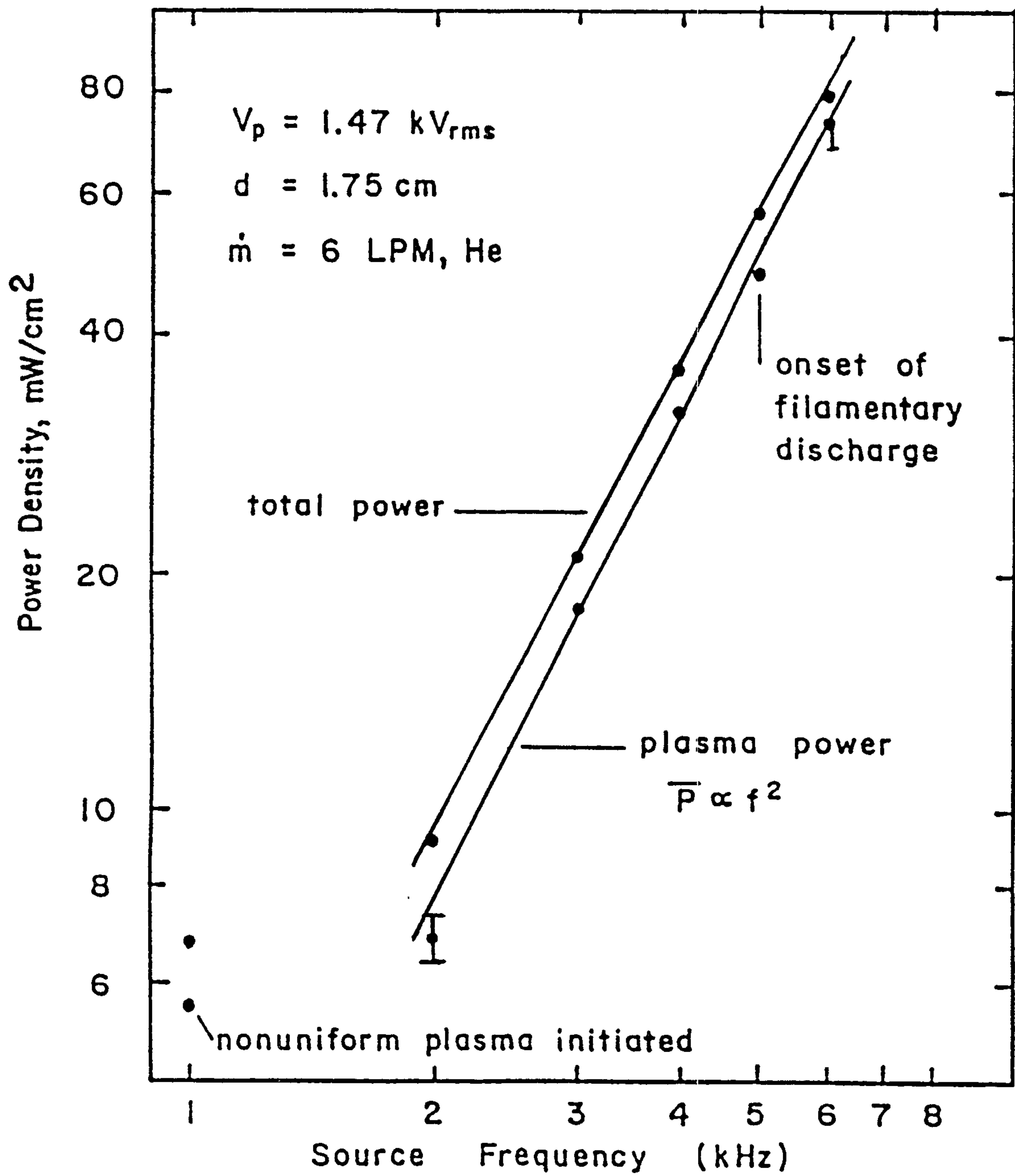


FIG. II

FIG. 12

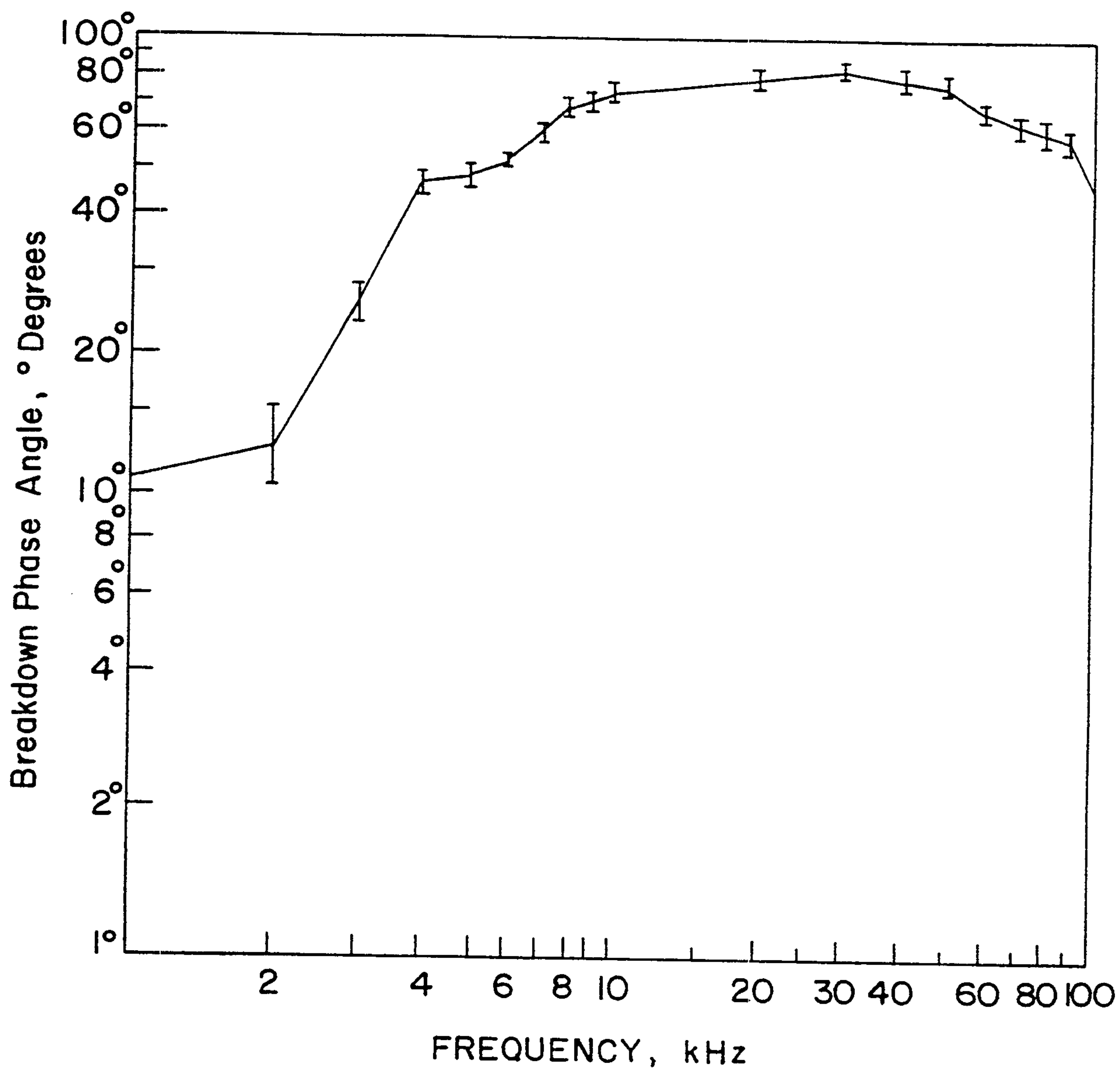
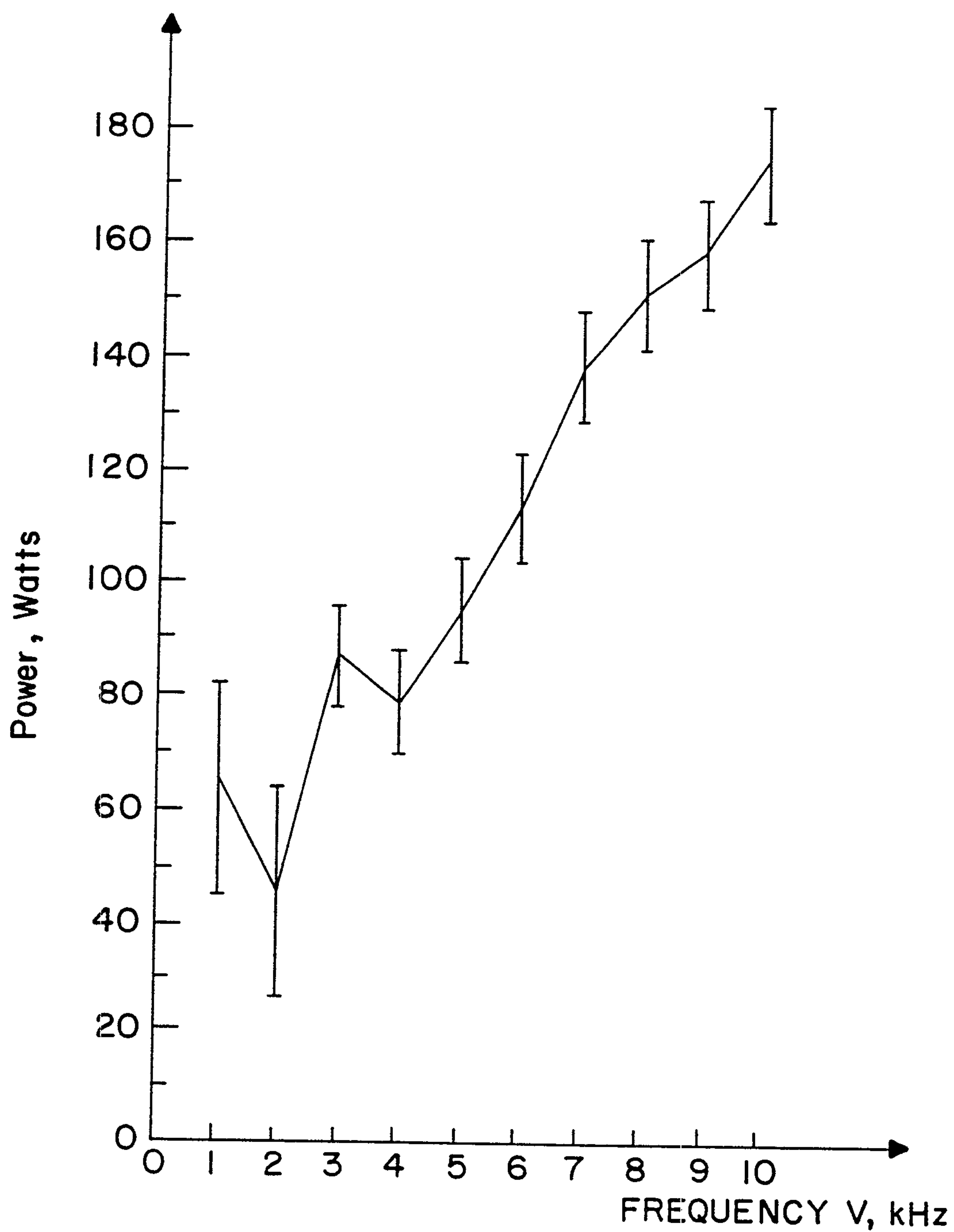


FIG. 13

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SUBSTITUTE SHEET (RULE 26)

