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Substantiation of a method for increasing the efficiency of the electrosynthesis of ozone by using periodic voltage pulses

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Abstract. The article analyzes the main directionsresearch to improve process efficiencyozone electro synthesis: research to improvestructures and materials of ozone generators; research influence of form, frequency, type of voltage. The article analyzed the process of ozone electro synthesis during nutrition sinusoidal voltage and identified significant disadvantages of this method. Process analyzed electrosynthesis of ozone when fed by periodic pulse stress with a drainage capacity of more than 5 and a significantincrease in efficiency this method.

1. Introduction

Since its discovery at the end of the 18th century, ozone has attracted constant interest of specialists in various fields and researchers due to its unique properties, first of all, its high oxidizing and disinfecting capacity [1]. In terms of its oxidizing ability, ozone (oxidizing potential 2.07 V) ranks third among known oxidants, inferior to fluorine (oxidizing potential 2.41 V) and oxygen fluoride, while chlorine (oxidizing potential 1.73 V) is eighth, and ordinary oxygen (O_2) is only thirteenth place [2].

Research on increasing the efficiency of the ozone electrosynthesis process is carried out in two main directions: research on the creation of the design of ozone generators; research on the creation of new power supplies [3].

The invention of the first designs of ozone generators is associated with the names of E. Siemens (E. Simens, 1857) and N. Tesla (N. Tesla, 1896). In 1897, E. Siemens developed the design, and the ideas embodied in it anticipated all subsequent ones, which were implemented in further attempts to modernize barrier discharge generators in volume for ozone electrosynthesis, up to the present day. Ozone generators with one dielectric layer were proposed by E. Frolich (E. Frolich, 1891). The cylindrical (tubular) generators to one dielectric layer, also called generators Velsbaha (H.Welsbach).

The construction of the ozone generator with the flat (plate) electrodes proposed A. Vostmaer (A. Vostmaer, 1916 g of.). For the operation of barrier discharge ozone generators in the volume, the difference in the shape of the electrodes (cylindrical or flat) is not essential.

In the synthesis of ozone in industrial conditions, generators with discharge gaps of 0.1–4.0 mm and dielectric layers 0.2–3.0 mm thick (with a relative dielectric constant of 5–50) are used. As materials for the dielectric layers are most often used different types of glasses and vitreous, at least - glass ceramics, ceramics, plastics and laminates [4]. The materials for the electrodes are stainless steel, aluminum or titanium and their alloys. The power supply voltage for the ozone generators is 1–30 kV (power is supplied through a matching and decoupling transformer), and the frequency is 0.05–20 kHz. The pressure of the oxygen-containing gas can be 0.02–0.2 MPa, and the maximum flow rate can reach 200m/s. These are essential conditions from which it follows that the barrier discharge occurs in a gas flow at relatively high pressures and relatively low velocities. Thus, the properties of an oxygen-

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containing gas can be considered close to those of an ideal gas. Gas flows are laminar (low Reynolds numbers) [5].

Even in the first electrical theories of E. Warburg (E. Warburg, 1903), A. Wartenberg (A. Wartenberg, 1908), G. Lechner (G. Lechner, 1915), as well as in later T . Manley (T. Manley, 1943 y of.), E. Brin (E. Briner, 1953 y of.), the ozone generator was considered as nonlinear system of two or three series-connected capacitors [5]. The most famous of modern concepts is the electrical theory, which was developed by Yu. Filippov [1]. It is based on component (equivalent circuit) and graphical (current-voltage characteristic) models of a barrier discharge ozone generator in volume.

The second direction of research to increase the efficiency of the process of ozone electrosynthesis is the use of various types of periodic, unipolar, high-frequency voltages. However, in existing industrial devices for ozone electrosynthesis, high sinusoidal voltages with a frequency of 500 Hz are mainly used [6]. The Exergy Efficiency of the implemented technological processes of ozone electrosynthesis is low (1–2%). A significant part of the energy is converted into heat, which leads to overheating of the electrodes and the need to cool them with running water [7].

2. Theoretical Basis

Consider the process of ozone electrosynthesis when fed with sinusoidal voltage (Figure 1). Due to the supply of the capacitive load, the current is ahead of the voltage by 90 electrical degrees. In the discharge gas gaps, in which self-sustained discharges occur, space charges (ions) are formed [7]. The amount of these charges turns out to be sufficient to prevent an increase in the current simultaneously with an increase in the voltage of the counter voltage half-wave. Therefore, at points 1-2, a slight increase in current is observed. Neutralization of space charges ends at point 2, and then an abrupt increase in the discharge current is observed. This corresponds to point 3 on the voltage curve. The process of ozone electrosynthesis is carried out at points 3 4 and 5 of the voltage curve. Hence the low efficiency of ozone generators powered by sinusoidal voltage. It is impossible to increase the performance of these devices by increasing the voltage, due to their operation at pre-breakdown voltages U_{br}.

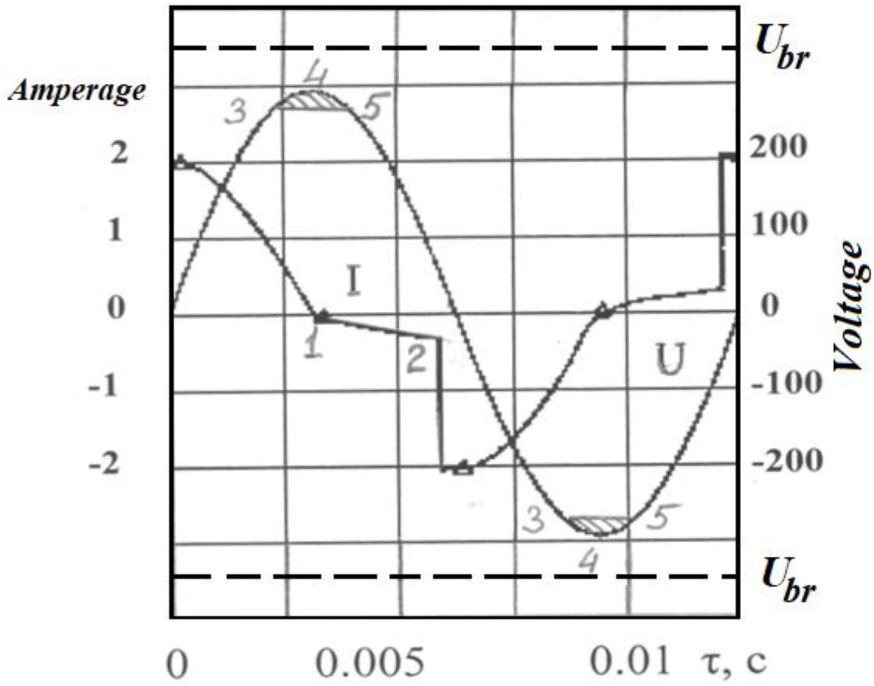

Figure 1. Average curves of instantaneous voltage and current through the ozone generator

Based on the analysis performed, it can be concluded that the ozone generators powered by sinusoidal voltage are brought to the limit of their capabilities. It should also be noted that self-sustained discharges are unstable in terms of the amplitude of the discharge current; accordingly, the time for neutralizing space charges will take different times. Hence, the instability of the process of ozone electrosynthesis can be occurred [8]. Hereof, the working hypothesis: it is possible to increase the efficiency of the ozone electrosynthesis process by using other types of voltage, for example, periodic pulses of a large duty cycle.

A number of studies in this direction are known [9, 10], but they have not been brought to their logical conclusion. In these works, the formation of high voltage pulses is carried out on the high side using capacitive energy storage [11]. The operation of these devices is determined by the electrical properties of the discharge gaps. Pulse voltages with a frequency of 20 ... 40 kHz are used. Generation schemes are complex and otherwise [12].

The development of a new method for ozone electrosynthesis is due to the shortcomings of existing devices. As already repeatedly mentioned [12], self-discharge currents of bits randomly distributed in time and are from bout function of the discrete random process whose implementation of amp litude and frequency random. In the barrier discharge, as in all types of electric discharges, occur simultaneously occurring about the various elementary processes [13]: appearance, movement and destruction of charged particles. It has been possible to quantitatively derive the properties of discharges on the basis of laws only in some cases, and then only under the condition of introducing essential assumptions [14]. This is due to the mathematical difficulties that arise when combining various patterns. These types of discharges at customarily called independent. The listed properties of a barrier discharge of an alternating voltage lead to instability of discharge currents in amplitude, to blocking of the discharge, and a transition to a spark or arc form. Obviously, by ensuring the stability of the discharge processes, the efficiency of ozone electrosynthesis can be increased.

The specificity of the electric fields of a barrier discharge is the presence of a flow of space charges in the discharge gap. The electric field created by these charges is directed opposite to the main electric field [15]:

$$E(x) = E_0(x) + \Delta x, \tag{1}$$

where $E(x)$ *is the* true electric field strength;
$E_0(x)$ is the main field strength;
Δx - field strength created by space charges.
The Δx value is determined based on the laws of electrostatics:

$$\Delta x = 4\pi q_t\{[\exp\alpha x / (\exp\alpha d - 1)] - 1/\alpha d\}, \tag{2}$$

where q_t is the time-dependent total number of positive ions per unit surface of each electrode in the discharge gap.
The voltage across the electrodes also changes by:

$$\Delta U = \int_0^d \Delta x dx, \tag{3}$$

Since $E(x)$ depends on distance, α also depends on distance. We mark this with the index x:

$$\alpha_x = Ap\exp\,[-Bp/(E_0(x) + \Delta x)] = \{-Bp/E_O(x)\,[1/1+\Delta_x/E_O(x)]\}, \tag{4}$$

where A and B are constants equal to 14.5 and 365, respectively, for air in the field of application E/p = 160 ... 600 V / cm·mm.Hg.
After expanding into a series to the number Δ/E_O squared, we get:

$$\alpha_x = \alpha_0\{1 + (Bp\Delta/E_0^2) + [Bp\Delta^2/E_0^4\,(0.5Bp - E_0)]\} \tag{5}$$

For cancellation by α_0 we denote $\alpha = Apexp\,(-Bp/E_0)$. Accordingly, the total number of ionizing collisions of a primary electron in a distorted field will be:

$$\int \alpha_x dx = \alpha_0 d + (\alpha_o Bp / E^2{}_0) + \left[\alpha_o Bp / E^4{}_0 (0{,}5Bp - E_0)\right]\Delta^2 dx \tag{6}$$

The integral in the last term is positive in all cases, since Δ^2 must always be positive. Thus, the last term is positive if $0.5Bp > E_0$, and vice versa. If the field distortion occurred at a constant voltage across the electrodes $(\Delta U = 0)$, then:

$$\int_0^d \alpha_x dx - \alpha_0 d > 0 \text{ for } E_0/p < 0{,}5B \tag{7}$$

$$\int_0^d \alpha_x dx - \alpha_0 d < 0 \text{ for } E_0/p > 0{,}5B \tag{8}$$

If, on the contrary, look for such changes in the voltage at the electrodes that again return the ionization in a distorted field to its original value in an undistorted field

$$\int_0^d \alpha_x dx - \alpha_0 d = 0 \text{ then:}$$

$$\Delta U = (E_0 - 0{,}5Bp)1/E_0^2 \int_0^d \Delta^2 dx, \tag{9}$$

hence

$$\Delta U < 0 \text{ for } E_0/p < 0.5\,B, \tag{10}$$

$$\Delta U > 0 \text{ for } E_0/p > 0{,}5B. \tag{11}$$

Equations (7) and (10) indicate that the uniform field E_0 is less than the critical value of 0.5, due to the distortion of the field, it becomes favorable for ionization at a constant voltage across the electrodes. In this case, to maintain ionization in a distorted field at the same level as in an undistorted field, a lower voltage is required at the electrodes.

Equations (8) and (11), respectively, show that the distortion of the field is unfavorable for ionization if the undistorted field is greater than the critical value. A feature of equations (7) ... (11) is that the conclusions from them are completely independent of how the field is distorted in each particular case.

It follows from the analysis performed that the stability of the discharge processes can be achieved in the case when the next voltage pulse of opposite polarity is applied in the absence of space charges in the discharge gap or when their number does not significantly affect the distortion of the main electric field.

The process of ozone electrosynthesis can also be intensified by exceeding the pulse amplitude of the breakdown threshold of sinusoidal voltage. In this case, the regularity of an increase in the electric strength of gas discharge gaps with a decrease in the time of exposure to voltage is used [16].

This pattern is determined by the overvoltage factor:

$$K = U_a/U_{br} \tag{12}$$

where U_a- voltage pulse amplitude;
U_{br} - breakdown voltage of the discharge gap at sinusoidal voltage.

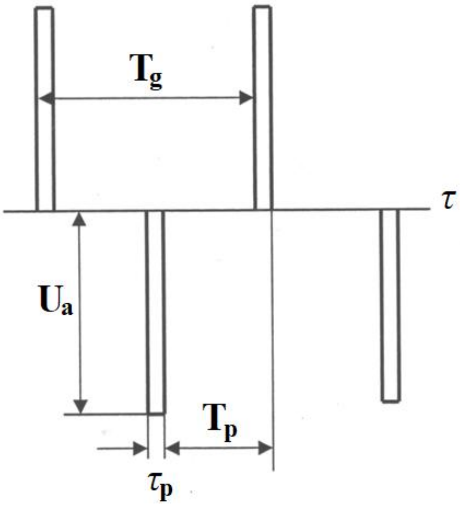

Figure 2. Parameters of periodic impulse voltages

Parameters of periodic voltage pulses (Figure 2):

- voltage pulse amplitude - U_a, V;
- pulse duration – τ_{puls},C;
- pulse repetition period in a half-period - T_{puls}, C;
- pulse duty cycle – $Dc = T_{puls}/\tau_{puls}$;
- period of voltage pulses - T_p;

Because of the applied nature of our research, it is advisable to select the type of voltage pulse and generates a real scheme of their tion. In this case, the parameters and shape, duty cycle, duration and front of the pulse will be characterized by a generation circuit that must satisfy the following requirements:

- ensure the stability of the frequency, shape and amplitude of voltage pulses;
- have minimal dimensions, simplicity and reliability, at the lowest cost;
- eliminate the possibility of transition of incomplete breakdown of air into spark and arc discharges;
- in the circuit for generating voltage pulses, it is necessary to form on the low-voltage side of the step-up transformer;
- meet the requirements of electrical and fire safety, industrial sanitation;
- do not create radio interference.

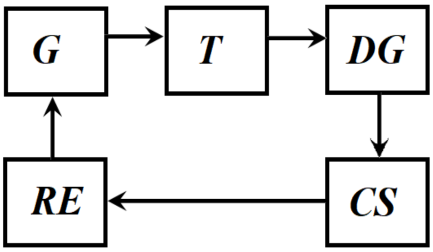

Figure 3. Block diagram of the high voltage periodic pulse generator**:** G - periodic voltage pulse generator; T - step-up transformer; RP - technological discharge gap; D - discharge current control sensor; RE is a regulating element.

As the analysis of existing devices for ozone electrosynthesis has shown, due to the instability of the discharge processes, automatic control of the processes turns out to be an impossible task. With the stabilization of the discharge processes, it becomes possible to automatically control the processes of ozone electrosynthesis by the value of the discharge current. What can be implemented according to the block diagram shown in Figure 3.

Of interest is the process occurring in the discharge gap in the pause between pulses under the influence of the constant component of the charge accumulated in the discharge gap [17].

The issue of stabilizing the discharge process in terms of currents (in our case, currents arising under the influence of a voltage pulse and currents in the pause between pulses act) can be solved by choosing such a pulse repetition rate at which, during the pause between pulses, all processes in motion and recombination charged particles will be brought to the extent that they practically do not affect the conductivity of the discharge gap, i.e. the current through the discharge gap at the end of the pause must be zero. The presence of space charges in the discharge gap distorts the picture of the main electric field, which characterizes the instability of self-sustained discharges.

After the application of a voltage pulse of one of the polarities, which caused a barrier discharge, volume charges with a density τ (the number of space charges per unit volume of the discharge gap) are formed in the discharge gap. Since the density τ decreases in the gas volume due to the recombination and transfer of space charges, the current density through the discharge gap correspondingly decreases:

$$j = eb\, E\, \tau\, (t) \tag{13}$$

where is the electron charge, $1.6\text{x}10^{19}$C;

b - ion mobility, $m^2/V\cdot s$;

E is the electric field strength, V/m;

$\tau\,(t)$ is the density of space charges decreasing with time, C/m^3.

Thus, in the discharge gap at the time when there are no ionization processes, the current density is proportional to the field strength, i.e. conductivity is linear. The nature of the change in the current density will be determined by the change in $\tau\,(t)$. The latter, in turn, will be determined by the parameters of the electrical circuit to which the discharge gap is connected.

Based on the above, the process in the discharge gap in the pause between pulses can be analyzed by the transient process in the power supply circuit. In this case, the discharge gap can be considered as an element of the electrical circuit.

Generation of unipolar high voltage pulses in the form shown in Figure 2 can be carried out according to the scheme shown in Figure 4, where the periodic voltage pulses generated by the generator G are increased by the transformer T and fed to the technological discharge gap. The circuit provides a sensor for monitoring the discharge current D and a regulating element R.

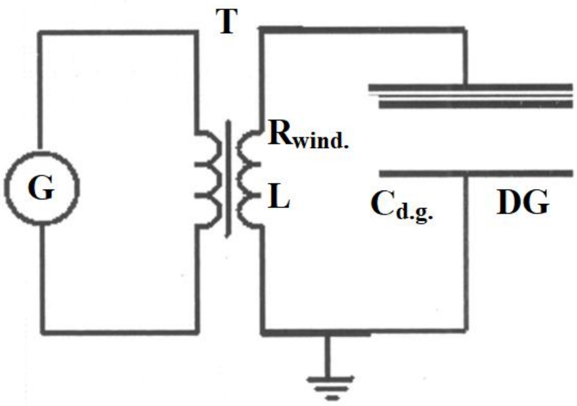

Figure 4. Schematic diagram of the ozone electrosynthesis process

An ozone generator is connected to the output of the circuit (Figure 5), which has its own capacity $C_{d.g}$. One of the advantages of the proposed method of ozone electrosynthesis using periodic voltage pulses over the existing method of ozone electrosynthesis with sinusoidal voltage is the possibility of considering the technological discharge gap as an element of the supply circuit.

G - generator of periodic voltage pulses; T - step-up transformer; $C_{d.g.}$ - capacity of the discharge gap; DG - discharge gap

Let us analyze the transient process in the electrical circuit of the source of high-voltage pulses in the pause between pulses. According to the equivalent circuit (Figure 5), we have a closed loop of the series-connected capacitance of the discharge gap $C_{d.g.}$, active $R_{wind.}$ and inductive L resistances of the secondary winding of the step-up transformer.

Let's analyze the process in the circuit in the pause between pulses. After the impulse is applied, the capacitor $C_{d.g.}$ ill be charged to the amplitude value of the voltage pulse.

To determine the law of voltage and current variation of the discharge gap in the pause between pulses, we compose the characteristic equation of the circuit in a complex form [9]:

$$Z = R_{wind.} + j\omega L + 1/(j\omega C_{d.g.}) \tag{14}$$

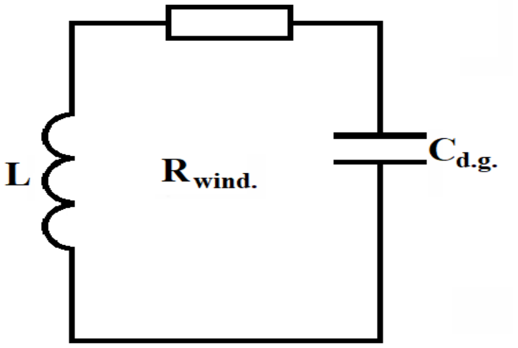

Figure 5. Equivalent circuit of the high-voltage circuit of the ozone generator: *L* - inductance of the secondary winding of the step-up transformer; $C_{d.g.}$ - capacity of the discharge gap; $R_{wind.}$ - active resistance of the secondary winding of the transformer

We replace the factor $j\omega$ with the operator p and the resulting expression $Z(p)$ equate to zero:

$$Z(p) = R_{wind.} + pL + 1/(pC_{d.g.}) = 0, \tag{15}$$

or

$$p^2(C_{d.g.} L) + pC_{d.g.} R_{wind.} + C_{d.g.} = 0. \tag{16}$$

The roots of the characteristic equation (1.23) are determined by the equality:

$$p_{1,2} = \{-C_{d.g.}R_{wind.} \pm [(C_{d.g.} R_{wind.})^2 - 4 (C_{d.g.} L) (C_{d.g.})^{0.5}\} / (2C_{d.g.} L), \tag{17}$$

Hence the free component of the voltage across the capacitor $C_{d.g.}$:

$$U_{C\mathrm{fr}} = (A_1e^{1t} + A_2e^{p2t}), \tag{18}$$

and the current in the circuit:

$$i_{sv=} [C_{d.g.}\, d\, (U_{C\mathrm{fr}})]/dt = C\, (A_1p_1e^{p1t} + A2p_2e^{p2t}), \quad (19)$$

Initial conditions for calculations:

$$U_{Cd.g} = U_a,\ i_a = i_{\text{fr.}o},\ t = 0, \tag{20}$$

where U_{c2} - voltage amplitude across the discharge gap with capacity C_2;

U_a - voltage amplitude at the output of the step-up transformer;

U_{c1} - voltage across capacitor C_1;

i_a is the amplitude of the discharge current;

$i_{Ct.\,0}$ - initial circuit current;

t is the integration time.

Taking into account the accepted assumptions and initial conditions, we obtain:

$$U_a = A_1 + A_2,\quad i_a = A_1p_1 + A_2p_2, \tag{21}$$

from here

$$A_1 = (p_2U_{pul}\, i_a)/\,(p_2 - p_1) \tag{22}$$

$$A_2 = (p_1U_{pul}\, i_a)\,/\,(p_2 - p_1). \tag{23}$$

With these values of the integration constants, the laws of change in the voltage and current of the discharge gap in the pause between pulses have the form:

$$U_{C2.\text{fr}} = [1/(p - p_1)]\ [(p_2U_a - i_a)\, p_1e^{P1} - (p_1U_a - i_a)\, p_2e^{P2}\,], \tag{24}$$

$$i_{\text{fr}} = [C_{d.g.}/\,(p_2 - p_1)]\ [(p_2U_a - i_a)\, p_1e^{P1t} - (p_1U_a - i_a)\, p_2e^{P2}\,]. \tag{25}$$

3. Results

The problem was solved on a PC for the following values of the circuit parameters: L = 7 H; $R_{wind.}$= 3.5x10^3 Om; $C_{d.g.}$ = 10^{-9} F;U_a = 2x10^4 V. Integration step 0.001 s. In view of the adequate nature of the change in current and voltage in the pause between pulses, the problem of changing the current was not solved. Based on the results of calculations, graphs of changes in the voltage of the discharge gap in the pause between pulses were constructed (Figure 6).

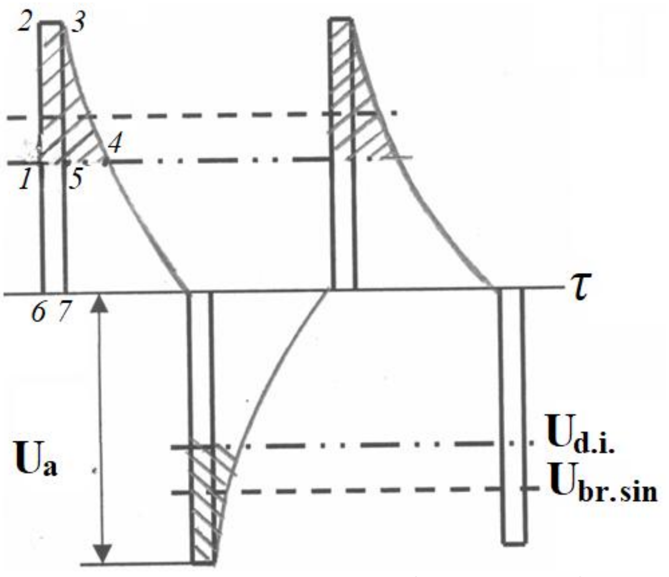

Figure 6. Changes in the periodic impulse and free voltages of the discharge gap

Analysis of changes in the periodic pulse and free voltages of the discharge gap (Figure 6) shows that the barrier discharge occurs in the area 1,2,3,4. This area starts from the discharge ignition voltage $U_{z.r}$. The amplitude of the pulses exceeds the breakdown voltage, which is observed when the ozone generator is powered with a sinusoidal voltage – $U_{br.sin}$. The energy of the impulse voltage is described by the area enclosed in points 1,5,6,7. This area is less than the area occupied by the barrier discharge. Hence, when powered by periodic voltage pulses, the efficiency can significantly exceed the efficiency, sinusoidal voltages.

The energy expended in the ozone electrosynthesis process can significantly exceed the energy consumed by the step-up transformer.

4. Conclusions

1. Efficiency of ozone generators, when powered by sinusoidal voltage, is 1 ... 2%. The rest of the energy is converted into heat, for the removal of which the electrodes are cooled by running water.
2. Analysis of the processes in the discharge gap revealed that due to the excess of the voltage pulse amplitude of the dielectric strength of the discharge gap at sinusoidal voltage and the supply of the next pulse after the complete recombination of space charges, the energy associated with the discharge processes exceeds the energy converted into heat. Therefore, a significant increase in efficiency is expected.
3. The energy consumed for the process of ozone electrosynthesis can significantly exceed the energy consumed by the step-up transformer.

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