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# Heterogeneous Effects in the Process of Ozone Synthesis in Electrical Discharges

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*Catalytic effects of solid surfaces in the synthesis of ozone have been examined under semicorona discharges conditions. It was found out that in the presence of a granular dielectric (silica) in the discharge gap, the ozone formation was accelerated and higher ozone concentrations were obtained. The mechanism of catalytic effects of silica is discussed.*

**KEY WORDS:** Ozone synthesis; heterogeneous catalysis; silica; semicorona discharges.

## 1. INTRODUCTION

As is known, ozone production efficiency per input energy is rather low in commercial reactors applied up to now.$^{(1,2)}$ One of numerous attempts to improve the efficiency is very interesting. This concerns catalytic phenomena which were observed during the interaction of electric plasmas with solid surfaces. At the plasma-solid interface various processes may occur,$^{(3-5)}$ such as ion neutralization, deactivation of excited species, and sorption, which is often followed by dissociation of molecules absorbed. In most of these processes the exchange of energy of the solid surface and plasma species is observed. The rates of the processes mentioned above, occurring at the solid surfaces, are often much higher than those of the similar processes in the plasma phase itself. It has been shown in some research that the solids may act under plasma conditions as catalysts in the chemical meaning, i.e., they may accelerate chemical reactions of the gas components. This was first proved in Russian works on the catalytic action of some metals in the synthesis of ammonia, of hydrazine, or of nitrogen oxides under silent and glow discharge conditions.$^{(6-9)}$ Very distinct catalytic

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effects of metals such as W, Mo, and Co, as well as their oxides, were observed when oxidation of nitrogen or decomposition of ammonia was carried out under conditions of low-pressure radio-frequency plasmas.(10,11) The theoretical interpretation of experimental data mentioned above was given.(10) It was founded on the theory of absolute reaction rates,(12,13) which was applied to heterogeneous processes.(14) It was indicated that catalytic phenomena occurring under conditions of nonequilibrium plasmas should be connected with the distribution of the molecular energy among different degrees of freedom. Chemical reactivity in those systems is controlled by vibrational or translational energy of reagents when the determining step of the reaction is, respectively, endothermic or exothermic, according to the Polanyi rules.(12,13)

Under ozone synthesis conditions in silent discharges heterogeneous effects were observed long ago. One of the earlier works(15) gave clear evidence that long-lasting changes in the ozone concentrations during the experiments performed were due to the sorption of some unidentified active species on the surface of the dielectric barrier (glass). This effect was especially distinct when ozone synthesis was carried out in the presence of nitrogen, e.g., in air. In a later investigation absorption of nitrogen oxides (especially of $N_2O_5$) was examined and its connection with ozone production drop was observed in a glass ozonizer.(16) The mechanism of all these surface phenomena has not been explained so far, although the effect of "poisoning" of ozone production by nitrogen oxides has been well known for a long time.(17,18)

The influence of the solid surfaces of dielectrics (or metals) on the reaction rates was clearly shown due to experiments in which the distributions of the ozone concentrations were measured across the discharge gap of an ozonizer.(19-21) It was found that the ozone concentration is much higher near the surface of the glass than in the center of the gap. Thus the effect of solid surfaces on ozone production was evident. Several experimental studies(22-24) of the ozone synthesis in silent and corona discharges gave clear evidence of the fact that the material of the electrodes used had a strong influence on the ozone production. On the other hand, it is known that a high energetic production yield was observed when electric conductors were introduced to the discharge gap of an ozonizer, e.g., a twisted stainless wire or a piece of wire gauze.(25,26) It seems quite possible that it was a catalytic action of metals (or of the metal oxides) demonstrated in these experiments.

In previous work(22) we examined ozone formation in a silent discharge ozonizer with a gap filled with some granular dielectric materials. We have found out that in the presence of granular dielectrics the ozone concentrations might be higher or lower than without packing, depending on the kind of dielectric used. For example, in the presence of alumina the ozone generation was accelerated and its concentrations rose. In one(2) recent work effects were examined of some metal oxides (CuO, FeO, $TiO_2$, ZnO) on ozone formation in silent discharges. In the presence of these oxides a significant increase in ozone generation rates was observed, while other metals oxides did not demonstrate any effects or even resulted in decreased ozone formation.

It is impossible to predict which kind of substances will act as a catalyst in the ozone synthesis process. There are not sufficient data on this matter up to now. However, many substances are known as catalysts of ozone decomposition(27,28) and so they are considered to be useless from the point of view of the scope of our investigation. It should be added that some substances which inhibit ozone decomposition are known as well.(29) In this paper we present the first experimental data on the catalytic effects of silica on ozone formation under semicorona discharge conditions. The material we have examined is often used as a sorbent, carrier, or catalyst of some chemical reactions.

## 2. EXPERIMENTAL

### 2.1. Apparatus and Measurement

The experiments were carried out in a semicorona ozonizer with a dielectric barrier (Fig. 1). The high-voltage central electrode (1) made of stainless steel had a diameter of 8 mm, and its surface was specifically formed by threading. A tube of Pyrex glass (3), of internal diameter 22 mm, constituted the dielectric barrier. The discharge gap between the electrode and the barrier had a width of 7 mm. The Pyrex tube was placed in a glass jacket with a cooling liquid, diluted sodium carbonate solution, flowing through it. The liquid filling the jacket at the same time acted as a ground electrode. Its temperature was controlled by a thermostat. A perforated insert of dielectric material maintained the electrode in a coaxial orientation with respect to the Pyrex tube. The bed of granular material filling the ozonizer was supported by the same insert.

The high-voltage electrode was connected to the high-voltage transformer (up to 20 kV) (Fig. 2.) This was a measuring transformer of class 0.5. This system was supplied from a 50-Hz network by means of a stabilizer and an autotransformer controlling the voltage in the primary circuit of the high-voltage transformer. The following electrical parameters were measured: (1) voltage in the primary circuit (low voltage), (2) current in the ground lead of the high-voltage transformer, (3) power supplied to the high-voltage transformer.

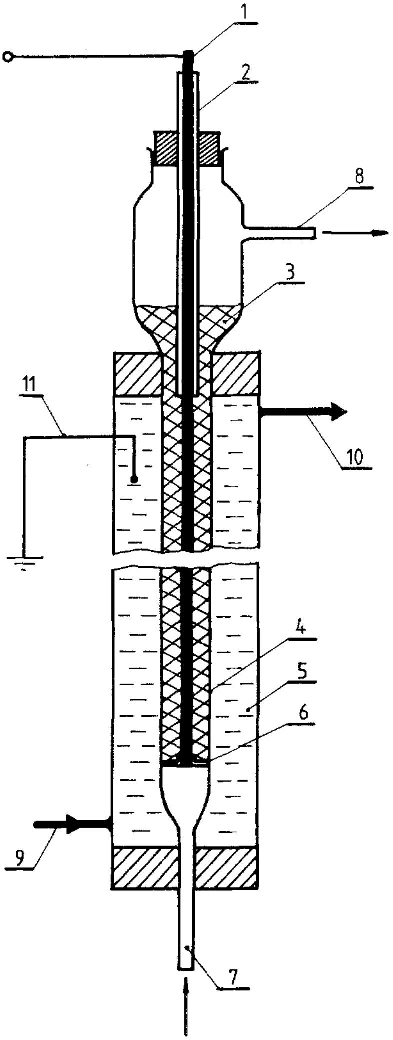

**Fig. 1.** Semicorona ozonizer. (1) High-voltage electrode; (2) insulator; (3) bed of granular dielectric (silica); (4) dielectric barrier (Pyrex tube); (5) cooling liquid; (6) perforated insert; (7) oxygen inlet; (8) oxygen and ozone outlet; (9) cooling liquid inlet; (10) cooling liquid outlet; (11) ground lead.

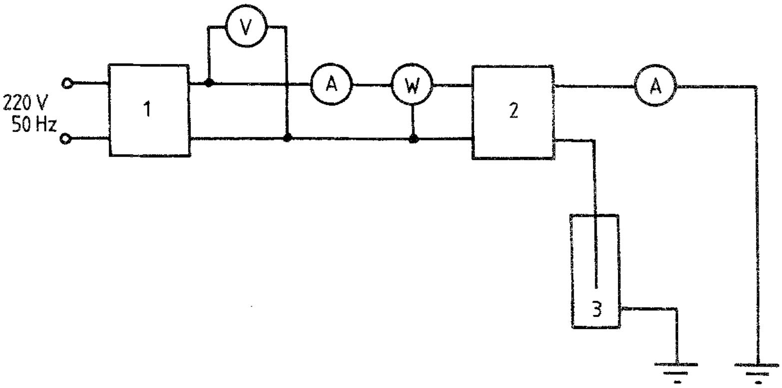

**Fig. 2.** Electric circuit. (1) Autotransformer; (2) high-voltage transformer; (3) ozonizer; (A) ammeter; (V) voltmeter; (W) wattmeter.

The ozonizer was supplied with oxygen (from a cylinder), which was passed through a column packed with silica gel for additional drying.

The ozone concentration in the stream leaving the ozonizer was determined by three methods:

(a) iodometric analysis—by ozone absorption in a solution of potassium iodide and titration with thiosulfate;
(b) the interferometric method; and
(c) the photometric method—by absorption in the 255-nm band (ultraviolet).

An interferometer (Carl Zeiss, Jena) was used, with a 1 m-long cuvette to which a constant gas stream from the ozonizer was introduced, as in Ref. 30. A similar method is known from another paper.(31) Instruments applied in methods b and c were calibrated by method a (unfortunately we do not have equipment suitable to measure absolute values of the ozone concentration).

Heterogeneous effects occurring in the process were detected by comparing the results of two series of experiments, with the ozonizer without packing and with packing, prepared from silica. This material was chosen from literature data(27,32) as well as from our observations,(22) indicating that silica does not catalyze ozone decomposition. The material used in our experiments consisted of irregular grains of 1.25 to 3.2 mm dimensions. The experiments were carried out at voltage $U = 8$–$20$ kV, rate of oxygen flow $\dot{V} = 10$ and $26\ \mathrm{dm^3/hr}$, and temperature of liquid cooling the ozonizer $t_L = 2$, 25, and 50°C. At the beginning of the measurement series the oxygen flow was switched on and settled, the temperature of the liquid in the cooling circuit was controlled, and finally the voltage value was settled. During the initial working period of the ozonizer the concentration of ozone in the stream leaving the ozonizer changed for some time (usually not exceeding 1-2 hr) and then became steady. With a higher rate of oxygen flow this period was shorter. However, there was no direct relation of this period to the residence time of reagents in the ozonizer gap, which was 7 sec at $\dot{V} = 26\ \mathrm{dm}^3/\mathrm{hr}$ and 18 sec at $\dot{V} = 10\ \mathrm{dm}^3/\mathrm{hr}$ (considering the whole gap volume along the active part of the electrode). Certain, insignificant delay of analytical instrument indication resulted from the volume of leads connecting the ozonizer to these instruments. However, the changes in ozone concentration observed in the initial working period of the ozonizer were the results mainly of changes of the process conditions within the ozonizer itself. It seems most probable that it was absorption of ozone (or other species) on the surface of the packing (silica) which was responsible for these effects.

Sometimes, especially at high ratio values of the energy stream to the mass stream of reagent, changes in ozone concentration lasting many hours were observed. And therefore, we started our measurements after the experimental system had settled to a stationary state each time, i.e., when the ozone concentration was stable. Examples of changes of ozone concentration during series of measurements are given in Fig. 3 and 4.

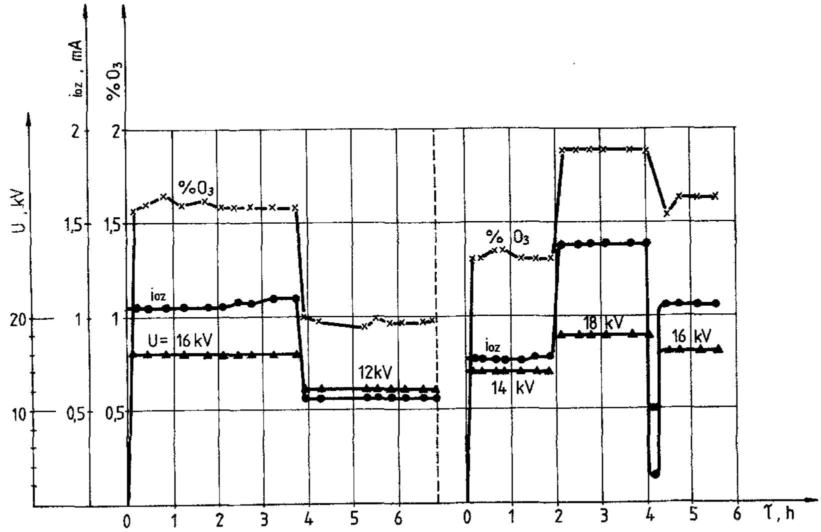

**Fig. 3.** Ozone concentration, voltage $U$, and current in ozonizer circuit $i_{oz}$ during a run of an experiment with silica, 1.25-3.2-mm grain (example). Oxygen flow $\dot{V} = 26\ \mathrm{dm}^3/\mathrm{hr}$; cooling liquid temp. $t_L = 25°\mathrm{C}$.

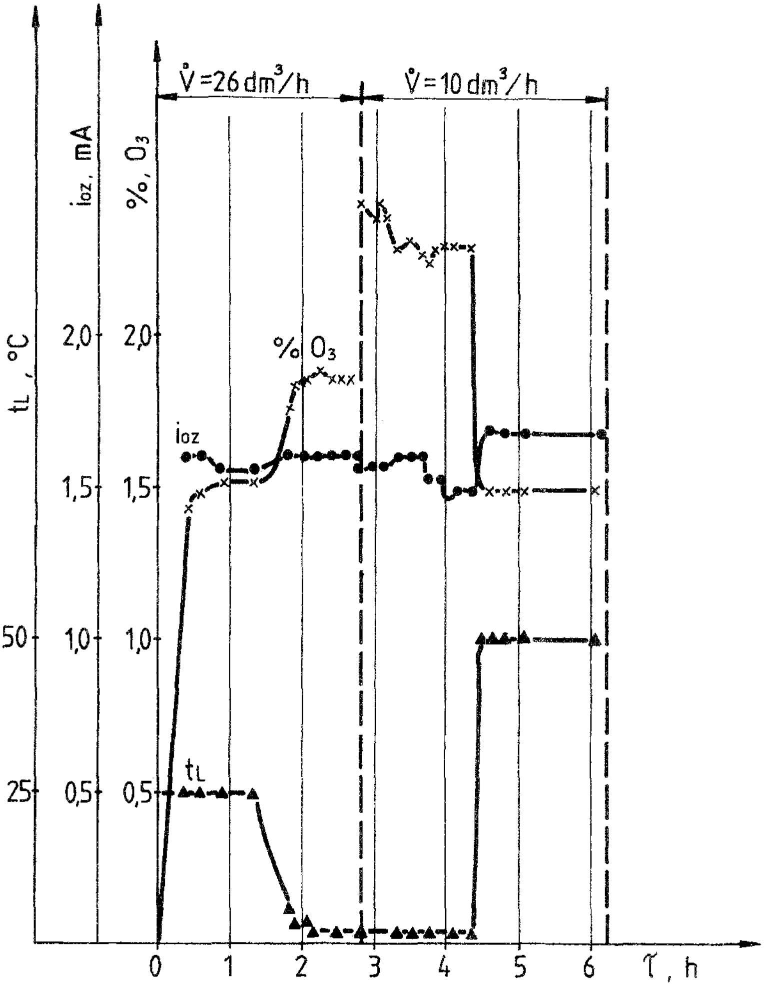

Fig. 4. Ozone concentration, cooling liquid temp. $t_L$, and current in ozonizer circuit $i_{oz}$ during a run of an experiment without packing (example). Oxygen flow $\dot{V}$ = 10 and 26 $dm^3$/hr; voltage $U = 20$ kV.

## 3. RESULTS

Current–voltage characteristics of the ozonizer are given in Fig. 5. The current through the ozonizer $i_{oz}$ was determined by measurements in the ground lead of the high-voltage winding of the transformer, with a correction taken for the no-load current. In additional measurements it was found that the current intensity calculated in such a manner corresponds to the current flowing through the ozonizer.

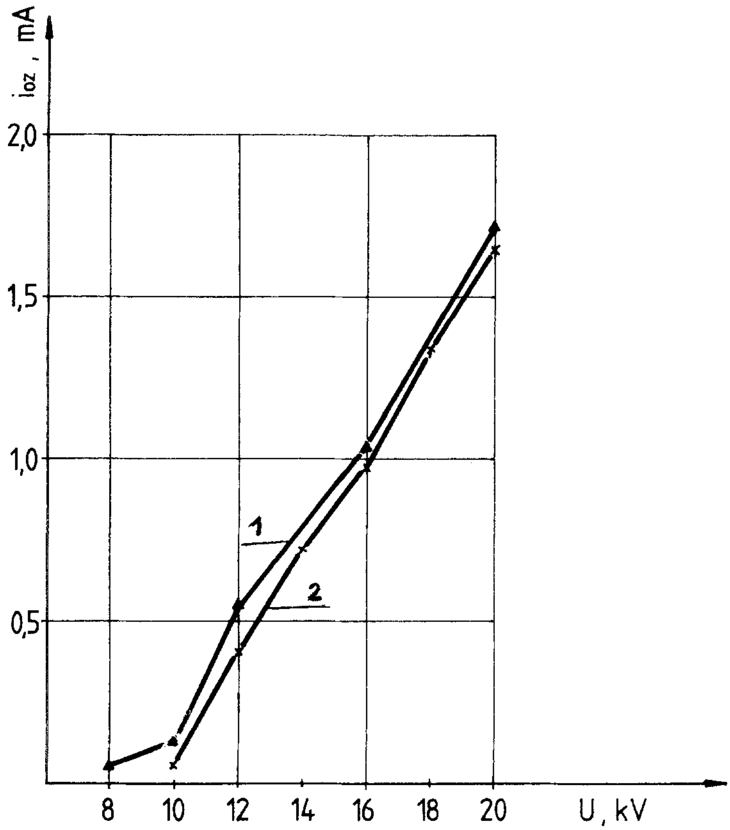

**Fig. 5.** Current-voltage characteristic of the ozonizer. Oxygen flow $\dot{V} = 26\ \mathrm{dm}^3/\mathrm{hr}$; cooling liquid temp. $t_L = 25°\mathrm{C}$. (1) With silica, 1.25-3.2 mm; (2) without packing.

As can be seen, the characteristics of the semicorona ozonizer used in our experiments are similar to the characteristics of the silent discharge ozonizer. A specific feature of the semicorona ozonizer is its high starting voltage, which should be connected with the large width of the discharge gap. The current-voltage characteristics of packed and nonpacked ozonizers do not differ significantly except for the fragment lying near the starting voltage. It is worth mentioning that in the presence of packing, the starting voltage was clearly lower.

As our ozonizer was made of glass, we could precisely follow the structure of the discharge, which significantly differed from the structure of a typical silent discharge. We have noted that it is marked by a clear heterogeneity easily visible with the naked eye. Filamentary microdischarges were less numerous than in the silent discharge, and at the same time they were clearly visible due to strong emission of light. Therefore it is evident that each of them transfers a much larger electric charge than that in the silent discharge. It is worth mentioning that they did not end at the surface of the dielectric barrier (glass) but continued their way on the surface in a form of individual sharply outlined filamentary channels, kind of sparks of irregular (zigzag) shape. The length of these sparks "sliding" on the surface of glass was different (and it was dependent on the voltage), however, it often reached a few centimeters. And so it exceeded multifold the width of the gap itself, which was about 7 mm.

When we introduced a granular material, being dielectric like silica, to the discharge gap, the discharge did not change much of its form. However, its structure became less homogeneous. In certain "privileged" parts of the gap, bundles of filamentary microdischarges gathered. They appeared much more seldom in the remaining parts of the gap, where quite a uniform glow of a low intensity could be seen.

The influence of the process conditions on the ozone concentrations in the stream from the ozonizer is shown as a temperature dependence (Figs. 6–8). Controlled parameters of the experiment were temperature of the liquid in the cooling circuit of the ozonizer ($t_L$), voltage ($U$), and rate of oxygen flow ($\dot{V}$).

The results obtained show dependences easily understood: increases in ozone content with increases in $U$ and with decreases in $T_L$. However, some exceptions were noticed at $U = 12$ kV, that is, near the starting voltage. In these cases an increase in ozone content with temperature rise (Fig. 8) most probably results from a significant increase in current intensity in the ozonizer, that is, from 0.58 mA at 2°C to 0.82 mA at 50°C.

The influence of the packing is evident. Much higher ozone contents were obtained at both values of the flow rate (10 and 26 $\mathrm{dm^3/hr}$) in the ozonizer with packing. In order to compare the ozone generation rates in the presence of silica with those without packing in the gap, the ozone concentrations ($\% O_3$) in the gas stream from the ozonizer are presented as a function of energetic density $E_V$ (Figs. 10–13).

$$E_V = \frac{P}{\dot{V}_N} \qquad (\mathrm{kJ/Ndm^3})^2 \tag{1}$$

Where $P$ is the power introduced to the ozonizer (kW) and $V_N$ is the oxygen flow ($\mathrm{Ndm^3/sec}$).[2]

The power $P$ introduced to the ozonizer was caluclated from measurements in the low-voltage circuit (with a watt meter) taking a correction for

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[2] 0°C, 760 mm Hg.

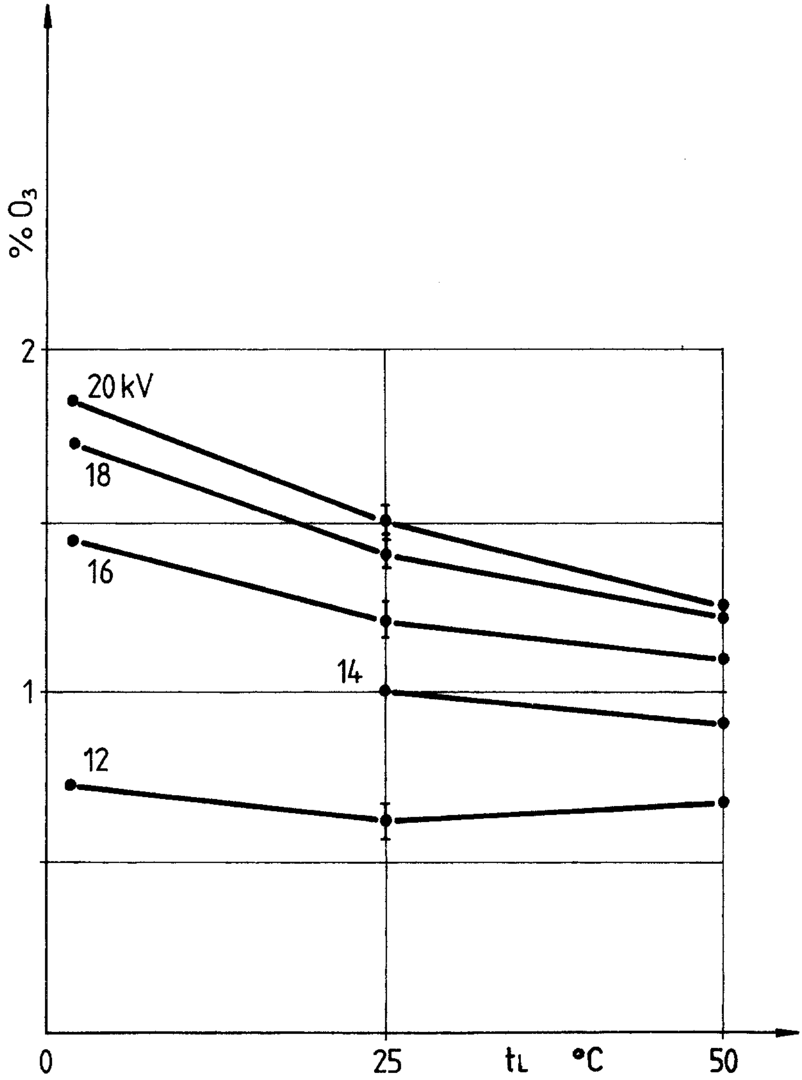

**Fig. 6.** Dependence of ozone concentration on cooling liquid temp. $T_L$, without packing. Oxygen flow $\dot{V} = 26\ \mathrm{dm}^3/\mathrm{hr}$; voltage $U = 12\text{–}20\ \mathrm{kV}$.

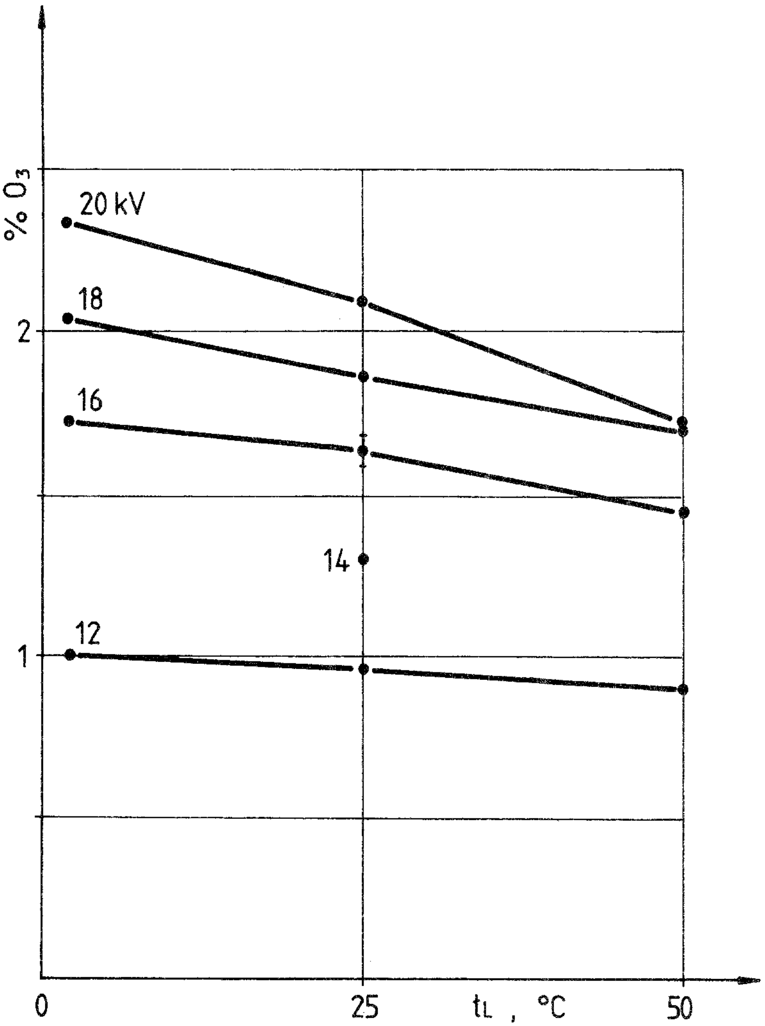

Fig. 7. Dependence of ozone concentration on cooling liquid temp. $t_L$; with silica, 1.25-3.2 mm. Oxygen flow $\dot{V} = 26$ dm$^3$/hr; voltage $U = 12$-$20$ kV.

losses of energy in the high-voltage transformer winding. Energetic production of the ozonizer is shown in Table I.

As can be seen from Fig. 9, parameter $E_V$ does not unequivocally describe the process conditions of ozone synthesis, as for each value $\dot{V}$ the results are arranged along a different curve. These observations are consistent with earlier experimental date and detailed analysis of the process

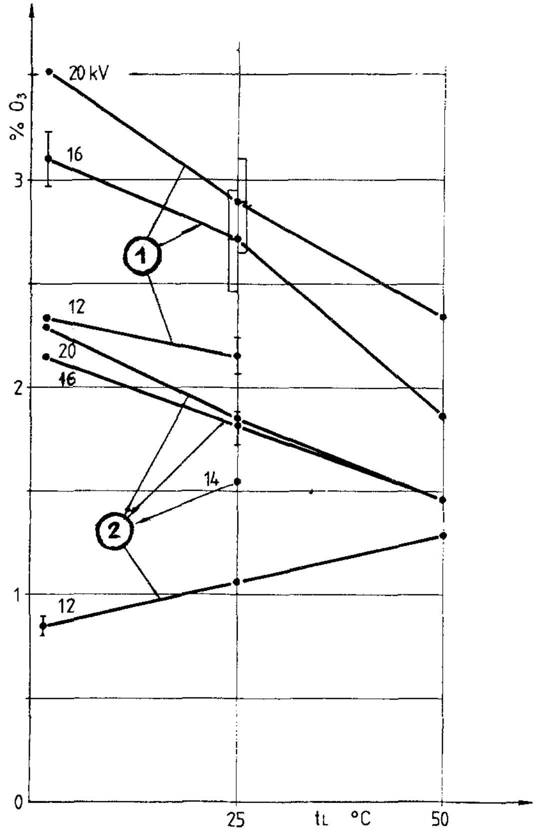

**Fig. 8.** Dependence of ozone concentration on cooling liquid temp. $t_L$. Oxygen flow $\dot{V}=10\ \mathrm{dm^3/hr}$; voltage $U=12\text{-}20$ kV. (1) With silica, 1.25-3.2. mm; (2) without packing.

**Table I.** Energetic Yield $\eta$ of the Ozonizer with Silica Grains and Without Packing: $t_L=25°\mathrm{C}$

| $\dot{V}$ (dm$^3$/hr) | $U$ (kV) | With packing | | Without packing | |
|---|---|---|---|---|---|
| | | % O$_3$ | $\eta$ (g O$_3$/kW hr) | % O$_3$ | $\eta$ (g O$_3$/kW hr) |
| 10 | 12 | 2.2 | 79 | 1.1 | 86 |
| 10 | 16 | 2.7 | 50 | 1.7 | 31 |
| 10 | 20 | 2.9 | 30 | 1.7 | 18 |
| 26 | 12 | 1.0 | 91 | 0.6 | 65 |
| 26 | 16 | 1.6 | 75 | 1.2 | 57 |
| 26 | 20 | 2.1 | 54 | 1.5 | 38 |

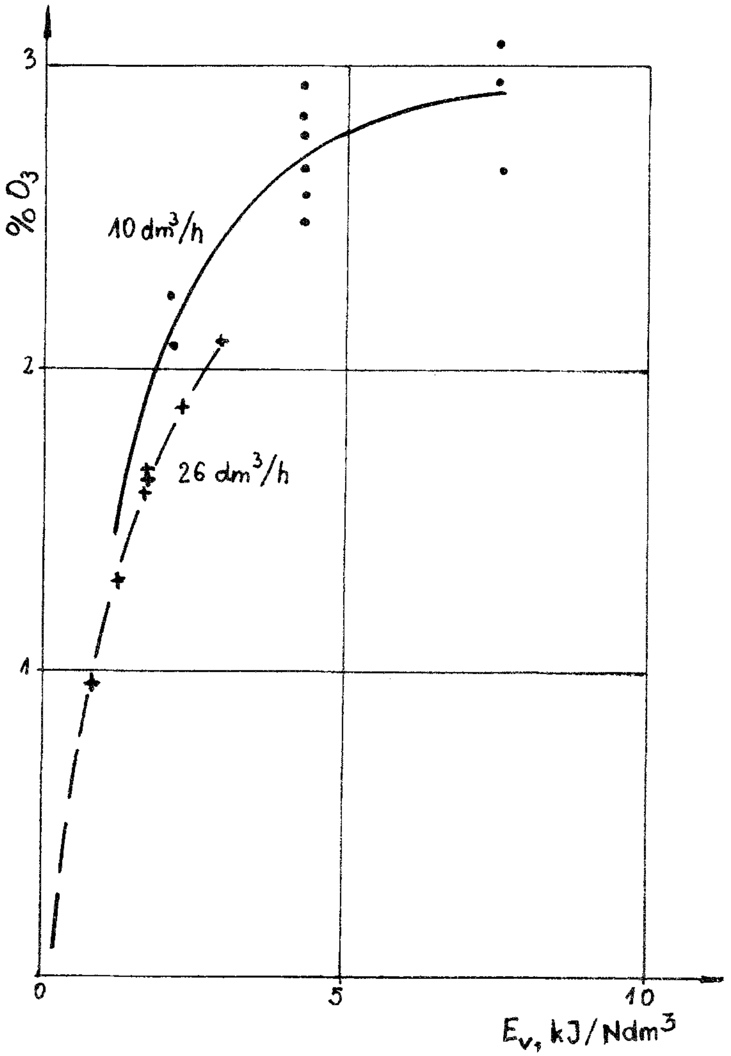

Fig. 9. Dependence of ozone concentration on $E_V$; with silica, 1.25-3.2 mm. Oxygen flow $\dot{V} = 10$ and 26 dm³/hr; cooling liquid temp. $t_L = 25°C$; voltage $U = 12$-20 kV.

in the ozonizer.(33) The ozone content obtained with packing is much larger—sometimes even one and a half times or more—than without packing at the same $E_V$ value (Figs. 10-13). This regularity occurred in all our experiments. It is worth noting that at large values of $E_V$ (for $\dot{V} = 10$ dm³/hr),

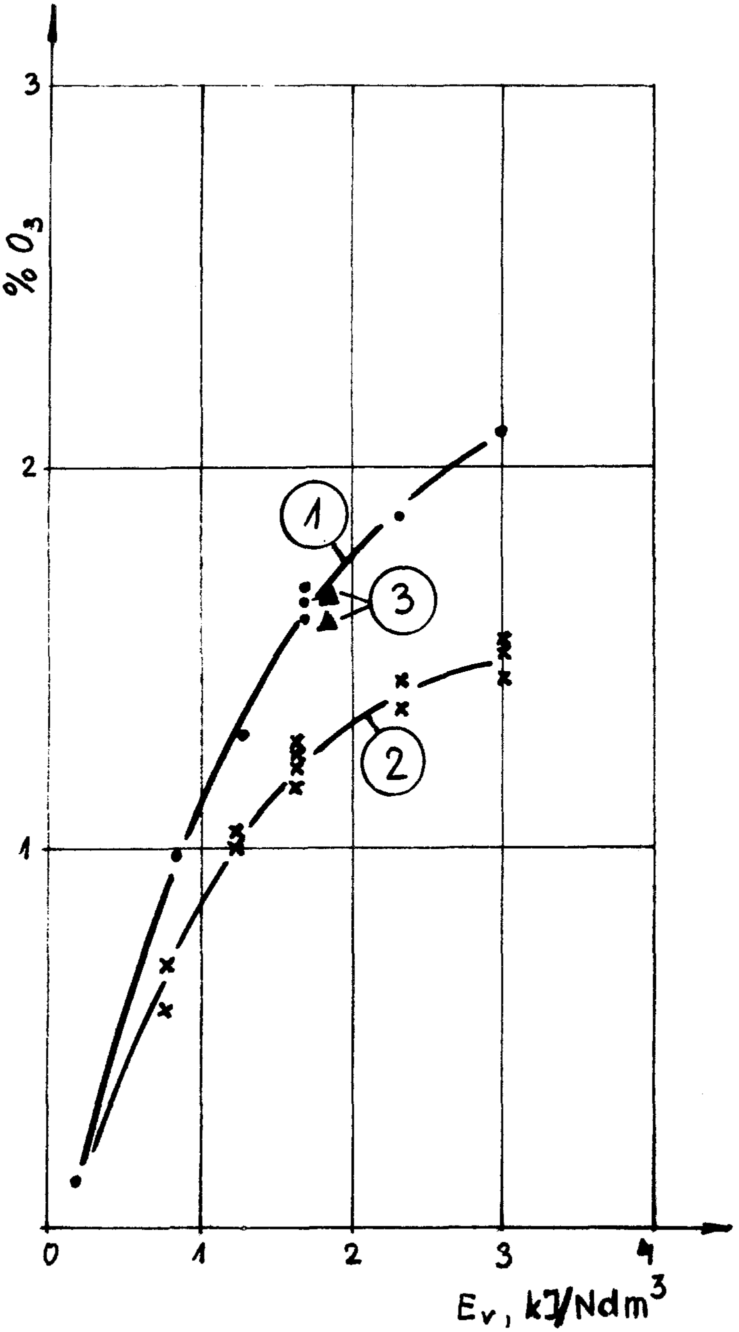

**Fig. 10.** Dependence of ozone concentration on $E_V$. Oxygen flow $\dot{V} = 26\ \mathrm{dm^3/hr}$; cooling liquid temp. $t_L = 25°C$; voltage $U$ = 12–20 kV. (1) With silica, 1.25–3.2 mm; (2) without packing; (3) with silica, 0.5–1.25 mm.

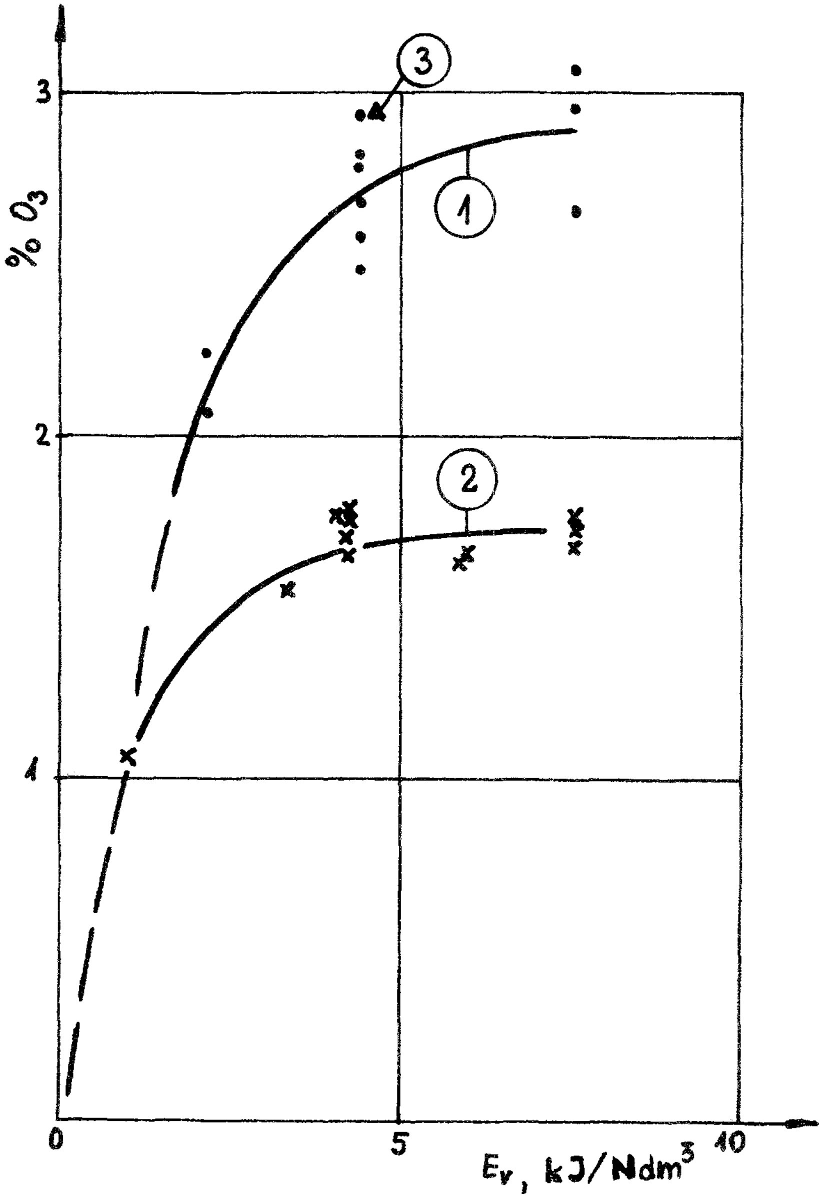

**Fig. 11.** Dependence of ozone concentration on $E_V$. Oxygen flow $\dot{V} = 10\ \mathrm{dm^3/hr}$; cooling liquid temp. $t_L = 25°\mathrm{C}$; voltage $U = 12\text{-}20\ \mathrm{kV}$. (1) With silica, 1.25-3.2 mm; (2) without packing; (3) with silica, 0.5-1.25 mm.

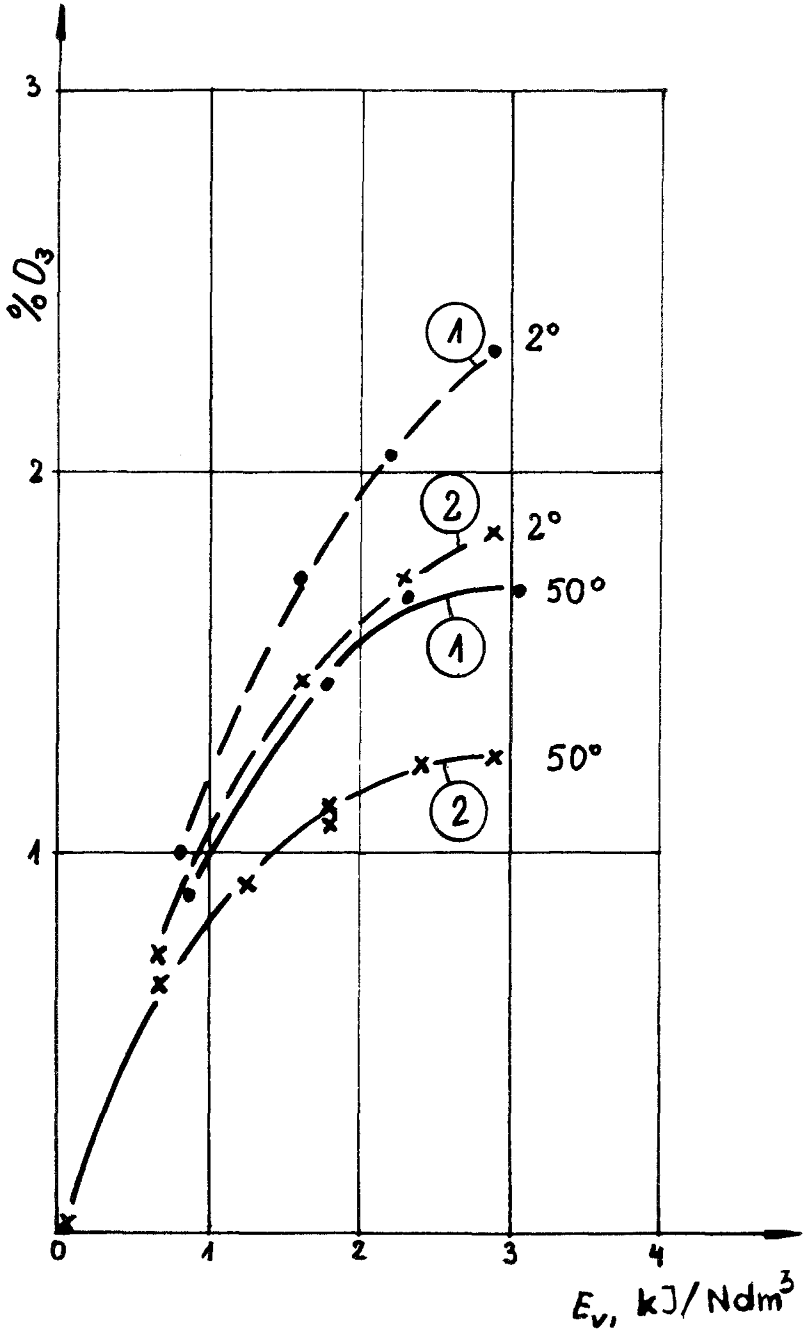

**Fig. 12.** Dependence of ozone concentration on $E_V$. Oxygen flow $\dot{V} = 26\ dm^3/hr$; cooling liquid temp. $t_L = 2$ and 50°C; voltage $U = 12$–$20$ kV. (1) With silica, 1.25–3.2 mm; (2) without packing.

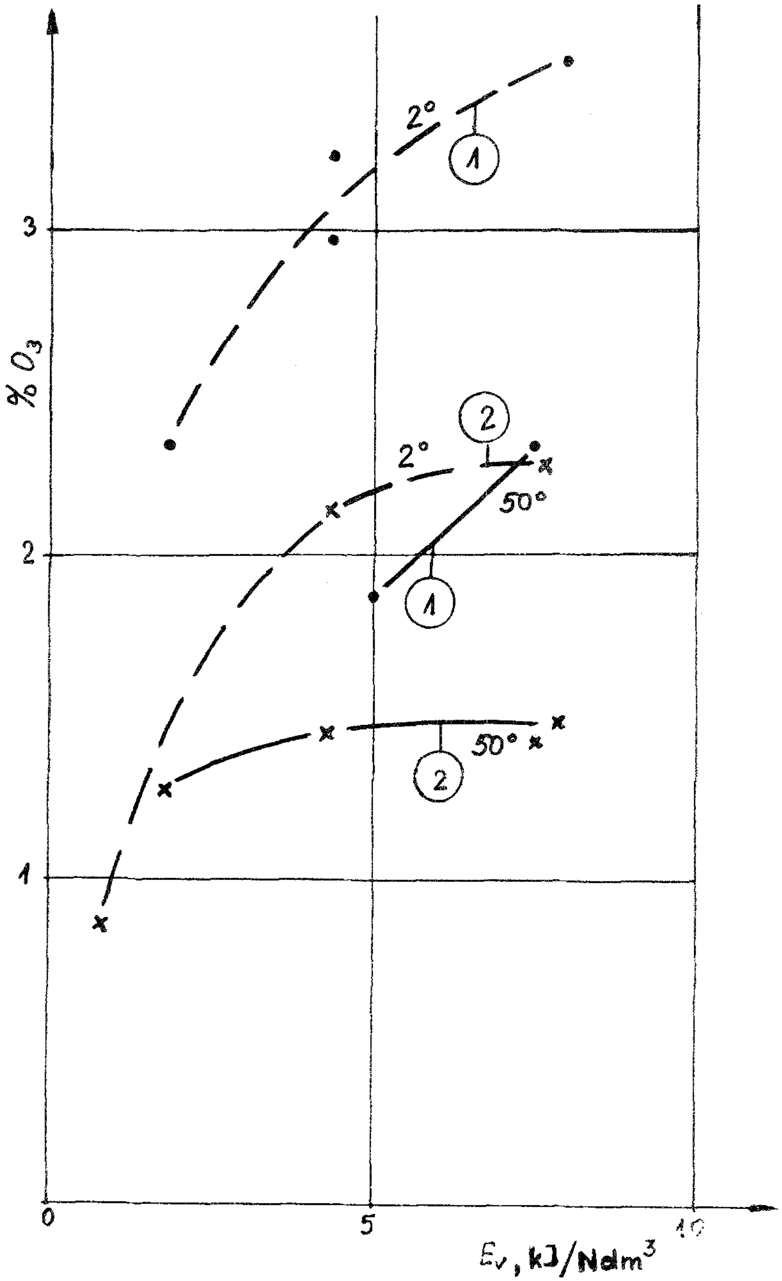

Fig. 13. Dependence of ozone concentration on $E_V$. Oxygen flow $\dot{V} = 10\ dm^3/hr$; cooling liquid temp. $t_L = 2$ and 50°C; voltage $U = 12–20\ kV$. (1) With silica, 1.25–3.2 mm; (2) without packing.

the ozone content does not increase any more with increases in $E_V$; a dropping tendency is even observed. The occurrence of an ozone content maximum like that is well known and is usually explained as an effect of a temperature increase in the reagent stream. Our results seem to confirm this interpretation. This is clearly visible in the dependence of ozone content on temperature $t_L$ (Figs. 6–8). It should also be taken into account that the temperature of the reagent stream in the ozonizer might be much higher than the temperature of the cooling liquid—by, e.g., several tens of degrees.

It is worth mentioning that in experiments with packing the increase in ozone content with increases in $E_V$ occurred in the range of large values of $E_V$, whereas without packing the ozone content within this range of $E_V$ did not increase any more (Fig. 13).

A number of parameters should be considered when discussing the influence of the packing on the ozone synthesis process. The majority of them have been presented earlier.(22) These are as follows.

(1) Shortening the residence time (at $\dot{V} = \text{const}$) as a result of a significant decrease in the free volume in the discharge gap.
(2) Change of hydrodynamic conditions in the stream as a result of an increase in flow velocity and of the irregular shape of channels between grains. These should result in much better intermixing of the stream in the cross section of the gap than without packing.
(3) Change of conditions for heat transfer (connected with effects mentioned in point 2). It should be expected that in the presence of packing, a more uniform temperature distribution occurs in the stream.
(4) Changes in the discharge structure, especially its nonuniformity due to gathering of microdischarges paths in some channels between grains, in certain "privileged" places.
(5) Effect of heterogeneous processes occurring on the solid surface.

Analysis of our results indicates that factor 1 can be neglected in the discussion.(22) However, a certain part is played by factor 2 and, especially, factor 3. The influence of temperature has been clearly marked in our experiments. If the packing facilitated heat transfer to the cooled ozonizer wall, this of course should favorably influence the result of the process. However, the observed increase in ozone content caused by the presence of packing seems to be rather too large, if it is to be attributed only to the favorable conditions of heat transfer.

The changes in the discharge structure in the presence of the packing might give various effects. The observed decrease in starting voltage resulted in a significant increase in ozone content at $U = 12$ kV. On the other hand, if the more nonuniform structure of the discharge had any influence on the ozone concentration, then it would be rather negative.

In our opinion, those were heterogeneous effects, occurring on the solid surface, that had the largest influence on the ozone formation in the presence of packing. The synthesis of $O_3$ particles may occur on this surface, e.g., according to the mechanism

$$O + O_{2ad} \rightarrow O_{3ad} \tag{2}$$

$$O_{3ad} \rightarrow O_3 \tag{3}$$

The subscript ad marks an adsorbed particle.

It seems probable that reactions with excited molecules $O_2^*$ occur as well,(34,35) e.g.,

$$O_2^* + O_{2ad} \rightarrow O_{3ad} + O \tag{4}$$

However, it may be assumed that the surface is a place for the formation of intermediates, from which ozone is formed in the gas stream.

However, there may be some doubts about the interpretation given above, which should be discussed here. First, it is well known that chemical reactivities of atoms, radicals, excited molecules, and other active particles are extremely high. Characteristic times of reactions in which the species mentioned above take part are very short, e.g., under pure oxygen plasma conditions they last no longer than 1-2 $\mu$sec.(16) Thus the lifetime of the active species might appear too short for them to reach the plasma-solid interface by diffusion from the place where they were generated, i.e., from the filamentary microdischarge channels. In our experiments the size of the silica grains was 1.25-3.2 mm, and the width of the gaps between them was of the same order.

Second, in our experiments with the silica grain size significantly decreased (from 1.25-3.2 to 0.5-1.25 mm), and thus the interface area much increased, we found that this change did not affect the ozone concentrations (Figs. 10 and 11). It was clear that the significant increase in the interface area did not result in any changes in the reaction rates, in spite of what is usually observed when heterogeneous processes occur. So a question arises: Did the heterogeneous processes really influence the ozone formation rates in our experiments? It seems, after all, that the answer is yes. There is no discrepancy between such a conclusion and the findings mentioned above if it is assumed that the discharges in our semicorona ozonizer partially were a kind of surface discharge, as has been presented earlier. This kind of discharge is thought to influence the ozone formation in conventional ozonizers.(21) The discharge structure we have observed during the experiments seems to confirm this conclusion. In the absence of the packing the filamentary microdischarges crossed the entire gap width and continued their paths over the surface of the dielectric barrier (glass). When we put the silica packing into the gap a glow, visible at the surfaces of grains, indicated that many of the microdischarges chose their way over these surfaces instead of following the paths through the gas volume. In our opinion, a significant part of the electric charges involved were engaged in a kind of surface discharge.

In such circumstances the active particles might be generated in the microdischarges passing just over the gas–solid interface, and so in spite of their short lifetime, they could take part in the heterogeneous reactions which occurred at the solid surface.

When discussing the second point it must be taken into consideration that the increase in the gas–solid interface area could influence the ozone formation rates, but only in the case when it occurred together with an increase in the number of active particles which were able to reach the solid surface. However, when a majority of these particles had already been engaged in the heterogeneous reactions at the interface, the subsequent increase in the area would not affect the ozone formation rate. Thus it should be assumed that the whole interface area did not take part in the ozone formation process, but only those of its portions which were nearby the microdischarge channels. It is quite possible that such circumstances occurred in our experiments with small silica grains.

We think that the findings presented above give sufficient evidence of the catalytic activity of silica in ozone formation, although some questions cannot be answered yet.

## 4. CONCLUSIONS

(1) It was found that a granular dielectric, e.g., silica, introduced into the discharge gap of a semicorona ozonizer can accelerate ozone formation and result in an increase in its concentration with stable energy consumption.

(2) Responsible for this are heterogeneous effects occurring on the solid surface of silica, which shows some catalytic activity in the formation of ozone.

(3) In the presence of granular dielectrics semicorona discharges may have a feature of surface discharges.

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