*The Chemical Reaction in Silent Electric Discharge. III. The Effect of the Packings on Ozone Formation**

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In the previous reports on ozone formation in a silent electric discharge, the relation between the gap length, the electrode area and the pulse current was studied[1,2].

For the present paper, an investigation of the ozone formation from oxygen has been carried out using a special type discharge tube with some adequate fillings to serve as dielectrics.

Experimental

The apparatus and the procedure, except for the packings, are essentially the same as in the previous report[1]. The space between the electrodes was filled with a granular packing of titanous oxide ceramics whose dielectric constant varied in accordance with the percentage composition of the ingredients, such as barium oxide, or tin(IV) oxide. Ordinary soda glass packings with the same geometry were used as a check standard. The packings were made by "one time baking" to an amorphous mass, then by crushing the granules to 0.75~1.00 mm. size mesh, which is an adequate size for filling. The ozonizer was again of a Siemens type, which has a gap length of 2.6 mm. and an effective electrode area of 250 cm^2. The voidage of gap space with the packing was 47% of the total gap volume in each case.

The stoichiometric composition of the ceramics and their dielectric constant, at room temperature and at 1 kc, are given in Table I.

TABLE I

Number of runs	Composition of the packings	Dielectric constant
I	Blank	1
II	Soda glass	6
III	$2MgO/TiO_2$	20
IV	TiO_2	100
V	$BaTiO_3$	1200
VI	$95BaTiO_3/5SnO_2$	5500~6000

The frequency of the electric source for silent discharge was 50 c/sec. The electric circuit that provided a high tension to the discharge tube and the whole flow system with its detecting device for ozone were similar to those described in the previous work[1,2]. Through a packed tube a discharge current can be raised to such a value that eventually damage will occur to the usual ozonizer. For example, in the case of titanous oxide packing, a stable discharge will be established up to around 8 mamp. current, while the maximum ozone concentration will be somewhat over 6.5%. The pulse current

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1) K. Morinaga and M. Suzuki, This Bulletin, **34**, 157 (1961).

2) K. Morinaga and M. Suzuki, ibid., **35**, 204 (1962).

was measured by the device of the oscillogram with an integral circuit that inserted a series to the earth line of discharge tube. The pulse current will be less than that of an ozonizer of the same type without any packing.

Results

All measurements were carried out with a residence time of the reactant gas of 1.5~80 sec. in the ozonizer.

Figure 1 represents the saturated state ozone concentration under a certain constant total discharge current, and Fig. 2 represents the saturated state ozone concentration under a certain constant pulse current. In both figures, the results are plotted against the value of the dielectric constant of the packing materials, and the location at the value of 1 on the abscissa represents the results that were obtained in a blank discharge tube without any packing fill. Under a constant discharge current, the maximum value of the saturation ozone concentration appears at the packing of titanium(IV)

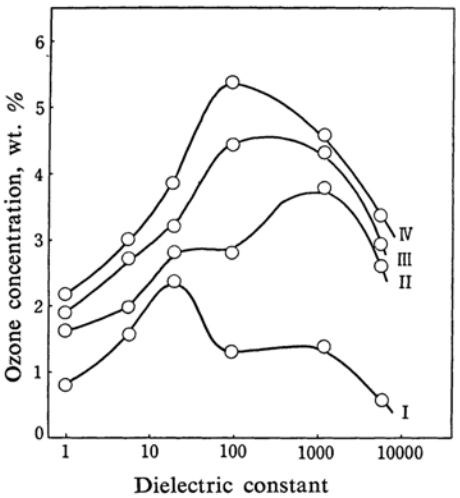

Fig. 1. The saturated state ozone concentration under a given total discharge current, against the dielectric constant of the packing materials.
(I) Total discharge current 1 mA,
(II) 2 mA, (III) 3 mA, (IV) 4 mA

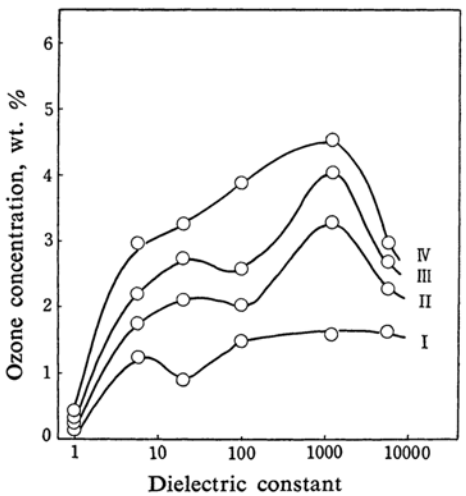

Fig. 2. The saturated state ozone concentration under a given pulse current, against the dielectric constant of packing materials.
(I) Pulse current 7μA, (II) 14 μA,
(III) 21 μA, (IV) 28 μA

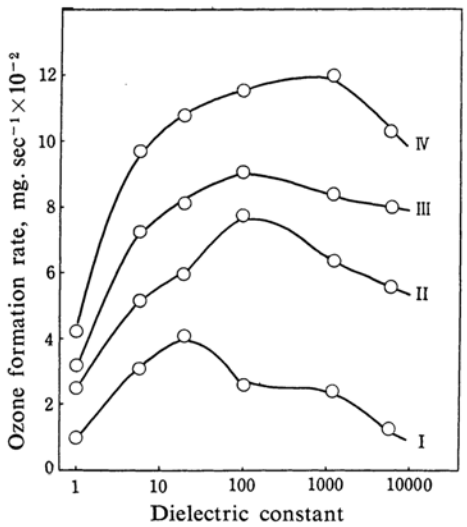

Fig. 3. The ozone formation rate under a given total discharge current, against the dielectric constant of the packing materials.
(I) Total discharge current 1 mA,
(II) 2mA, (III) 3 mA, (IV) 4 mA

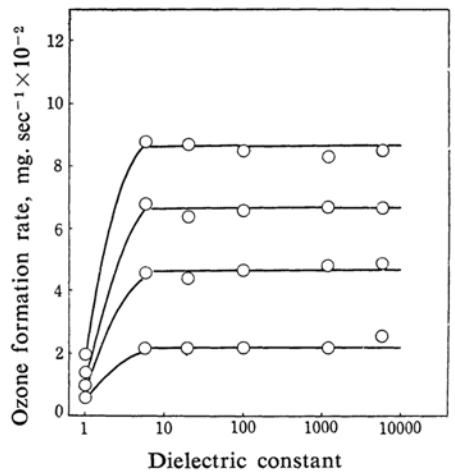

Fig. 4. The ozone formation rate under a given pulse current, against the dielectric constant of the packing materials.
(I) Pulse current 7 μA, (II) 14 μA,
(III) 21 μA, (IV) 28 μA

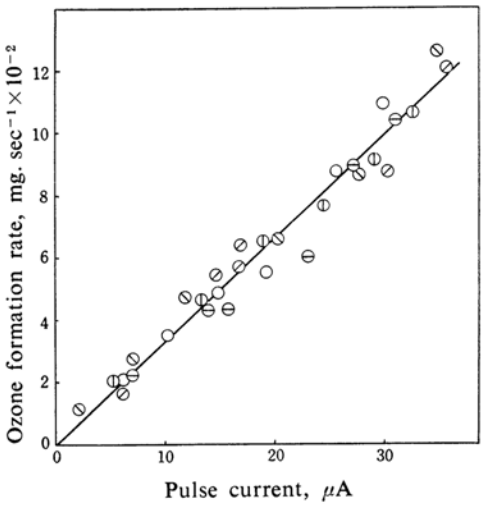

Fig. 5. The rate of ozone formation under various packing against pulse current.
○ Soda glass, ◐ TiO_2,
◔ $95BaTiO_3/5SnO_2$,
⊖ $2MgO/TiO_2$, ◴ $BaTiO_3$

oxide, whose dielectric constant is around 100. In the case of a constant pulse current, the maximum saturation ozone concentration occurs at the dielectric constant value of about 1200 of $BaTiO_3$.

Under the same conditions as in Figs. 1 and 2, the rate (mg./sec.) of ozone formation is plotted in Figs. 3 and 4 against the same abscissa as before. The curves in Fig. 3, where the parameter of each diagram is the discharge current, do not show any regular feature, whereas in Fig. 4, where the parameter is pulse current, the rate of ozone formation at a higher value of dielectric constant is nearly independent of the dielectric constant value of the packing materials. In Fig. 5, the ozone formation rates for various ceramics fillings of different dielectric constants against the pulse current are shown. The rates for each packings, independent of the dielectric constant values, are represented by a straight line whose inclination has a value of 3.3×10^{-3} mg. sec^{-1} μamp^{-1}.

The observed number of hairs of the packing fill ozonizer is more than that of the usual ozonizer without packings where all other conditions are the same.

Discussion

It is highly conceivable that the surface of the dielectric packing is partly electrically conductive. The conductivity will increase in accordance with the higher value of the dielectric constants. At the application of some electric tension between the electrodes, the current will be carried in two ways, one by the discharge current through the gas phase, and the other along the surface leakage. In the oscillogram pattern, the discharge current will manifest itself as pulse current or hair on the base current pattern, where the leakage current is implied together with the basic current.

The presence of the packing is equivalent to the larger value of the electrode area and the small value of gap length, which leads to the conclusion that rate of ozone formation should be higher with a packing-filled ozonizer.

The mean value of the ozone formation rates per unit pulse current for discharge tubes with a filling whose dielectric constant in each case has a different value, was 3.3×10^{-3} mg. sec^{-1} μamp^{-1}.

In the case of 50 c/sec. discharge and for unit A/d, the corresponding rate is 7.0×10^{-7} mg. sec^{-1} μamp^{-1} [1], were A is the electrode area and d is the gap length.

The experimental conditions are about the same for both cases, the exception being the packing fill. The rate value should be proportional to the A/d value in both cases. The assumed A/d value for the packed discharge tube is 4.7×10^{3} cm., which means a very large electrode area and/or a very small gap length. In the above pattern of discharge in packed ozonizers, the discharge potential, then, will be appreciably smaller than in the usual ozonizer, which fact accounts for the larger number of hairs and the larger value of the formation rate. The discharge current involves two contributions, the gas discharge and the surface leakage. For a certain fixed value of discharge current, the discharge contribution will increase at first with the increase of ozone formation, because in an ozonizer, absorbed electric energy which is to be proportional to the ozone formation is proportional to the total capacity C, where C is given by

$$1/C=1/C_g+1/C_a$$

in which C_g is the capacity of glass or dielectrics, which is proportional to the value of the dielectric constant, and C_a the capacity of the air gap. On the other hand, the surface leakage effect will increase in company with the increase of the dielectric constant of the fillings, and above a certain value of the ozone formation rate it will begin to decrease according to the increasing leakage current under a certain fixed discharge current, because the leakage current does not benefit the ozone yield. These patterns explain the features of the diagrams in Figs. 1 and 3.

The pulse currents represents only the quantity of discharge electricity through the air gap space, while the base current, in an oscillogram, implies the leakage electricity. For a certain

amount of discharge electricity, or pulse current, the ozone formation should be the same no matter what the value of the dielectric constant of the filled packing, because the rate is referred to the value at zero time of residence and is, therefore, governed solely by the discharge quantity of electricity.

The ozone concentration is the complicated results of reaction under which the gas is exposed for a certain period of residence. It is, therefore, no wonder that the diagram in Fig. 2 does not show any regularity. However, it arouses rather a practical interest that the packing of titanium(IV) oxide under a certain constant total discharge current shows the maximum value. Rummel also uses in his patent** layers of ceramic substances containing titanium(IV) oxide with a dielectric constant of 80 for the preparation of ozone.

In conclusion, the application of the packing in an ozonizer makes two contributions to ozone formation, the one due to the shortening of the gap distance, which is equivalent to the expansion of the electrode area, and the other corresponding to the enhancement of the dielectric constant on the wattage absorbed in the ozonizer and on the leakage current along the surface of the packing. These effects benefit the ozone formation by exempting the adverse effect of leakage current, which will increase according to the increasing value of the dielectric constant.

** T. Rummel, German Pat. 1028544 (April 24, 1958).

Summary

1. The ozone formation rate was increased in a packed discharge tube more than in the same type of ozonizer without packing.

2. The linear relationship, which has been proved before, between the pulse current and the ozone formation rate was also obtained in this case, independent of the dielectric constant value of the packing materials.

3. The ozone concentration shows a maximum value at a certain value of the dielectric constant.

4. The rate of ozone formation is independent of the dielectric constant at the higher values of the dielectric constant.

5. A tentative mechanism which is plausible for the elucidation of the results has been discussed.

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