Investigation of corona-resistant coatings for the dielectric surface in a plasma-chemical ozone generator on the base of dielectric barrier discharge

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Abstract. The results of the study on the development of corona-resistant coatings for dielectric barriers in plasma-chemical ozone generators on the base of dielectric barrier discharge are presented. The influence of the binder and filler material on the service life of the dielectric barrier is studied. The best corona resistance result was achieved using an organosilicon binder. Inorganic fillers are effective for increasing the corona resistance of the coating: Al₂O₃ powders, talc and others. The studies were performed in air at atmospheric pressure.

1. Introduction
Dielectric barrier discharge (DBD) is widely used in various industries and in scientific research. Technologies based on application of plasma generated in discharge cells of surface, coplanar and volume DBD are developing intensively. Plasma and plasma-chemical technologies can be effective, in particular, in case of methods development for plasma etching, technologies for surface layers formation, methods for purposeful changes of the physicochemical properties of materials surface layers. Technologies of nanoparticles synthesis in low-temperature plasma, generated in DBD cells are actively developed. In particular, the DBD is used for effectiveness improvement of energy conversion in case of development of dye-sensitized solar cells as the relatively inexpensive photoelectric converters. Also, the near-surface plasma attracts significant interest for creation of control technologies by the high-speed air flows, that flow around the moving in air bodies, by affecting on boundary layer characteristics by electric discharges. For example, plasma-chemical generators of the barrier type are effective for ozone producing. The disadvantage of such ozone generators is an unsatisfactory service life due to fairly rapid destruction of the dielectric due to the effects of micro-discharges, an electric field, as well as ozone synthesized in the discharge cell, which is a strong oxidizer [1-8]. Therefore, the development of a corona-resistant coating of the dielectric barrier is relevant. It should be noted that there are a significant number of publications that have studied the effect of DBD on various materials: plasma atmospheric pressure treatment of the surface of aluminium nanoparticles (nAl) to reduce the inactive amorphous shell Al₂O₃ [9]; improving the dielectric properties of cross-linked polyethylene in plasma CF₄ [10]; surface activation of textile fibres [11]; the electrical and mechanical characteristics of surface linear DBD actuators [12]; the surface modification of aromatic polymers [13]; the influence of surface charges on the structure of a dielectric barrier discharge [14, 15] and many others.

This paper presents the results of a study of the effect of corona-resistant coating fillers on the durability of the dielectric barriers of plasma-chemical ozonizers based on DBD.
2. Pilot plant
The effect of micro-discharges in the DBD cell (figure 1) in the air at atmospheric pressure was subjected to a corona-resistant coating (film) deposited on the surface of the dielectric barrier. As a dielectric, glass-bonded (reinforced) dielectric material was used, which is a layered composite material based on fibreglass and a polymeric binder. The fibreglass plate has dimensions 10x15 cm and a thickness of 0.5 mm. A 0.1 mm thick film consisting of a binder and a filler was deposited on the upper surface of the fiberglass dielectric.

Powders of the following materials were used as fillers: alumina oxide $\text{Al}_2\text{O}_3$, titanium dioxide $\text{TiO}_2$, talc $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, mica $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}] (\text{OH})_2$, asbestos $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

The air gap between the upper metal electrode and the dielectric with a corrosion-resistant coating (see figure 1) is 1.5 mm. The metal electrodes in the DBD cell were supplied with an alternating voltage with an effective value from 7.5 to 8 kV and with a frequency of 50 Hz. The effect of micro-discharges on the film in the air at atmospheric pressure continued until the breakdown of the dielectric (glass-bonded (reinforced) dielectric material) occurred.

![Figure 1. Schematic diagram of a dielectric barrier discharge cell: 1 — flat plate-shaped metal electrodes; 2 - dielectric plate; 3 corona-resistant coating (film) on the surface of the dielectric.](image)

The voltage was selected in such a way that the dielectric barrier without corona-resistant protective coating functioned for without a breakdown from 15 to 60 minutes. In order for the ozone output to be no less than in the case of using the dielectric without protective coating, the current of the same value was also established in the experiment with a protective coating of the dielectric barrier. The total thickness of the dielectric barrier increased due to the protective layer. Therefore, experiments with dielectric barriers with a corona-resistant coating were carried out at higher voltages.

As a binder, heat-resistant “Certa” enamel, heat-resistant varnish KO-85 and white enamel PF-115 were used. By composition, KO-85 varnish is a mixture of a solution of modified organosilicon resins and glyphaltic varnish in aromatic and aliphatic solvents. Heat-resistant anticorrosive enamel “Certa” is a suspension of aluminium powder or black heat-resistant pigment, polyphenylsiloxane resin, micro talc in a solution of toluene and butyl acetate. The quantitative composition of enamel “Certa” is as follows: polyphenylsiloxane resin-50 %, heat-resistant pigment (various colors) – 15 %, micro talc – 10 %, butyl acetate – 5 %, toluene-20 %. White enamel PF-115 contains: semi-finished varnish-28%, rutile form of titanium dioxide-62%, Stoddard solvent-10%. Semi-finished varnish is a solution of pentaphthalic resin modified with semi-drying oils in volatile organic solvents. Percentages are shown by weight. The names of varnish and enamels indicate Russian brands.

3. Results and discussion
The dielectric barrier discharge observed in the discharge cell is shown in figure 2. Uniform discharge takes place in the entire air gap of the flat electrode system (see figure 1).

The test results of the DBD cells for different corona-resistant coatings of glass-bonded (reinforced) dielectric material are presented in table 1. The average time of functioning of the DBD cell before breakdown was determined by the results of three experiments.
Table 1. Results of tests of a plasma-chemical ozone generator with a different composition of a corona-resistant coating of the glass-bonded (reinforced) dielectric material.

| Fillers | RMS current value $I$, mA | RMS voltage value $U$, kV | Duration of the ozone generator functioning before the dielectric barrier breakdown, Minutes |
|---------|---------------------------|---------------------------|---------------------------------------------------|
| Talc    | 2                         | 8                         | 241.6                                             |
| Al$_2$O$_3$ | 2                       | 8                         | 233.3                                             |
| TiO$_2$ | 2                         | 7.5                       | 163.3                                             |
| Asbestos| 2                         | 7.5                       | 128.3                                             |
| Mica   | 2                         | 7.5                       | 125.0                                             |

In the experiments, a mixture in the ratio of 50% “Cetra” enamel and 50% KO-85 varnish by volume was used (see table 1). This was done because when using only KO-85 varnish it was not possible to create a continuous coating. The reason is that after drying, the filler crumbles at any it’s concentration.

A typical surface coating is shown in figure 3. Target-oriented approach was utilized for the optimization of the analytic measurements [16]. Before measurements the sample was mounted on a 25 mm aluminum specimen stub and fixed by conductive silver paint. Metal coating with a thin film (13 nm) of carbon was performed using magnetron sputtering method as described earlier [17].

The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 30 kV accelerating voltage and at working distance 8-15 mm. Morphology of the samples was studied taking into account possible influence of metal coating on the surface [17].

It should be noted that the coating morphology depends on the duration and intensity of exposure to micro-discharges in separate local areas of the barrier surface.

The average duration of operation of the DBD discharge cell without a breakdown in the case of
using a dielectric barrier (glass-bonded (reinforced) dielectric material) without covering with a corona-
protecting film was equal to 33 minutes.
When the surface of glass-bonded (reinforced) dielectric material is covered with corona-
resistant coating a significant increase in the service life of the dielectric barrier takes place (see table 1). The
best results were observed when using Al₂O₃ and talc powders as filler. This is because based on these
materials the most uniform coating was obtained since these fillers had small rounded granules. Mica is
a flake, arranged randomly. Channels of micro-discharges pass along the surface of the scales,
destroying the protective coating and, in the future, the dielectric barrier. A similar situation with
asbestos. Asbestos is a fibrous material, and destruction occurs on the surface of the fibres. Of interest
is titanium dioxide. This material has an increased dielectric constant compared to other fillers examined
but is more hygroscopic.

4. Conclusion
Inorganic materials have sufficient mechanical and electrical characteristics and a high melting point of
about 2000°C. Thus, the requirement of heat resistance and corona resistance of the coating is satisfied.
The use of inorganic filler also increases the thermal conductivity of the surface of the dielectric, which
provides a more uniform distribution of temperature over the surface, reducing local overheating.
In this study, it was used as a binder, in particular, varnish on an organosilicon basis. Organosilicon
varnishes and enamels are characterized by the stability of the coating at high temperatures of 200–
800°C, which is comparable with the softening temperature of glass enamels; high electrical insulation
performance; water-oil-petrol resistance; high corrosion protection properties.
The high efficiency of organosilicon-based binders in terms of increasing the corona resistance of
the dielectric barrier in DBD cells used as ozonizer has been established. This is due to the high heat
resistance of this material. It was found that the effect of the binder material on the corona resistance is
more significant compared to the influence of the filler material. Interaction effects are of little
importance. It has been shown that talc is the best filler. At the same time, the presence of any of the
coatings studied significantly increases the life of the dielectric barrier. This led to the conclusion that
the use of multilayer barriers with a corona-resistant coating significantly increases the service life of
the dielectric barrier discharge cell.

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