An affordable way to get silver nanoparticles for conductive inks and pastes

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Abstract. In this paper, we study the process of obtaining silver nanoparticles by the method of electrospark erosion of silver electrodes in distilled water with a significant overvoltage of the electrode gap. Studies were conducted on the previously developed experimental setup. The results showed that when the air discharge gap FV₁ is much larger than the working discharge gap FV₂, their exact ratios do not affect the particle size of the nanopowder. The particle size of the nanopowder is determined by other, not yet established process factors. Manufactured nanopowders have the same average size for all production modes and are characterized by a small scatter of particle sizes. The development of the process of obtaining silver nanoparticles by the method of electrospark erosion will reduce the cost of conductive inks and pastes in the future.

1. Introduction
Printed electronics is one of the new and actively developing areas of production of electronic devices. Conductive inks based on silver nanoparticles are used in printed electronics for printing. Currently used conductive inks are organic silver compounds, which decompose during heat treatment and further form silver nanoparticles. With prolonged thermal effects, the nanoparticles combine with each other to form conductors and other elements of electronic devices. Such conductive inks, for example, smart'Link s-CS01130 ink from Sigma-Aldrich have a high cost, more than $ 400 per 25 ml.

In our experiments, we want to obtain silver nanoparticles directly from metallic silver. This should reduce the cost of conductive ink in the future. To obtain powders of conductive materials of micron sizes, it was proposed to use the phenomenon of electric-spark erosion of materials during electrical breakdown of a liquid dielectric between two working electrodes [1]. However, when attempting to obtain nanometer-sized powders by the method of electrospark erosion, a serious drawback was identified. The disadvantage is the large variation in the particle size of the nanopowder, which complicates their use in conductive inks.

In our previous work [2], we reported on experimental confirmation of the assumption made by us that a possible way to solve this problem is to create an electric spark erosion process with significant overvoltage on the discharge gap. To implement this approach, it was necessary to abandon the use of the conventional EDM machine and we developed an experimental EDM with overvoltage on the working discharge gap (OV-EDM). The experimental setup demonstrated stable generation of a spark discharge in the discharge gap with a discharge pulse energy of less than 100 mJ. Using the...
experimental setup OV-EDM, silver nanopowder with a narrow scatter of nanoparticle sizes was obtained. The functional diagram of the experimental OV-EDM installation in comparison with the standard EDM installation scheme is shown in figure 1.

![Functional diagrams standard EDM (a) and experimental OV-EDM (b)](image)

**Figure 1.** The functional diagrams standard EDM (a) and experimental OV-EDM (b) [2].

It is important to note that our first results showed the possibility of using distilled water as a liquid dielectric for producing silver nanopowder. Silver was not oxidized during the electric spark discharge in distilled water. This eliminates the use of liquid nitrogen or other inert, primarily cryogenic liquids as a working liquid [3, 4]. The use of cheap liquid dielectric further increases the attractiveness of obtaining silver nanopowders by the method of electric spark erosion.

2. **Experimental**

The most interesting feature of the OV-EDM is the presence of an air discharge gap FV1, which provides for the creation of an overvoltage on the working discharge gap FV2. These two discharge gaps form a voltage divider when the capacitor C is discharged. At first glance, the voltage divider should have a significant impact on the operation of the OV-EDM. Possibly, it will allow controlling the process of electrospark dispersion of materials. Thus, for the OV-EDM at the first stage it was most interesting to study the influence of the ratio of the sizes of the discharge gaps FV1 and FV2 on the process of obtaining nanopowders.

To quickly measure the size of the obtained silver nanoparticles, it was decided to use the well-studied effect of plasmon resonance, which allows determining their average size from the spectrum of a colloidal solution of silver nanoparticles [5]. Measuring the size of silver nanoparticles in this way has previously been used by other researchers and experimentally proved its adequacy [6, 7].

For experiments, the high-voltage capacitor (C) with a capacity of 1500 pF was installed in OV-EDM to study the effect of the size of the discharge gaps FV1 and FV2 on the process of obtaining nanopowders by the method of electric spark erosion. The capacitor was charged from a high voltage AC transformer with a frequency of 50 Hz to a voltage of 10 kV. Capacitor C charged to maximum voltage, had an energy of 75 mJ. If the breakdown of discharge gaps FV1 and FV2 occurs at a lower voltage, the stored energy was less. The charge rate of the capacitor was set by the resistance R of the charging circuit, the resistance of the resistor was 50 kΩ. Both dispersible silver electrodes, which form the FV2 gap, were completely immersed in distilled water, 1 liter in volume. For uniform dispersion of the electrode material in the process of spark erosion, the working electrodes were rotated relative to each other.

The size of the gap of the air discharge gap FV1 varied in the range from 1 to 1.3 mm, the gap FV2 between the dispersible electrodes varied in the range from 50 to 100 μm. The dispersion time for each mode without changing distilled water was 120 seconds. It was established that during this time there is no accumulation of nanopowder in the working fluid, in amounts that can influence the process of electric spark discharge.

Experiments have shown that an increase in the interelectrode discharge gaps of FV1 and FV2 leads to an increase in the breakdown voltage, which was expected. In figure 2 shows oscillograms of discharge voltage pulses, measured on capacitor C, obtained with the minimum value of the discharge gap FV2 and the minimum and maximum value of the discharge gap FV1.
Figure 2. Oscillograms of discharge pulses, FV2 – 50 microns, FV1 – 1.0 mm (a) and 1.3 mm (b).

Figure 3. Spectra of a colloidal solution of silver nanoparticles, FV2 – 50 μm, FV1 – 1.0 mm (a) and 1.3 mm (b).

It is seen that the value of the breakdown voltage of the discharge gap system FV1-FV2 increases from ~6.5 kV to ~8.0 kV. The absorption spectra of the working medium with suspended silver nanoparticles obtained in these modes are shown in figure 3. From the spectra, it can be seen that the peak of the resonance for all the above operating modes of the experimental setup is 393 nm, which corresponds to an average size of silver nanoparticles of ~10 nm [5]. The small half width of the resonance indicates a small scatter in the size of nanoparticles. At the same time, different modes of the experimental setup correspond to different values of the resonance value, which is determined by the concentration of nanoparticles in the measured medium. With an increase in the discharge gap FV2 from 1.0 to 1.3 mm, the magnitude of the resonance is halved.

In figure 4 shows the oscillograms of the discharge voltage pulses measured on the capacitor C, obtained with the maximum value of the discharge gap FV2 and the minimum and maximum value of the discharge gap FV1. It can be seen that in this case, as the interelectrode discharge gaps FV1 and FV2 increase, the breakdown voltage also increases from ~6.5 kV to ~8.0 kV. An increase in the breakdown voltage is accompanied by an increase in the level of electromagnetic interference, leading to a failure of the measuring equipment, which is also seen in the oscillograms.

The absorption spectra of the working medium with suspended silver nanoparticles obtained in these modes are shown in figure 5. It can be seen that, for all the above operating modes, the resonance peak is 393 nm, as in previous experiments. Also, there is a difference in the concentration of nanoparticles depending on the ratio of the discharge gaps FV1 and FV2. It should be noted that in this case more intense absorption is also observed in the ultraviolet region of the spectrum, which is especially visible in figure 5(a).
Figure 4. Oscillograms of discharge pulses, FV2 – 100 microns, FV1 – 1.0 mm (a) and 1.3 mm (b).

Figure 5. Spectra of a colloidal solution of silver nanoparticles, FV2 – 100 microns, FV1 – 1.0 mm (a) and 1.3 mm (b).

Typical TEM images of silver nanopowder particles for different modes are shown in figure 6. It is seen that the majority of particles have a spherical shape, and their size varies between 10–20 nm.

Figure 6. Typical TEM image of silver nanoparticles, FV2 – 50 microns, FV1 – 1.0 mm (a) and 1.3 mm (b).

3. Conclusions
Experimental studies have shown interesting and hard to predict results. As a result of research, it was found that in the case when the size of the discharge gap FV1 is much larger than the size of the working discharge gap FV2, their exact ratios do not affect the nanoparticle size. The size of
nanoparticles is determined by other process parameters. A small scatter of particle sizes characterizes the resulting nanopowders. At such ratios of the discharge gaps, the voltage divider formed by the dischargers FV1 and FV2 regulates only the productivity of the process of producing nanopowders of conductive materials.

The results show the opportunity to develop an affordable technology for producing silver nanopowders. For this purpose, further investigation of the process of OV-EDM is necessary.

Acknowledgement
The Ministry of education and science of Russia, project № 8.7552.2017/8.9, supported the work.

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