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Synthesis of Conductive Silver Ink with a Low Sintering Temperature for Inkjet Printing Applications

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Abstract: **Transparent silver ink based on silver amino complex for inkjet printing has been developed. 1,2-diaminopropane, which acts as a solvent and complexing agent, significantly lowered the decomposition temperature of the silver salt and ensured the chemical stability of the resulting ink at room temperature. The annealed films were characterized by close packing and low electrical resistance values (8.5 μOhm·cm at an annealing temperature of 150°C). The ink provides productive inkjet printing while maintaining stable operation of the print head nozzles.**

Keywords: **silver, conductive inks, organic silver complex, inkjet printing, low-temperature sintering, printed electronics**

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1. INTRODUCTION

Printed electronics is a relatively new area for the production of various electronic components and printed circuit boards based on them. It is successfully used in such areas as: the manufacture of RFID tags [1], NFC modules [2], in the production of "flexible electronics", including various sensors [3]. The main advantages of this technology are the simplicity and speed of manufacturing the final products. It is especially useful in prototyping tasks, when one needs to quickly and cheaply make product mock-ups or test the viability of many ideas regarding the design of a device or product. Another advantage of printed electronics is the wide choice of a suitable substrate (glass, ceramics, polymeric materials, etc.).

Currently, inks based on carbon nanoparticles (nanotubes, graphene, etc.) [4] or inks containing metal nanoparticles (silver, gold, copper, platinum, etc.) are most often used as conductive materials for printed electronics [5-7]. The selection of the rheological parameters of the ink is very dependent on the intended printing method. Of the many application technologies, three main types of printing can be distinguished: screen, inkjet and aerosol. In this article, we will talk about inkjet printing using a commercial inkjet printer Dimatix DMP-2831 from Fujifilm Inc., USA.

The most popular type of conductive inkjet ink is silver nanoparticle ink. This is due to the optimal ratio "price-quality". The needs of the market dictate the need to create and produce high-precision small-sized universal and cheap conductive elements on light and flexible substrates. Nanosilver is a readily available source of low electrical resistance at low post-processing temperatures for printed structures. This is due to the lowest electrical resistivity of silver as a metal, the relative ease of obtaining and concentrating silver sols, and resistance to oxidation in air. The conductivity of such ink is provided by the effect of lowering the melting temperature of particles with a decrease in their size [8].

However, often silver ink, which is concentrated silver sols, tends to coagulate and form various kinds of aggregates. This is facilitated both by the properties of the nanoparticles themselves and by the hydrodynamics of the printing process of the flow of ink through narrow capillary channels inside the printer cartridge, as well as the process of drop formation and printing itself, in which a build-up of a silver layer can be observed at the base of the nozzles near the meniscus of the liquid due to evaporation. volatile components of the solvent.

One of the potential solutions to these problems can be the so-called particleless ink - ink containing complex silver salts, which are destroyed by heating, irradiation with UV light or other activation method with the formation of metallic silver. This forms a conductive coating. Such inks do not contain silver particles and are true solutions, so they are largely devoid of the disadvantages of inks containing particles. When creating such inkjet inks, it is important to observe the following criteria:

- the composition of the ink must be selected in such a way as to ensure long-term chemical stability and optimal rheological parameters (viscosity, surface tension);
- print stability (stable formation of ink droplets without clogging the nozzles

of the print head during the printing process);
- the silver concentration should ensure maximum conductivity of the printed and annealed structures;
- low annealing temperature (for creating flexible electronics elements).

In connection with the above, the main goal of this study was to develop a stable conductive silver ink with a low sintering temperature for inkjet printing on equipment similar to a Dimatix DMP printer (Fujifilm Inc., USA).

2. EXPERIMENTAL PART

The following materials were used to perform this work: silver nitrate (chemically pure, Petronit LLC), potassium oxalate (chemically pure, RusChem LLC), 1,2-diaminopropane, (Purity 99%, CAS Number 78-90-0, Sigma-Aldrich), 2-propanol (high purity grade, JSC EKOS-1), deionized water (resistivity 18 MΩ cm), hydrazine hydrate (100%, RusChem LLC), polyethersulfone syringe membrane filter (PES 0.22 μm, Millipore), polyimide film (PI, 40 μm thick).

For inkjet printing on Dimatix DMP equipment, the synthesized ink must have the following characteristics: viscosity – 10-12 mPas, surface tension – 28-33 dynes, low solvent volatility (boiling point above 100°C) and density ≤ 1.

The silver ink used in this study was synthesized by dissolving silver oxalate in organic solvents.

Silver oxalate was obtained under laboratory conditions by an ion-exchange reaction by mixing aqueous solutions of silver nitrate and potassium oxalate, taken in stoichiometric ratios. The resulting white precipitate was centrifuged, washed several times with deionized water, and dried at 40°C.

The preparation of the ink was carried out by dissolving 2 g of silver oxalate with cooling and intensive stirring on a magnetic stirrer in 1.5 ml of deionized water and 2.5 ml of 1,2 diaminopropane until a clear solution was formed. The resulting composition contained 36 wt.% silver and was characterized by a viscosity of more than 120 mPas and a density of 2.96 g/cm^3. These parameters significantly exceeded the optimal physical criteria for inkjet printing. In this regard, to achieve the necessary rheological properties, the original ink was diluted with a mixture of deionized water and isopropyl alcohol.

Thus, in this study, by selecting the ratio of solvents, it was possible to synthesize transparent silver ink with suitable rheological parameters for inkjet printing (viscosity – 10 mPas, surface tension 33-35 mN/m, density 1.01 g/cm^3). The final ink was filtered using a 0.22 μm syringe filter for further testing and research.

The absorption spectra of silver ink were recorded on a Leki SS2107UV spectrophotometer (ZAO LOIP, Russia) in the wavelength range from 200 to 1100 nm. The sample volume was 3 ml, the optical path length was 1 cm.

The thermal behavior of the ink was studied on a thermogravimetric analyzer (TGA) from Perkin Elmer (Germany) using aluminum trays. 20 μl of ink (m = 20 mg) was placed in the bath, dried at a temperature of 90°C until a film was formed (m = 8.6 mg), and then heated in the analyzer to 300°C in an air atmosphere with a heating rate of 10°C/min.

Ink testing in printing was carried out on a Dimatix DMP-2831 inkjet printer. During the printing process, Model DMC-11610 cartridges with a drop volume of 10 pl, equipped with a piezoelectric print head with 16 nozzles with a diameter of 21 microns, were used. Printing was carried out at room temperature without substrate heating, using standard settings (Wave 2 waveform, nozzle voltage 23 V).

The formation of printed elements (squares 7×7 mm, lines 20 mm) was performed by layer-by-layer printing with ink (5 layers) on PI film. To improve the wettability and adhesion of the ink to the substrate, the PI was preliminarily cleaned of contaminants, degreased, and hydrophilized by keeping the film in hydrazine hydrate for 1 min. The printed structures were annealed at various temperatures for 30 min. The cured square films were used for surface morphology, print quality, and electrical measurements.

The identification of the phase composition of the annealed samples was carried out on a Bruker D8 Advance facility (Germany) operating in reflection mode on Cu-Kα radiation (40 kV, 40 mA, $\lambda = 1.54056$ Å) with a scanning step of 4^{o} min^{-1}.

The morphology and thickness of the silver film on the surface of the polymer substrate was studied using a Prisma E scanning electron microscope (Thermo Scientific, Czech Republic) in a high vacuum mode (~$5 \cdot 10^{-4}$ Pa) with an accelerating voltage of 3.5 kV. The sample was frozen in liquid nitrogen for 20 min, then a cut was made with a sharp scalpel from the side opposite to the deposited silver layer. The sample was fixed on an *L*-shaped holder with carbon tape in such a way that the resulting cut was perpendicular to the optical axis of the microscope.

The viscosity of silver ink was measured on an AND SV 10A vibratory viscometer (Japan).

The surface tension of the ink was evaluated by stalagmometry.

The resistance of silver films was measured using a JG WeChat Support Type ST 2258C four-point probe system (Suzhou Jingge Electronic Co, China). The resistivity (ϱ) of the printed silver films was calculated as $\varrho = R_s \times W$, where R_s is the sheet resistance and W is the film thickness.

To measure the adhesion strength of silver films to a polyimide substrate, a standard test method, the adhesive tape method (test method B), was used. To do this, cuts were made on the film in the form of a lattice: four cuts in both directions up to the substrate. A pressure-sensitive adhesive tape was applied to the "lattice" and then torn off. Adhesion strength was determined by comparative analysis of the film before and after tearing off the adhesive tape.

3. RESULTS AND ITS DISCUSSION

An important factor in the creation of conductive ink in this work was the choice of the correct compound as a precursor. Most of the non-metallic phases must leave the system during thermolysis and evaporation. The chemical precursor must be designed in such a way that the chemical transformation into a pure metal phase occurs at a sufficiently low temperature to ensure the elimination of inorganic and organic compounds.

Following the above and relying on the achievements of studies described in scientific publications over the past few years [9-14], in this work, the process of complexation between a silver salt and an organic amino compound was used to form silver ink.

Silver oxalate was chosen as a precursor, the advantage of which is a high content of silver among carboxylates and, according to experimental data [15], a relatively low decomposition temperature (T_{dec} = 210°C).

According to literature sources, amino compounds, entering into donor-acceptor interaction with silver ions, form $Ag(R\text{-}NH_2)^{2+}$ complexes, which contribute to a significant decrease in the thermal decomposition temperature of the silver precursor [16]. This property is especially pronounced in silver complexes with bidentate amines. In this regard, 1,2-diaminopropane was used as a complexing agent. This compound has an optimal boiling point (120°C), has good solubility in water, alcohols and is characterized by chemical stability.

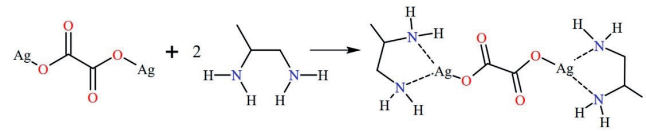

Fig. 1. *Formation reaction of a complex of silver-1,2 oxalate-diaminopropane.*

The advantage of the synthesis of the silver oxalate-1,2-diaminopropane complex is its ease, simplicity and cheapness. A schematic reaction for the formation of a silver organocomplex is shown in **Fig. 1**.

On the basis of the synthesized compound, an ink formula was developed that satisfies the requirements attached to a liquid for inkjet printing on a Dimatix DMP unit. Such organic silver ink was a transparent liquid with a solid metal content of 15 mass%. When keeping the ink for a month at room temperature, no degradation elements (precipitation, color change) were noticed, the transparency of the liquid remained unchanged. These observations are confirmed by spectral studies. In the spectra of the UV-visible absorption region, recorded with freshly prepared ink and kept for a month at room conditions, there are no plasmon resonance bands in the range of 390–600 nm, which are characteristic of nanosized silver (**Fig. 2**).

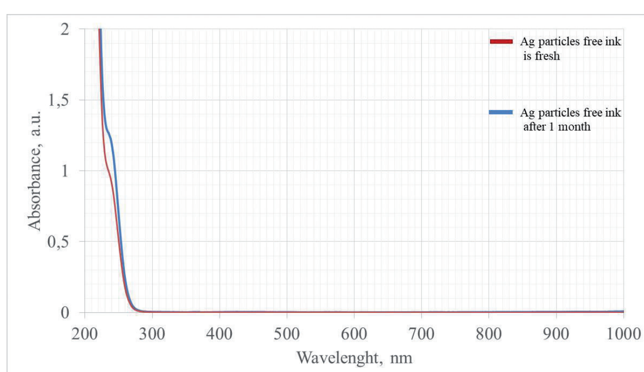

Fig. 2. *UV-visible absorption spectra of ink: 1 – freshly prepared, 2 – aged at room temperature for a month.*

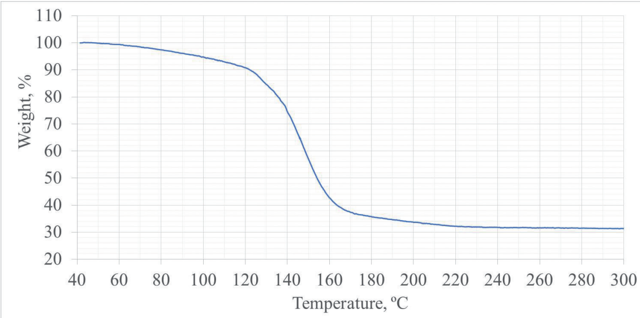

Fig. 3. *TGA curve of organic silver ink.*

Chemical resistance is an indisputable advantage of the ink obtained in this study. In addition, the absence of silver particles in the composition of the liquid is an advantage for using this ink in inkjet technology, as this will eliminate the risk of clogging of the print head nozzles.

The thermal behavior of silver organic ink is shown in **Fig. 3**.

The TG curve shows two main stages of weight loss. First stage between 40°C and 120°C, corresponds to the evaporation of residual volatile components in the film: water, acetic acid and traces of alcohol. The second stage (120-165°C) is due to the decomposition of the silver oxalate-1,2-diaminopropane complex with the formation in the ink composition that is capable of destructing with the formation of a metal component at sufficiently low temperatures, in comparison with the decomposition temperature of silver oxalate. The recommended temperature for annealing is 150ºC, because many polymer substrates cannot withstand higher temperatures.

The remaining metal phase must be of high purity in order to provide high electrical conductivity. To find this out, samples of annealed films were studied by *X*-ray phase analysis.

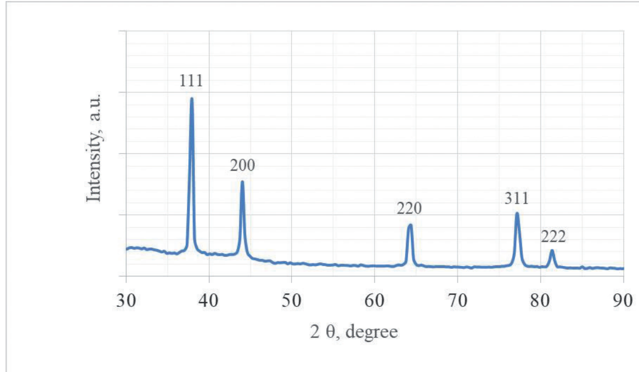

Fig. 4. *X-ray diffraction pattern of a silver film obtained upon annealing at 150°C.*

The diffraction pattern (**Fig. 4**) of the film formed at 150°C contains strong reflections at angles of 38.1°, 44.7°, 64.3°, 77.5°, and 81.2°, which correspond to the (111) planes, (200), (220), (311) and (222) silver crystals. These characteristic diffraction peaks confirm the single-phase composition of the sample, which is silver with a face-centered cubic structure.

Another important criterion that an ink must have is stability during the printing process.The ink obtained in this work has a suitable rheology for piezo inkjet printing on a Dimatix DMP machine (viscosity ~10 mPas, surface tension 33–35 mN/m, density 1 g/cm^3). The cartridges for your printer are designed for one-time refilling only, without the possibility of cleaning the print head nozzles with flushing liquids at the end of the printing process. Therefore, the ink is forced to remain in a closed system until it is completely used up.

After refilling the cartridge, the silver ink was in it for 24 hours and seven days with active use. Every day, observations were made of the appearance of the ink and the process of formation and departure of drops from the nozzles from the video camera was monitored in real time. It was

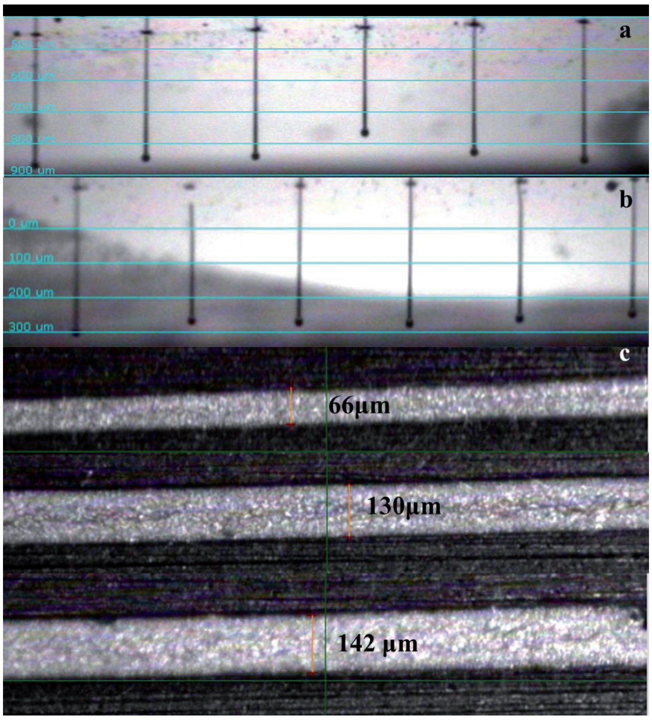

Fig. 5. *Departure of drops from the nozzles of the print head: a – the first day of printing, b – is the seventh day of printing. c – silver lines of various widths.*

noted that during the entire period the cartridge worked properly, the printing liquid remained invariably transparent and provided stable printing. On **Fig. 5***a,b* show photographs of droplet departures on the first and seventh days of printing. The droplets are round without satellites (satellite droplets) and are characterized by a straight projection. The printed lines (Fig. 5*c*) have clear edges, which also confirms the straightness of the droplets, the stable operation of the printing nozzles, and also indicates the satisfactory wettability of the surface of the polyimide material by liquid drops.

When the ink is annealed above 120ºC, a rapid evolution of gaseous products is observed, which can contribute to the loosening of the silver film and the violation of its integrity. To ensure the maximum conductivity of the material, the annealed structures must be densely packed. In this regard, the heat treatment of the printed squares was carried out in a stepwise manner. First, the films were heated to 100°C, kept under these conditions for 5 min to remove volatile components, and then the heating temperature was increased to the required one (120-200°C) and annealed for another 30 min.

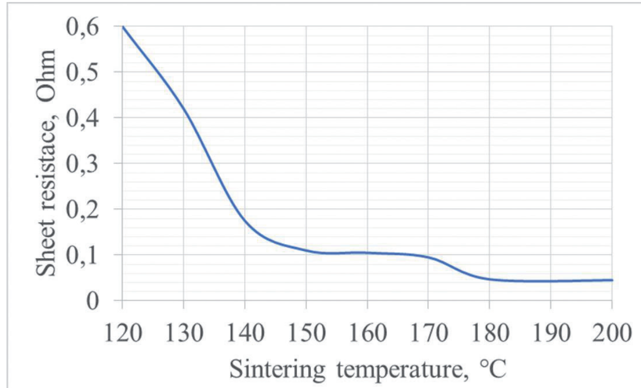

Fig. 6. *Surface resistance of silver films annealed at different temperatures.*

Fig. 6 describes the effect of sintering temperature on the surface resistance of the silver layer. There is a clear dependence of the resistance on the processing temperature. The higher the annealing temperature, the lower the resistance of the silver element. When films are sintered at 180ºC and higher, the resistivity values differ little from each other.

Cured silver films annealed at 130°C, 150°C and 180°C were examined by SEM to study morphology and structure at the micro/nano scale. At the micro level, the surface of the films (**Fig. 7***a,b*), regardless of the annealing temperature, has an integral relief structure (multiple branched folds are found). The width and height of the folded formations lies in the range of 1-2.5 microns. The microphotographs

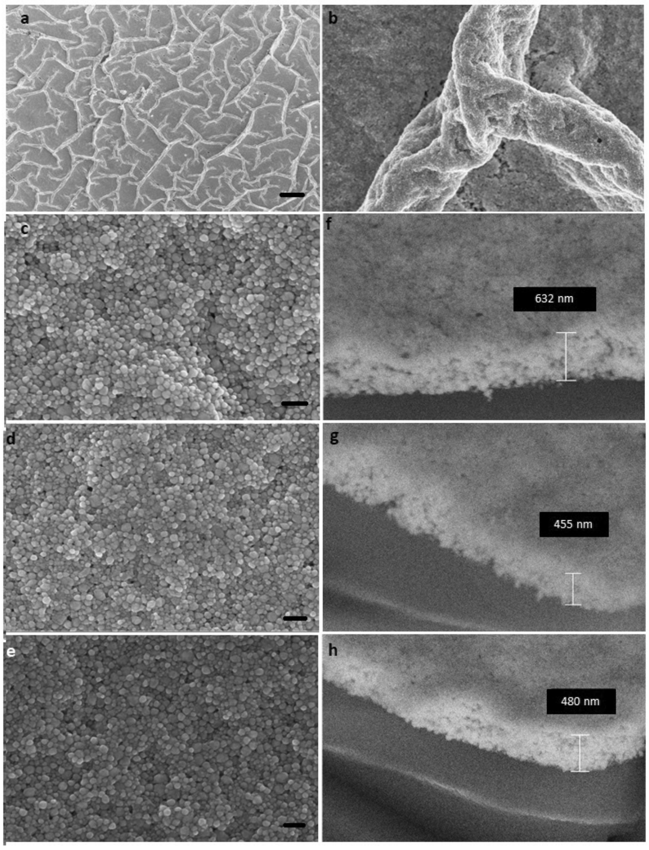

Fig. 7. *SEM images: a – surfaces of the hardened silver film on a microscale (reference 20 μm), b – folds; the surface of films on the nanoscale (reference 200 nm) annealed at different temperatures: c – 130°C, d – 150°C, e – 180°C; thickness of films annealed at f – 130°C, g – 150°C, h – 180°C.*

obtained at a higher resolution show that the structure of the silver films is formed by spherical nanoparticles (Fig. 7*c-e*), which are closely adjacent to each other. Their formation is due to the processes of nucleation and growth. The silver amino complex under the action of temperature (above 100°C) decomposes into ultra-small silver nuclei AgO, which, colliding with each other, form closely bound nanoparticles. These interconnected nanostructures provide many continuous channels for electron transport, which helps to reduce the resistance of the silver layer. Films have compact packing not only on the surface, but also in volume. The average height of the smooth sections of films annealed at 130°C is 650 nm, at 150°C and 180°C its value does not exceed 500 nm (Fig. 7*f-h*).

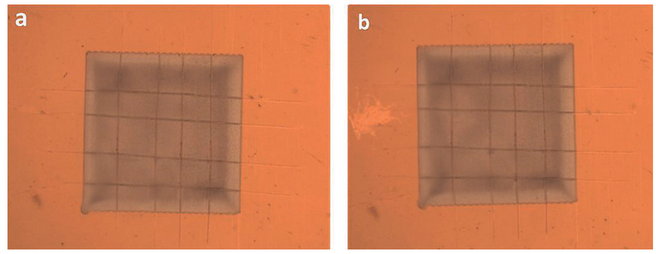

Fig. 8. *Photos of silver films: a – before and b – after tearing off the adhesive tape.*

Taking into account the geometric parameters, the electrical resistivity of the silver printed elements was calculated. The obtained values allow us to conclude that the annealed printed structures are characterized by low values of resistivity. For films annealed at 130°C, 150°C and 180°C on PI they are 13 μOhm·cm, 8.5 μOhm·cm and 6.5 μOhm·cm, respectively.

On **Fig. 8** the results are showed of a test of thermoset films to determine the adhesion of silver to a polyimide film. After tearing off the adhesive tape, the edges of the cuts retained their previous appearance, the integrity of the film remained unchanged. This indicates that the silver structures annealed on polyimide have high adhesive properties, which correspond to the 5V scale.

The resulting organic ink retains long-term chemical stability for more than 1 month when stored at +25ºC and more than 6 months at +5-10ºC.

4. CONCLUSION

As a result of the study, a conductive organic ink based on a complex of silver-1,2-diaminopropane oxalate with a suitable rheology for inkjet printing was developed.

The carefully selected formula ensures the chemical resistance of the ink, which makes it easy to work with them at room temperature.

The successful choice of the complexing agent provided a decrease in the decomposition temperature of the silver precursor and the formation of a high-purity metal component at sufficiently low temperatures.

Silver oxalate-1,2-diaminopropane complex inks have potential as a low cost alternative to nanoparticle inks. They can provide high conductivity at low annealing temperatures (8.5 μOhm·cm at 150°C). The formula is particle free and has been shown to provide consistent inkjet printing.

Thus, the developed silver ink is an inexpensive and promising material for low-temperature fabrication of high-performance printed electronics.

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