

Conductive Inks for Inkjet Printing Based on Composition of Nanoparticles and Organic Silver Salt

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Abstract—In this article, conductive inks for inkjet printing with high content of silver nanoparticles with the addition of organic silver salt and polymer additives are developed and investigated. Silver nanoparticles are shown to be stably dispersed in a solvent and the presence of a silver salt and a polymeric surfactant ensures the viscosity necessary for printing. A print of test images is performed using a laboratory inkjet printer equipped with an industrial small-droplet printhead followed by annealing of printed patterns at 150–250°C, and their structural and electrical properties are investigated. Simultaneous presence of polymer additives and silver salt is found to influence the structure of the forming conductive layer and the conducting properties.

Keywords: silver nanoparticles, organic silver salt, inkjet printing, printed electronics, conductive inks

DOI: 10.1134/S2075113315040243

INTRODUCTION

Lately, a lot of articles have dealt with the investigation and development of conductive inks for inkjet printing because of the active development of printed electronics [1]. Such metals as silver, copper, nickel, and aluminum serve as conductive elements of inks [2]. Development of conductive inks is a complex task, in which it is often necessary to take into account many contradicting factors. It is desirable that the inks be stable during storage and have low viscosity at high metal content [2]. To achieve this, stabilizers and surfactants should be used in the case of nanoparticles to prevent their aggregation and sedimentation in a solvent. In this case, when printing on thermal sensitive polymeric materials, it is desirable to perform curing of printed patterns at low temperatures or to use other post-treatment techniques in order to remove organic components and to form conductive layers [2, 3].

Today silver-based conductive inks are the most widespread owing to high conductivity and oxidative stability of silver [2, 4–14]. Mostly, the inks based on nanoparticles stabilized by different ligands, such as alkylamines, thiols, phosphorus-containing surfactants, and polymers [2, 4–7], are developed and investigated. Also, a large number of studies deal with the development of inks based on silver nanoparticles stabilized by carboxylic acids with different chain length [8–12] or on silver carboxylates [13, 14]. Unlike inks in which polymeric stabilizers are used, the annealing of nanoparticles modified with carboxylic acids and of

inks based on organic silver salt may be carried out at lower temperatures. According to some data, the inks based on nanoparticles coated with carboxylic acids are of low stability [13, 14]. As is noted in [8, 11, 12], the stability of dispersion increases with length of the methylene chain of carboxylic acid adsorbed on the surface of a silver particle. However, the use of the long-chain carboxylic acids leads to the increase in temperatures and curing times. The problem of the low stability of the dispersion of nanoparticles is solved by using inks based on the organic silver salt dissolved in a suitable solvent [13, 14]. However, as compared with the inks based on nanoparticles, when the inks based on silver carboxylates are used, there should be more printing passes owing to the lower concentration of silver in them. This leads to high complexity when printing thin elements.

In this article, for increasing of the stability of the inks and adhesion to the polyimide substrate, the combining in one composition of nanoparticles with organic silver salt with the addition of polymer additives has been investigated. An attempt has been made to combine the advantages which both nanoparticles and silver salt have when taken separately. A print of test images has been performed using a laboratory inkjet printer followed by the curing of printed patterns at 150–250°C, and their structural and electrical properties have been investigated in order to establish the dependence of the electrical conductivity on the print-

ing modes and thermal treatment, as well as to establish the influence of polymer additives.

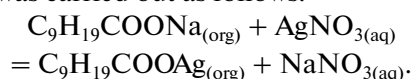
EXPERIMENTAL

Preparation of Nanoparticles and Organic Silver Salt

Silver nitrate of reagent grade (GOST 1277-75), nitric acid of special purity grade 27-5 (GOST 11125-85), sodium hydroxide of special purity grade 18-3 (OST 6-01-302-74), caprylic acid of high-purity grade (TS 6-09-529-75), neodecanoic acid $C_9H_{19}COOH$ (Versatic 10) with the mass fraction of the base substance more than 99%, ethylene glycol of analytical grade (GOST 10164-75), toluene of analytical grade (GOST 5789-78), isopropanol of analytical grade, and butyl glycol acetate of analytical grade were used in the experiments.

Silver caprylate was obtained in the exchange reaction between caprylic acid sodium salt and aqueous solution of silver nitrate. The synthesis of nanoparticles was carried out by heating of silver caprylate in ethylene glycol at 130°C. The procedures of the synthesis of silver caprylate and its reduction with the formation of silver nanoparticles were described by us in detail earlier in [15].

The solution of the organic silver salt (silver neodecanoate) was prepared according to the procedure described below. First, 380 mL of distilled water, 34 mL of sodium hydroxide, 180 mL of toluene, and 125 mL of neo-decanoic acid were loaded sequentially while stirring into a glass reactor with the volume of 2 L equipped with a stirrer made of stainless steel and bottom discharge. Then, 300 mL of previously prepared aqueous solution containing 110 g of silver nitrate were gradually added for 20 min to the sodium neodecanoate $C_9H_{19}COONa$ solution obtained. The mixture obtained was stirred for 1 h and the exchange reaction was carried out as follows:



After the phase immiscibility, the bottom silver-containing organic phase of silver neodecanoate with silver concentration of 240 g/L was poured through the bottom discharge.

Preparation of Inks, Printing and Posttreatment Conditions

First, 6 g of 33.3% solution of a polymer of polyol nature (containing OH groups in its structure) in butyl glycol acetate, 32.7 g of butyl glycol acetate, then 3.6 g of silver neodecanoate solution, and 5.4 g of an anionic polymeric surfactant Disperbyk 111 were added to 71.5 g of powder of silver nanoparticles. For thorough homogenization of metallic silver, the dispersion of the suspension was performed using an IKA T-25 homogenizer for 1 h at a rate of 5000 rpm followed by ultrasonication in a Sapfir ultrasonic bath for

1 h. Then the inks were filtered sequentially through a 1 μ m Minisart-GF syringe filter and 0.45 μ m NY-X Plus. The viscosities of the inks were measured using a Brookfield DV-II + Pro-CP viscometer in a cone/plate geometry with a CP40 measuring cone at 25°C and 100 s⁻¹. The surface tensions of the inks were measured using a LAUDA TD1C tensiometer by the anchor-ring method at 25°C.

Printing of conductive elements was carried out on DuPont Kapton[®] polyimide film with the thickness of 40 μ m. The printing was performed on a Neo Skat laboratory tablet printer equipped with a temperature-controlled printing table, vacuum clamp of material, and Konica Minolta 512 SHX small-droplet printhead (drop volume 4 pL, thermoregulation). The printing was performed at the printhead temperature of 25°C, the voltage of 14 V, the printing speed of 1000 Hz, and heating of the printing field up to 50°C. Printing was performed with different resolutions containing different amounts of the inks: 360 \times 720 dpi (dpi is the number of dots per inch in printing; 360 \times 720 dpi was achieved after two printing passes), and 360 \times 1440 dpi (four printing passes).

Drying and curing of the samples after printing were carried out at temperatures of 80–250°C in a ShS-80-01 drying box (OAO Smolenskoe SKTB SPU) with automatic control and maintenance of temperature. The resistance was measured using an Aktakom AVM-4403 digital multimeter. For the samples obtained under the same conditions (the printing mode, the curing mode), the resistance measurements were averaged over ten samples.

Examination of the samples by transmission electron microscopy (TEM) was performed on a JEM-2010 electron microscope (JEOL, Japan) operating at 200 kV and having a resolution of 0.14 nm. Examination of the samples by scanning electron microscopy (SEM) was performed using a Hitachi 3400 N scanning electron microscope (Hitachi Ltd., Japan).

RESULTS AND DISCUSSION

Preparation of Silver Nanopowder

We chose caprylic acid as a stabilizer. Silver nanoparticles coated with caprylic acid are well dispersed in organic solvents according to some data [12], the temperature of its removal from the surface of the nanoparticles being notably lower than for the long-chain carboxylic acids like stearic one [11, 15].

The transmission electron micrograph of silver nanoparticles used for the preparation of the inks is shown in Fig. 1. One can see that the particles have a shape close to spherical. The average size of the particles calculated from micrographs containing more than 100 particles is 50 nm.

As follows from the results of X-ray and thermal analyses carried out by us earlier in [15], silver is in the metallic state, the oxide phase is not detected, and the

content of organic impurities does not exceed 2%, and they may be removed by heating at a temperature of about 200–250°C.

Preparation of Inks

In most studies, toluene or xylene was used as the solvent for the inks based on silver nanoparticles stabilized with carboxylic acids or organic silver salts [9, 10, 12–14]. We also made attempts to disperse the nanoparticles obtained in toluene, including the use of sonication and intense mixing on laboratory disperser at 5000–15000 rpm. However, it was found that the particles are not dispersed even at low concentrations of 1–2 wt %. The colloids obtained have a high viscosity, and within a few hours, a precipitate of aggregated nanoparticles is observed. The instability of the colloid was one of the reasons that toluene was not used as a solvent in this work.

Another problem why it is not desirable to use toluene and xylene for piezo inkjet printing by industrial printheads is their high volatility and low boiling points. At the evaporation of the solvent, a solid precipitate of silver nanoparticles is formed on the surface of the nozzle plate and in the nozzles, which leads to instability of printing and to the outage of the printhead. Therefore, butyl glycol acetate, which has a high boiling point and relatively low evaporation speed and is often used by different manufacturers in the production of inks, was chosen as the main solvent for the preparation of inks.

The dispersion of silver nanoparticles in butyl glycol acetate, as well as in toluene, had a high viscosity. In preparation of inks, the best result on reducing the viscosity (to 10–11 mPa s) was achieved when silver neodecanoate solution and dispersant Disperbyk-111 were simultaneously added to the dispersion of nanoparticles. It should be noted that the stability of the dispersion of nanosilver was observed only when they were present simultaneously. The nature of this effect is not yet clear, and more detailed investigations should be carried out to clarify it. Presumably, a new polymer ionic structure is formed as a result of the exchange processes between these two components, which stabilize silver nanoparticles (simultaneous steric and electrostatic stabilization takes place). When the content of silver nanoparticles was 60 wt %, the inks obtained had a low viscosity of 11.0 mPa s and surface tension of 23.6 mN/m. The obtained values of these parameters fit well within the ranges recommended by manufacturers of this type of printheads for inkjet printing.

To improve the adhesion of the inks to the polymeric substrate, different polymers are introduced into the formula of inks [16]. To increase the adhesion of the inks to the polymeric films, a polymer of polyol nature, which is recommended for use in printing paints in order to improve the adhesion of inks to a wide range of polymeric materials, was chosen in this

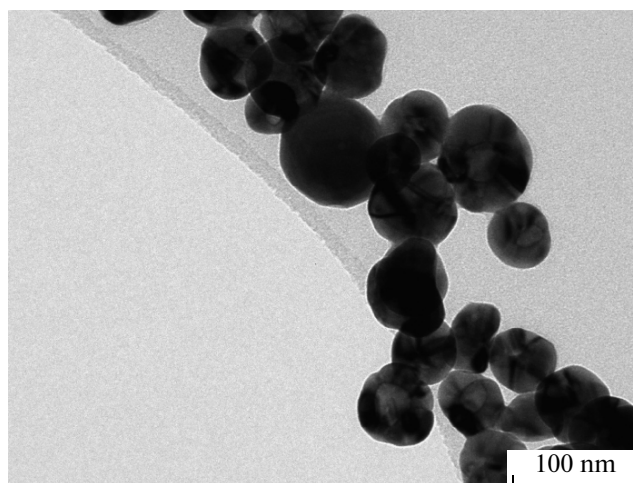


Fig. 1. Transmission electron micrograph of silver nanoparticles obtained by reduction of silver caprylate with ethylene glycol.

study. So, even when 2 wt % of this polymer were added to the formula, the adhesion to polyimide films after the heat treatment significantly increased, and without this additive, a metalized layer was easily removed from the surface during the test with adhesive tape, which was stuck to the surface and then removed.

Printing, Posttreatment, and Study of Prints

The inks obtained were used for inkjet printing of conductive elements on polyimide. The test image represented a set of bands of different widths: from 100 μm to 5 mm (Fig. 2).

Micrographs of the printed film after printing with resolution of 360×720 dpi followed by drying at 80°C for 15 min to remove the solvent and curing for 30 min at temperatures of 150, 200, and 250°C are shown in Fig. 3. The structure of the layer is not visible owing to the presence of the organic constituent (see Fig. 3a), which begins to be removed during the thermal treatment at 150°C. After the curing at 150°C, the nanoparticles forming the layer with sizes close to the initial sizes in the ink are seen (see Fig. 3b). Coalescence of the particles is observed after the thermal treatment at 200°C (see Fig. 3c). Here, it is seen that the structure of the layer is heterogeneous, and there are denser (see Fig. 3c, lighter areas) and less dense regions with smaller thickness of the layer. At 250°C, a further enlargement of the particles takes place, and a structure consisting of islands formed by large particles with the size of 0.5–1.5 μm surrounded by regions of smaller particles with the size of 50–150 nm (see Fig. 3d) is observed. It is also seen that the voids between the islands made of large particles are filled with smaller particles. Comparison with the micrographs of the structures of the layers given in a number of articles at

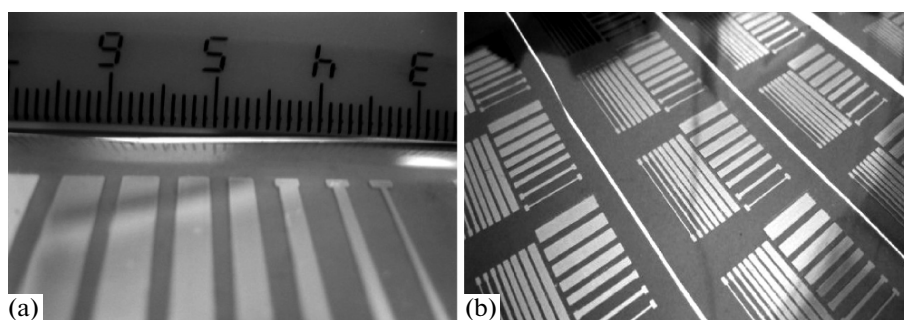


Fig. 2. (a) Test image printed on polyimide film by conductive ink with resolution of 360×1440 dpi containing nanoparticles and organic silver salt; (b) plain image of series of prints.

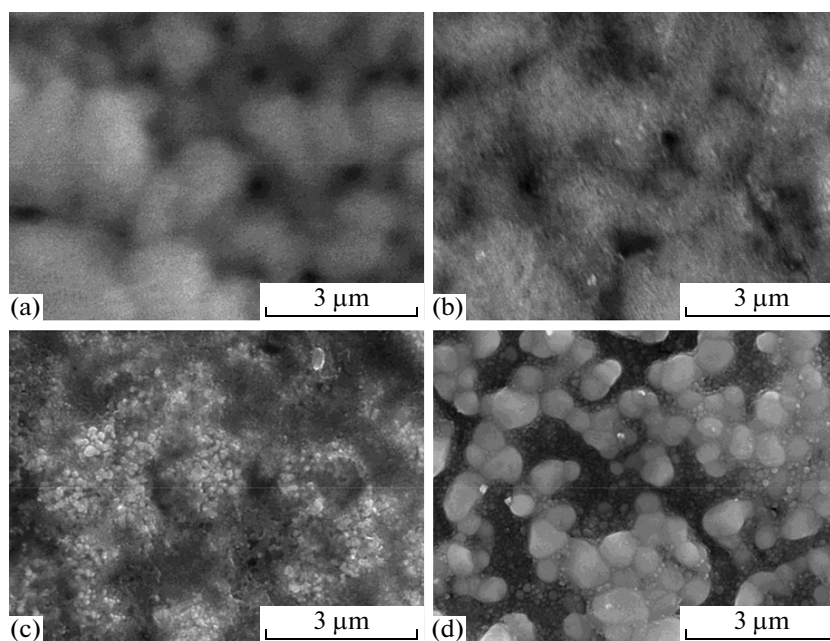


Fig. 3. Micrographs of printed film after printing with resolution of 360×720 dpi followed by (a) drying at 80°C for 15 min and thermal treatment for 30 min at (b) 150°C , (c) 200°C , and (d) 250°C .

the curing of printed patterns obtained by inks based only on nanoparticles or only on silver salt showed that a similar structure was not observed there [10, 12, 14], and distinct particles forming the layer were nearly the same size on the micrographs. The structure of layer obtained in this work is most likely due to the presence of both nanoparticles and silver salt in the inks. Apparently, the larger particles were formed as a result of the sintering of silver nanoparticles, which had already partially started at 200°C , and small particles were formed as a result of both sintering of silver nanoparticles and the decomposition of the organic silver salt.

In order to study the forming film depending on the print resolution, the printed patterns obtained at resolutions of 360×720 dpi and 360×1440 dpi after drying and annealing under the same conditions were compared. It was found that, when the resolution increases, both the compactness of the layer and the

layer thickness increase. The increase in the compactness of the layer is observed for the samples at all annealing temperatures studied; however, it is most noticeable for the samples after the thermal treatment at 250°C . Micrographs of the surface of the film obtained at different magnifications after printing with resolutions of 360×720 dpi and 360×1440 dpi followed by the thermal treatment at 250°C for 30 min are shown in Fig. 4. In the micrographs obtained with high magnification, it is seen (see Figs. 4a, 4b) that the layer after printing with the resolution of 360×1440 dpi is denser, the fraction of large particles is higher, and also the number of connections between them is higher; i.e., there are fewer isolated particles. In the plain micrographs obtained with smaller magnification, it is also seen that the film after the printing with the resolution of 360×1440 dpi is more continuous and homogeneous

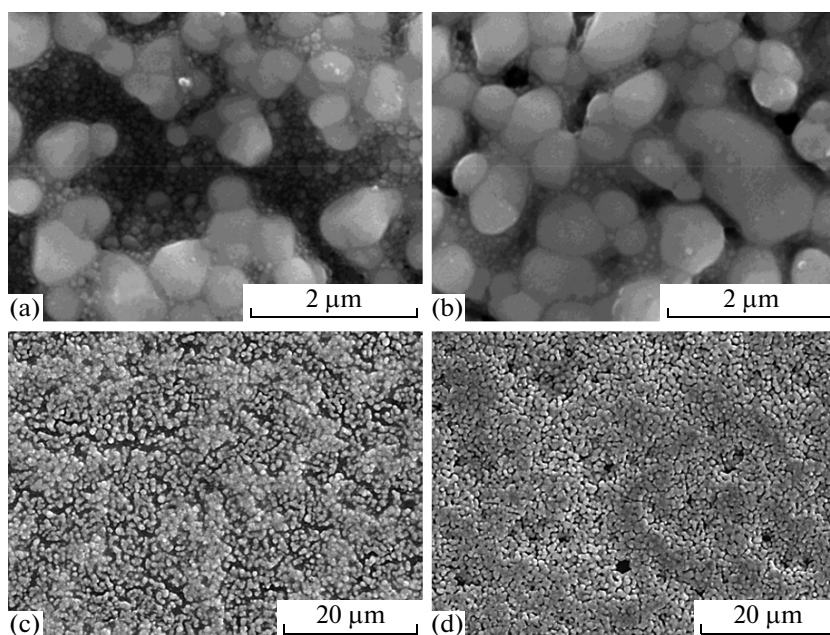


Fig. 4. Micrographs of surface of film after printing and annealing at 250°C for 30 min, (a, c) 360 × 720 dpi and (b, d) 360 × 1440 dpi.

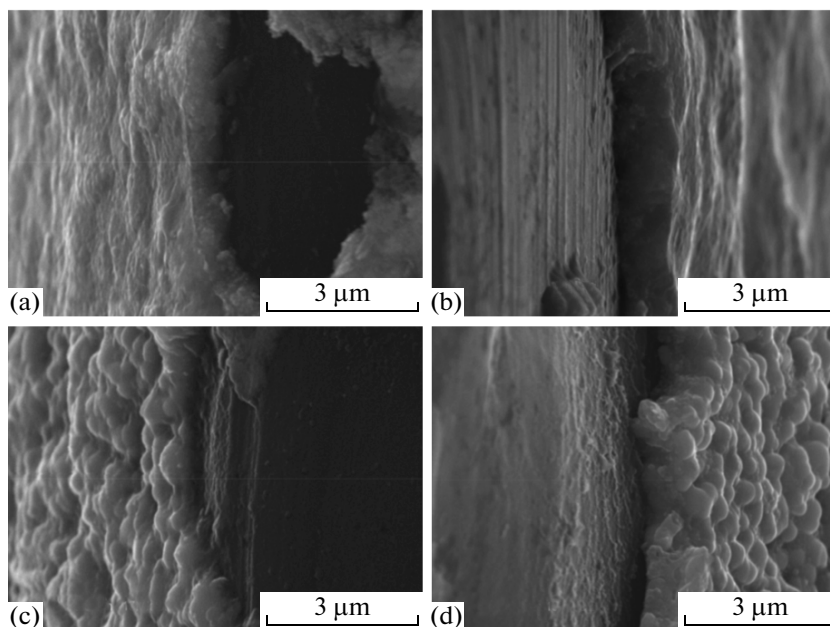


Fig. 5. Micrographs of cutoffs of layer after printing and annealing for 30 min at 200 and 250°C, (a, c) 360 × 720 dpi and (b, d) 360 × 1440 dpi, respectively.

in contrast to the film after the printing with lower resolution of 360 × 720 dpi (see Figs. 4c, 4d).

The thickness of the layers was measured using micrographs of the cutoffs for the samples obtained under the same conditions. When analyzing the micrographs of the cutoffs, the averaging of the values measured was carried out over several measuring

results (more than ten measurements of different parts of the cutoff). Examples of the cutoffs of layers after printing with resolution of 360 × 720 dpi and 360 × 1440 dpi followed by thermal treatment at 200 and 250°C for 30 min are shown in Fig. 5. It is seen that, after annealing at 200°C, the layers are represented by small particles in both cases (see Figs. 5a, 5b). The thickness of the layer after printing with resolution of

360 × 720 dpi is 0.7 μm, and the height difference is 0.2 μm. The thickness of the layer after printing with resolution of 360 × 1440 dpi is practically two times greater and is 1.2 μm, and the height difference is 0.3 μm. After the annealing at 250°C, the formation of large particles takes place. As is seen in Figs. 5c and 5d, the layer is represented by large particles surrounded by small particles. It is also seen that the surface roughness increases owing to the appearance of large particles in the layer. When the annealing temperature increases from 200 to 250°C, the compression of the layer and the decrease in its thickness are observed. Thus, the thickness of the layer after printing with a resolution of 360 × 720 dpi was 0.5 μm, and the height difference was 0.2 μm. The thickness of the layer after printing with a resolution of 360 × 1440 dpi was 1.0 μm, and the height difference was 0.4 μm. It is most likely that the decrease in the thickness of the layer observed is owing to the removal of the organic compounds and enlargement of the particles. In both cases, the layers look denser than in the case of the annealing of the printed patterns obtained as a result of the printing by inks based only on nanoparticles [2, 7, 12]. Similar layers were obtained in [16] in the case of printing by inks based on submicron particles with a polymer. The authors have drawn a conclusion that the dense layer is formed owing to the presence of the polymer, which when heated consolidates the particles. In our situation, the dense layer is apparently also formed owing to the presence of the polymer during annealing. During annealing, the compression of the polymer apparently takes place and because of this the convergence of silver particles takes place. However, in addition to this, it is possible that the presence of silver salt also leads to the formation of a denser layer since the salt partially fills the voids between the nanoparticles.

The electrical resistance of the films after printing with the resolution of 360 × 720 dpi and 360 × 1440 dpi followed by the thermal treatment at 150, 200, and 250°C was measured. The resistivity of the elements was calculated on the basis of the data on length, width, and thickness of the elements obtained using scanning electron microscopy and the results of measurements of resistance of the layer. The resistivity of the elements after annealing at 150°C appeared to be higher than 10000 μΩ cm (we did not succeed in the determination of the precise value). The resistivity of the elements after annealing at 200°C after printing with resolution of 360 × 720 dpi was 1638 μΩ cm, and after printing with resolution of 360 × 1440 dpi, it was 576 μΩ cm. These values are significantly higher than the values obtained for the layers formed individually of silver nanoparticles and of silver salt without additional polymer additives after thermal treatment under similar conditions [8–14]. Therefore, one can conclude that the main cause of high resistivity in our case is the presence along with the residues of caprylic and neodecanoic acids of the polymeric surfactant, which does not have time to decompose under these condi-

tions and hinders the sintering of the particles and the formation of the layer. At higher temperatures (>200°C), the decomposition and removal of the polymeric surfactant, residues of caprylic acid, and silver neodecanoate take place. The resistivity of the elements after annealing at 250°C falls sharply and is 24 μΩ cm after printing with resolution of 360 × 720 dpi and 4.7 μΩ cm after printing with resolution of 360 × 1440 dpi. It is seen that, at all annealing temperatures, the electrical resistance of the layer decreases with the increase in print resolution. On the basis of the analysis of the structures of the layers obtained after printing with different resolutions, one can conclude that the decrease in resistance is due to the increase in the compactness of the layer. The value of the resistivity obtained for the layer after printing with resolution of 360 × 1440 dpi and annealing at 250°C is comparable with or lower than that obtained under similar conditions for layers formed in printing by inks based only on silver nanoparticles or silver carboxylates [8–14]. A similar result was obtained in [16] in the case of printing by inks based on submicron particles with adhesive polymer after annealing at high temperatures (280°C, 1 h). In our situation, the low resistivity is due to the formation after annealing of a dense layer practically without voids consisting of large silver particles surrounded by small particles. Such a structure of the layer is formed owing to the presence of the adhesive polymer, which promotes agglomeration of the particles, as well as to the presence of silver salt, which partially fills the voids between nanoparticles.

CONCLUSIONS

In this study, conductive inkjet inks for inkjet printing with a high content of silver nanoparticles dispersed in butyl glycol acetate with the addition of an organic silver salt, polymeric surfactant, and polymer to improve adhesion to polyimide were developed and investigated. It was found that silver nanoparticles are stably dispersed in the solvent owing to the interaction between the organic silver salt and the polymeric surfactant, which also provides low viscosity (10–11 mPa s) necessary for inkjet printing. It was found that the presence of the polymeric surfactant hinders the formation of the conductive layer at temperatures below its decomposition temperature (approximately 220–250°C), which leads to a high electrical resistance of the layer. At annealing temperatures higher than the decomposition temperature of the polymeric surfactant, a dense layer with low electrical resistance is formed. Its formation is promoted by the adhesive polymer, as well as the silver salt, which forms contacts between nanoparticles and fills the voids between them.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 13-03-12157-ofi_m, and by the Ministry of Education and Science of the Russian Federation, project no. 16.578.2014/K.

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Translated by V. Kudrinskaya