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STABILITY PROPERTIES OF ELECTRICALLY CONDUCTIVE INK WITH NANOSIZE SILVER FOR INK-JET PRINTING TECHNOLOGY

The ink-jet is a noncontact technique for production very complicate electronic patterns like conducting points, lines and even 3D structures for electronic applications. There are two important components of the ink-jet printing technology: one is the printing system - the printer, and the other is the conductive material for printing - the ink. The greatest challenge is the ink formulation, because these inks have to meet strict physicochemical properties: viscosity, surface tension, adhesion to a substrate, etc. The most important is low viscosity and very homogeneous structure like molecular fluid with conductive nanosized particles [1]. This type of fluids must be stable for a long time to avoid sedimentation during printing process and to achieve optimal performance and reliability of the printing system and obtain the best printed pattern.

Stability parameter has been tested during long term of time and results are presented in the paper. In the first part of the paper the background of nanosilver production and its mechanism of stabilization in suspension are presented. The main part of the paper is devoted to viscosity measurement tests results and its influence for ink stability properties.

1. INTRODUCTION

Ink-jet printing is now widely used in many applications, such as fabrication of diodes, transistors and integrated circuits, conducting devices and many others. Its ability to deliver a precise amount of material in a quick, reproducible manner to predetermined locations under computer control is a desirable feature for such applications in electronic industry. Therefore the development of ink-jet printing technology grad-

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ually replaces the traditional etching and lithography technology due to their high cost, time-consuming and less environmental-friendly.

The critical issue that needs to be addressed when using the ink-jet printing to many applications is ink development. Inks must be formulated to fit the physical and rheological requirements of fluid flow during the printing process, with viscosity being the key factor. Additionally, slight variations in fluid properties must be compensated by adjusting printer driving settings to ensure printing reliability [2].

Low viscosity and very homogenous structure similar to „true fluid" are two the most important properties of inks for printing. Size, dispersion and stability of metallic nanoparticles are very crucial for the conductive ink system, because the nozzle of the printer would be clogged with larger particles due to their aggregation. To prevent agglomeration, precipitation and to obtain stable silver nanodispersions, number of special kind of protective substances must be added. This material covers the silver surface via physical and chemical bonding and creates a protective coating, which inhibits contact particle to particle and thus the agglomeration of the powder. So for the preparation of a concentrated silver suspension, which can be used as ink-jet ink, the crucial point is the selection of effective protective coating. It is necessary for keeping uniform and stable ink parameters [3]. In general, the protective layer can stabilize nanoparticles in a colloid by electrostatic or/and steric stabilization.

In the article we focus on the preparation of stable concentrated ink containing 20 and 30 wt.% silver with polymeric protective containing.

2. SILVER NANOPARTICLES FOR PRINTING CONDUCTIVE PATTERNS

2.1. SYNTHESIS OF SILVER NANOPARTICLES

There are several synthesis methods for the preparation of silver nanoparticles. The processing of nanosized silver particles can be briefly classified into several regimes: chemical reduction of silver ions in the presence of stabilizing agents [4-7], thermal decomposition [8,9], photoreduction [10,11], ultrasonic, laser ablation process [4], electrochemical process [8] and others.

Chemical reduction is the most frequently applied method for the preparation of nanosilver as stable, colloidal dispersions in water or organic solvents. Moreover, nanoparticles with different shapes can be easily prepared by controlling the reaction conditions. However, upon formation in powder form, the resulting particles tend to aggregate to form large particles [12,13]. Thus, the most important key in this method is to avoid the agglomeration of silver nanoparticles during the synthesis. The choice of the protective material rounded each silver particle is very critical because it determines the stability, solubility, reactivity, and even the size and shape of the nanoparticles. Protection layer is built during nano-Ag production process and is the most important key to avoid the agglomeration of these synthesized nanoparticles [13].

The present study reports the nanosized silver by a simple reduction of silver salt

using reducing agent and stabilizing polymeric agent also known as protective coating.

2.2. STABILIZATION OF SILVER NANOPARTICLES

When particles are of very small sizes - in range of several nanometers - the van der Waals forces and Brownian motion have great influence, while gravitational forces are not too important. Van der Waals forces are very weak and their range is very limited, however, Brownian motion makes nanoparticles collide and then, as a result of action of van der Waals forces, aggregates can be formed.

Thus, one of important functions of protective coatings is to prevent aggregation of metal nanoparticles, and this function is usually classified in two categories: electro-static (charged) or/and steric (polymer) stabilization.

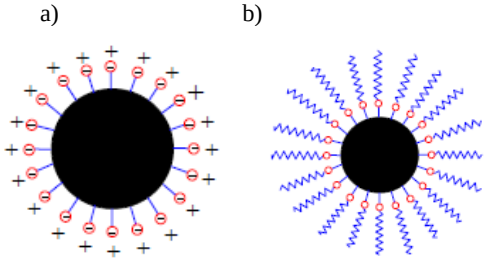

Fig. 1. Electrostatic (charged) (a), steric (polymer) (b) stabilization by same protective coating [14]

This method by which ions are attached to the silver particles to create a unified charge is called electrostatic stabilization. This charge around particles is known as a zeta (ζ) potential, measured in milivolts [3]. Zeta potential strictly depends on the pH of nanoparticle environment. According to S. Magdassi's study, the most stable AgNPs colloids have negative potentials (-33 mV) at a pH range of 6-8. Tests were made both for non-stabilized silver particles and those stabilized with sodium citrate [16]. Around these charged particle an electrical double layer is formed (Fig. 2).

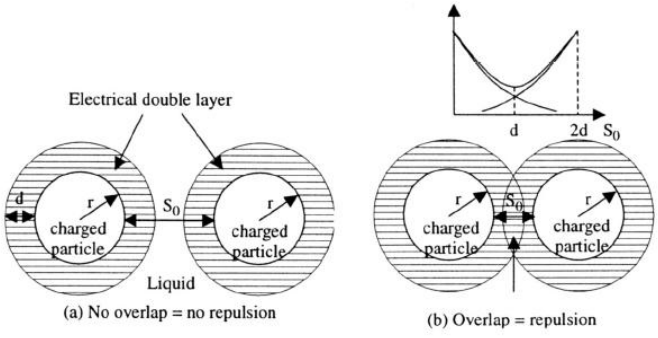

Fig. 2. Mechanism of electrostatic stabilization [17]

The examples of electrostatic stabilizers are the compounds containing such functional groups as: sulfo, carboxyl and amino, including citrates, SDS (sodium dodecyl sulfate), amines, amides, saccharides, fatty acids, surface active agents, as well as many others.

The method by which a polymer is attached to the silver particles in medium is called steric stabilization. One end of such a polymer can attach to the silver particles in suspension, while the other end points away from the particle, resembling a tail [3].

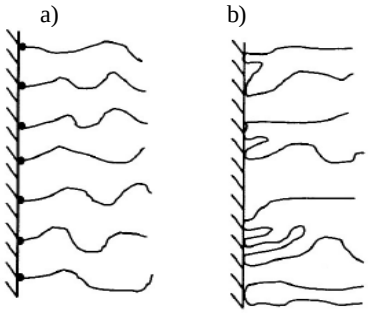

Fig. 3. Mechanism of steric stabilization; chemical attaching (a), physical adsorption (b) [16]

Polymer chains may be chemically attached to the surface of particle (Fig. 3a) or physically adsorbed on its surface (Fig. 3b). The mechanism of steric depends on the degree of coating the surface of particles with macroparticles, as well as on the type of solvent. Typical polymers used for protection against agglomeration include: polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG), poly(methacrylic acid) (PMAA), polymethylmethacrylate (PMMA), polyvinyl alcohol (PVA) and others.

In these two ways each particle is surrounded by protective layer. Since thanks to these coating molecules are not bind to each other, they will prevent the silver particles from agglomerating.

However, steric stabilization is used to stabilize colloidal suspensions more frequently than electrostatic, because:

- it is a more efficient stabilization, also in the case of very concentrated suspensions, e.g. inks with a concentration of conductive nanoparticles of 20-40%,
- it can be used for multi-component systems,
- is a thermodynamic method,
- the formed agglomerates can be split again into single nanoparticles.

While the use of electrostatic stabilization is limited because:

- it is effective only for diluted suspensions,
- it may not be applied in multi-component systems since different particles will produce different surface charges and different double layers,
- it is a kinetic method,
- if agglomerates are formed, it is practically impossible to split them.

Therefore for the further work to produce the stable conductive ink containing even 30 wt.% of silver, coated by polymer, was selected.

2.3. CHARACTERISATION OF SILVER NANOPARTICLES

Characterization of nanoparticles was important to understand and control stability of nanoparticles suspension by using the polymer coating. As is known that the protection layer is built during synthesis of nanosilver and kind of it depends from production materials and technology. For this purpose, the first step was to determine the content of this material on surface obtained nanosilver.

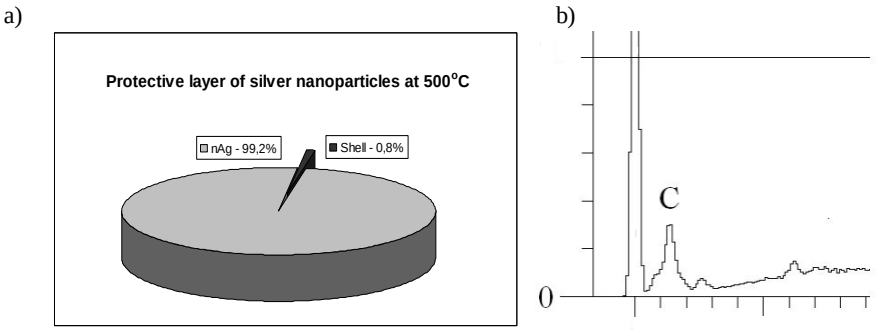

Fig. 4. Result of quantitative analysis for nanosilver with polymer coating (a) and fragment of EDX spectra indicated the carbon presence in the sample (b)

As is illustrated above, maximum protection layer can be about singles percentage of total nanosilver mass. In EDX studies (Energy Dispersive X-ray Spectroscopy), the polymer protective coating disclosed as a carbon which represents small part of the otal volume of the product (Fig. 4b), which confirms previous quantitative research.
The further characterization was performed using a variety of different techniques such as SEM (Scanning Electron Microscopy), Malvern Zetasizer and UV-Vis spectroscopy. These techniques are used for determination of different parameters such as particle size, their distribution (SEM and Malvern) and to confirm sample formation by showing the plasmon resonance (UV/Vis).

With respect to examination for basic parameters of prepared nanosilver, SEM and Malvern Zetasizer examinations were carried out in order to determine their morphology, shapes, dimensions and size distribution.

a) b)

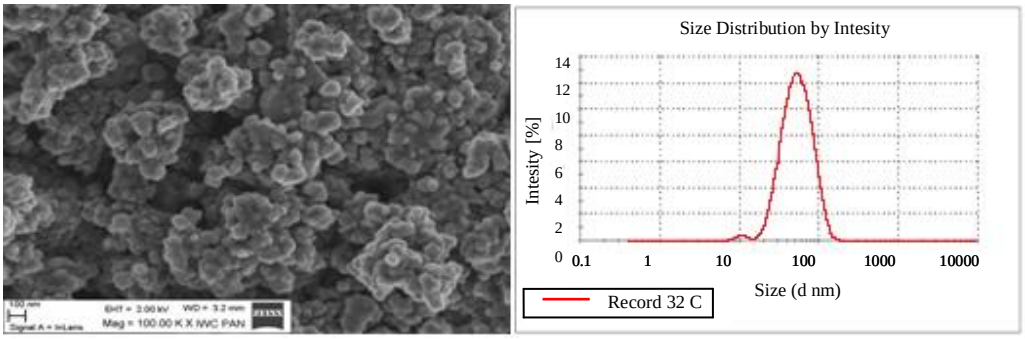

Fig. 5. SEM pictures (a) and distribution of nanosilver particles (b) [3]

Analysis of SEM image of patterns deposited on the substrate in a dry form, shows that the average size of the nanosilver covered by polymer material is 50-70 nm. The SEM-micrograph given in Fig. 5a reveals that these nanoparticles are quite uniform and have spherical shape [3].

For confirmation analysis of individual grains of nanosilver dimensions the more researches were carried out. Using Malvern Zetasizer allows to obtain images of the distributions of nanosilver particles. Exemplary obtained results were shown in Fig. 5b. In order to obtain presented graph of powder nanosilver grains, one needs to produce a preparation of significant dilution in the sample. The average diameters of tested grains of nanosilver is about 60 nm. The obtained results allowed for presenting them in this graphic form, while the intensity of occurrence of grains of the same diameter was expressed as percentage.

In order to examine the spectroscopic properties of nanosilver the UV/Vis analysis were carried.

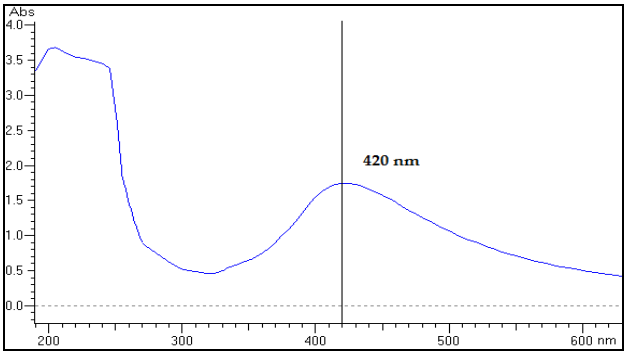

Fig. 6. UV/Vis spectra of nanosilver

The UV-vis absorption spectrum of silver nanoparticles with polymeric coating in ink medium exhibits the intense characteristic surface plasmon band located at 420 nm (Fig. 6). This peak maximum in absorption spectrum must be attributed to synthesized of silver atom Ag(0) from ion Ag+. The optical properties of a metallic nanoparticle depend mainly on its surface plasmon resonance, where the plasmon resonant refers to the collective oscillation of the free electrons within the metallic nanoparticle. It is well known that the plasmon resonant peaks and line widths are sensitive to the size and shape and surface of the nanoparticle, the metallic species and the surrounding medium [15].

3. CONDUCTIVE INK COMPOSITION

3.1. PREPARATION AND PROPERTIES OF INK-BASED SILVER NANOPARTICLES

Connected with our R&D work, a conductive ink was based on obtained Ag nanoparticles with polymer coating, using solvents mainly composed of ethanol and ethylene glycol, which are currently used in commercial ink. This composition is expected to be environmentally friendly. The base properties of produced ink formulation are presented in Table 1.

Table 1. Ink specifications

Number of components	One
Consistency	Very low viscous ink
Color	Dark green to gray
Percentage of silver filler [wt.%]	20-30
Viscosity [mPas]	5-6.5
Thixotropy index (1/10)	~1.0
Surface tension value [mN/m]	~35
Recommended curing & sintering conditions in convection oven	150 °C-60 min.
Storage	2 months in room temperature (do not keep it in temp. below 5 °C)

In order to determine the stability properties of electrically conductive ink we prepared two compositions with different contents of nanosilver. Concentration of this filler in the solution was 20% for ink 1 and 30% for ink 2. Both of inks containing such a large percentage amount of metal nanoparticles have very low viscosity and properties of the solution with a uniform structure. As will be shown later these compositions were also stable at room temperature and did not exhibit any sedimentation symptom. Therefore the conductive ink described in this work can be useful for future applications the electronic industry.

3.2. INK-JET PRINTED CONDUCTIVE PATTERNS

Inks with properties given in Table 1 have very good dispensing properties, some of deposited test patterns are presented in Fig. 7.

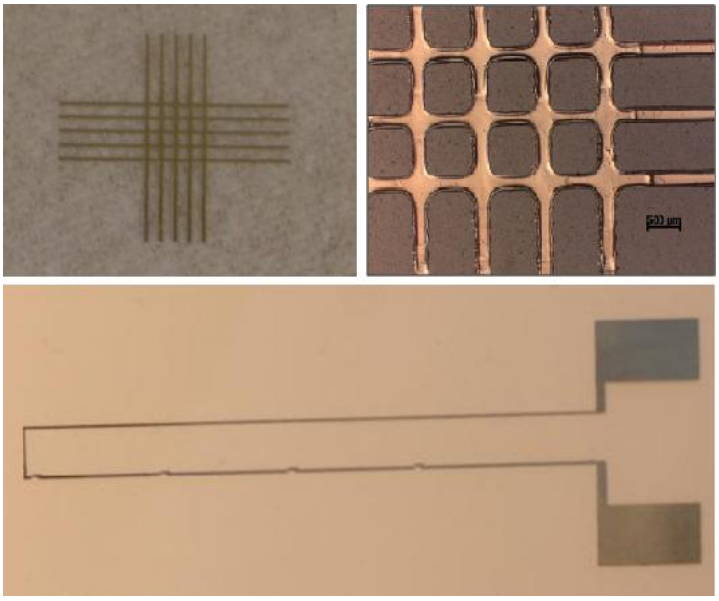

Fig. 7. Examples printout on the PE (polyethylene) foil using tested inks sintered at temperature 150 ˚C

4. STABILITY MEASURMENTS OF SILVER INK

4.1. VISCOSITY MEASURMENT RESULTS

In order to know more about the properties of such inks, the viscosity was measured during long period of time – two months. Viscosity of Ag suspensions was measured with a viscometer Brookfield type DV-II + Pro with 100 rpm rotor velocity (dynamic form measurement). The measuring temperature was maintained at 25±0.1 °C by a Brookfield TC 500 temperature controller.

For tests purpose, two sets of inks we have prepared with initial parameters of inks were introduced in Table 2:

Table 2. Initial properties of tested inks

Sample	Ink 1	Ink 2
Percentage of nAg [wt.%]	20	30
Initial viscosity [mPas]	5.81	6.08
Thixotropy index	~1.0	~1.0

All studied inks are kept at room temperature (about 22 °C). The viscosity measurement was made in two months every week. Fig. 6 presents the results of viscosity measurements.

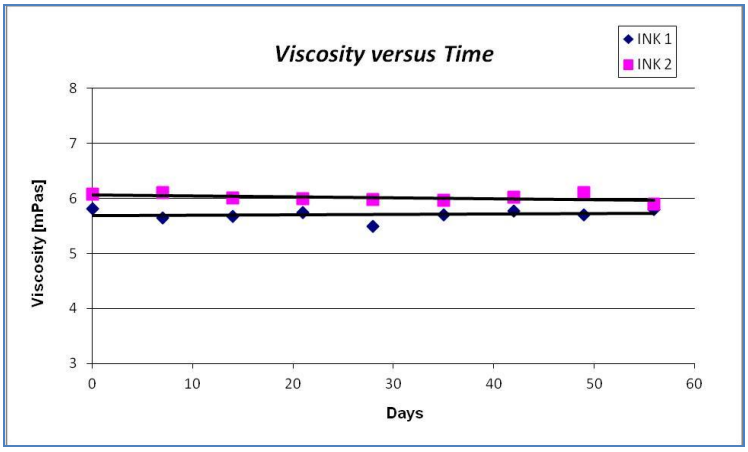

Fig. 8. Inks viscosity versus time

It was found that the viscosity of the tested silver inks is constant during two months. The viscosity value for ink 1 and ink 2 is very comparable in time and equal the initial viscosity. It increases only from the 5.7 (average value of viscosity for ink 1) to 6.02 mPas (average value of viscosity for ink 2) with the increase in concentration from 20 to 30%, respectively. Storage time till 60 days causes the viscosity value is still acceptable for ink-jet printing technology. We would like to add that the viscosity of the original inks for the commercially available printer (Microdrop Technologies GmbH) are in the range of 0.5-20 mPas.

4.2. TEST OF SEDIMENTATION PHENOMENON

The same time, for checking the stability of ink formulations, sedimentation tests were conducted. The main goal for these tests was checking percentage amount of silver filler inside formula as a function of time at storage room temperature (22 °C).

The sedimentation effect was studied for the same samples: ink 1 (20% nAg) and ink 2 (30% nAg).

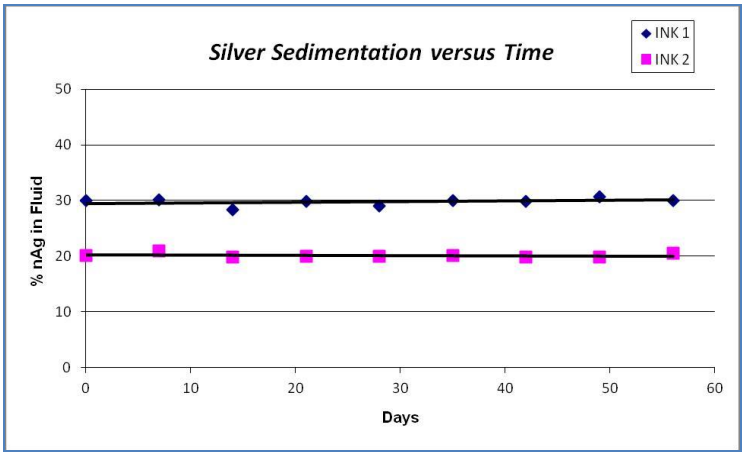

Fig. 9. Silver sedimentation versus time

This investigation showed (Fig. 9) that stored for 60 days of our inks are stable and suitable for ink-jet printing technology

5. CONCLUSION

The silver nanoparticles, even at a high concentration of 30 wt.% were dispersed efficiently in an ink medium. In this investigation, two physical properties of ink, viscosity and sedimentation phenomenon, were studied for determine the stability of these suspensions. The effectiveness of dispersion can be verified by measurement of particle size, viscosity, percentage amount of filler inside formulation and their thixotropical properties. Our experiment shows that Ag nanoparticles can be stable in formula very effectively in the presence of stabilizing agents. The field emission scanning micrograph of silver particle indicates the particle has a uniform size about 50-70 nm. It represents that the agglomerates were totally broken down by using the polymer coating which rounded each silver particle in production process. Studied suspensions containing 20 and 30% Ag nanoparticles show that their viscosity is constant during tested time. Silver filler with such nanosize of particle did not show also the phenomenon of sedimentation. It is essential for print head safe work and repeatability of printed structures.

We expect that inks containing nanosilver particles will find many applications as ink-jet inks in electrical industry, since they offer a system that behaves very stable before and during printing process. While after printing and sintering these inks will demonstrated highly uniform structure similar like in case of metal wire.

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