Research Status and Prospects of Particle-Free Silver Conductive Ink

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Abstract. Conductive inks are mainly used in the printed electronics industry. Particle-free conductive inks are prepared from organometallic compounds or complexes as precursors. They have the characteristics of preventing agglomeration and settling, not easily clogging the nozzles, and having a low heat treatment temperature, suitable for inkjet printing. Starting from precursors, the development statuses of conductive inks using silver acetate, silver citrate, silver neodecanoate, silver oxalate, silver tartrate, silver nitrate, and silver oxide as precursors were respectively introduced, summarized the main problems that existed, and put forward the outlook.

1. Introduction
With the continuous development of the information industry, printed electronics as an essential technical support for the information industry has also received more and more attention. As an important printing material in the printed electronics industry, conductive inks are widely used in RFID antennas, photovoltaic cells [1], flexible electronic devices, and wearable devices. Printing technology is essentially a process of depositing ink onto a substrate, and has attracted widespread attention due to its low cost, flexibility, and light weight. Compared with the traditional photolithography technology and screen printing, ink jet printing technology [2] has the characteristics of lower cost, high print resolution and good continuity, the substrate is not limited, and so is the preferred method for producing flexible electronic devices.

However, it is necessary to have a corresponding conductive ink for preparation by ink jet printing. Currently used conductive inks mainly consist of functional materials such as gold [3] conductive ink, silver [4] conductive ink, copper [5] conductive ink, and carbon [6] conductive ink. Among them, silver conductive ink is a mainstream in the prior art because of its high conductivity and good stability in the air. In recent years, due to the low price of copper, some copper conductive inks have also been researched and developed [7]. There are also some studies on conductive inks of other metal elements, such as tin conductive inks [8].

At present, the metal conductive ink is classified into particle-type conductive ink and particle-free conductive ink according to whether there is a direct function item in the ink. As the name suggests, particle-based conductive inks refer to the presence of conductive phases (ie, nano-metal particles) in the ink [9, 10]. Because these conductive inks are prone to agglomeration, they can easily clog the nozzle during inkjet printing and after printing. Film formation is not uniform. In order to improve the above situation, it is often necessary to add a lot of auxiliaries. The addition of these auxiliaries means a high post-treatment temperature. The high-temperature treatment is followed by the phenomenon that the
matrix is inappropriate and the conductive phase cracks and falls [11]. The non-particle conductive ink effectively avoids the above payment. Particle-free conductive inks are generally formulated with metal salts (oxides) as precursors, organic amines or ammonia as complexing agents, alcohols, organic acids as solvents and reducing agents, and studies have been made without direct preparation through complexation. For the ink, the precursor may be reduced to a metallic element by heating, light irradiation or the like at the time of use. This preparation method is simple, and the obtained ink has high stability, ink jet printing does not cause the phenomenon of clogging of the shower head, and the heat treatment temperature is low (mostly at 100 to 200°C).

Based on the above reasons, the choice of precursor is particularly important, first of all, the precursor must have sufficient stability at room temperature, so that the stability of the ink can be guaranteed; secondly, the reduction of the precursor must be simple, at a lower temperature, or add the simplest reducing agent to restore. The following describes the current status of the development of the current particle-free conductive ink according to the precursor.

2. Development status of non-particle silver conductive ink

2.1. Silver Acetate as a Precursor

Mohammad Vaseem [12] et al. used silver acetate as a precursor, and used ethylamine and ethanolamine as complexing agents and sintered at 150°C for 30 minutes results in a silver film having a uniform surface morphology and excellent adhesion, and the ink has high stability. To demonstrate the ink's performance, radio frequency inductance measurements were performed on the printed metal's conductivity, thickness, and roughness sensitivity. This is the first time that SOC inkjet printer inductors have demonstrated superior performance even at lower temperatures. This ink formulation has the potential for high-quality RF components to manufacture and print electronic products.

![Figure 1. Mechanism of reducing silver acetate by formic acid [13].](image)

U.S. Walker S. B. [13] et al. developed a particle-free conductive ink for reducing silver acetate with formic acid. In the research, an improved Duolun reagent was synthesized. First, silver acetate was dissolved in ammonia water, and formic acid was added dropwise to the system. After stirring and mixing, silver particles were generated at the bottom. After standing for 12h, the supernatant was taken as the desired conductive ink, wherein the silver content was 22wt. %. The silver ink has a viscosity of 2cP and is completely suitable for ink jet printing. Due to the reduction of formic acid, the decomposition temperature is greatly reduced. At 23°C, the conductivity of the ink was higher than $10^{-4}$ S•cm$^{-1}$ on the substrate. The silver film obtained by sintering at 90°C for 15 minutes had a resistivity of $1.6 \times 10^{-6}$ Ω•cm. The characteristics of low-temperature sintering make this ink suitable for various types of substrates, including flexible substrates such as paper and plastic.

Bhat, KS et al. [14] also used silver acetate as a precursor, using ethylamine and ammonia as complexing agents, formic acid as a reducing agent, and adding a mixture of ethanolamine and hydroxyethyl cellulose (HEC). In order to make it more spray able, a durable, particle-free, low-temperature sintered SOP ink is formed. Using PI and PET as substrates respectively, the ink was sprayed by a spin coating method and sintered at 90°C to obtain a silver film with good adhesion, high smoothness, and good electrical conductivity. The specific resistance was $1.98 \times 10^{-5}$ Ω•cm.
2.2. *Silver citrate as a precursor*

Yang Weidong [15] proposed a novel silver organic ink with a decomposition and self-reduction mechanism using silver citrate as a precursor (10wt% silver content). The ink was mixed with ethylenediamine as a complexing agent and sprayed on a polyimide substrate and then sintered at 155°C to obtain a uniformly conductive silver film with a resistivity of $7.94 \times 10^{-5} \Omega \text{cm}$. The activity of ethylene glycol and the potential chemical changes in the heating process are elucidated. At high temperatures, the ink undergoes simultaneous changes in the solvent composition and the decomposition/reduction of the silver complex. During the formation of the silver film, the use of decomposition and self-reduction mechanisms greatly reduce defects such as voids and cracks, as well as the coffee ring effect.

![Figure 2. Preparation of silver film by thermal reduction (a) and chemical reduction (b) [16].](image)

Yuan Gu [16] et al. compared two main methods (thermal decomposition of silver-containing organic salts and chemical reduction of silver salts). Using silver citrate as a precursor, ammonia as a complexing agent, propanol and hydroxymethyl cellulose as a solvent, and DMF as a reducing agent, inks containing a reducing agent and a reducing agent were prepared, respectively. SEM images show that the chemical reduction can make the silver film denser than thermal decomposition, and the porosity is low. This phenomenon may be due to volumetric shrinkage of the silver precursor decomposition after thermal sintering. Due to the low porosity, the resistivity of the silver film produced by the chemical reduction is also lower than that of the thermally decomposed silver film. At the same time, polymer additives make the silver film more uniform and easier to sinter. The resistivity was $6.6 \times 10^{-6} \Omega \text{cm}$ when the reducing agent was added to the ink for sintering at 160°C for 30 minutes. The study showed that the elemental silver can be reduced at 95°C. The decomposition of the additive was achieved by heating to 160°C. Volatilization temperature, that is, if the low boiling point and decomposition temperature of the additive is selected, the firing temperature of the ink will be lower. The ink was left at room temperature for three days with no significant changes.

In the article [17], Nie Xiaolei from Tianjin University also introduced the use of silver citrate as a precursor, 1, 2-propanediamine as a complexing agent, and methanol-isopropanol as a solvent to form a non-particle conductive ink. This ink can be reduced at 135°C, which is much lower than the 185°C decomposition temperature of silver citrate. Reduction at 150°C for 60 minutes gave a conductive silver film having a resistivity of $1.78 \times 10^{-5} \Omega \text{cm}$. Also get a good adhesion.

In addition, Jin-ju Chen [18] used silver citrate as a precursor to develop a particle-free silver ink suitable for inkjet printing. The ink has long-term storage stability. The article successfully printed on a flexible polyimide sheet using a commercial printer, confirming its excellent printability. Subsequently, the printed ink was electrolessly plated with copper. The rapid growth of the copper layer confirmed its effective catalytic activity for subsequent electroless plating. The obtained copper layer had a dense, uniform, and well-crystallized structure. The resulting resistivity is only 1.67 times greater than bulk copper.
Wendong Yang [19] et al. used silver citrate as a precursor, ethylenediamine as a complexing agent, and ethylene glycol and propanol as mixed solvents to prepare an organic silver ink with self-reducibility and decomposability. The thermal properties of the ink were studied. The results showed that the best decomposition temperature was 155°C and the resistivity value was $7.94 \times 10^{-5}$ Ω.cm. Due to the use of a mixed solvent containing the active ingredient, defects such as voids, cracks, and coffee ring effects formed by film formation of the ink are effectively reduced or eliminated.

2.3. Silver neodecanoate as a precursor

\[
\begin{align*}
\text{R}_1 + \text{R}_2 + \text{R}_3 &= \text{C8} \\
\text{O}^+ &+ \text{H}_2 \text{O}^- + 2 \text{H}^+ &\rightarrow &\text{Ag}^0 + \text{R}_1 \text{O}^+ + \text{R}_2 \text{OH}^- + \text{R}_3 \\
\end{align*}
\]

**Figure 3.** Reaction of hydroquinone with silver neodecanoate [20].

Valeton et al. [20] used a method that allows the ink to be reduced to silver at room temperature. Using silver neodecanoate as a precursor, an aqueous solution of ethanol as a solvent, the ink is applied to the substrate by a spin coating method, and the ink is reduced by ultraviolet irradiation and a hydroquinone solution. This process takes less than a minute and is performed at room temperature, allowing the use of low glass transition temperature polymer substrates such as PET. The main principle is that the latent image of free silver atoms is formed by ultraviolet light irradiation (the ink will change from colorless to brown at this time). After irradiation, the sample is immersed in a solution of 40% hydroquinone, and the silver element can be reduced. The resulting silver pattern had a conductivity of 10% of bulk silver, reaching a magnitude of $10^{-6}$.

Arnold [21] introduced a simple formulation consisting of silver neodecanoate, ethyl cellulose and solvents (aromatics and esters) to achieve better performance than current inks. The addition of ethyl cellulose can increase the viscosity of the ink, thereby increasing the adhesion and reducing the decomposition temperature of the precursor. The silver trajectory obtained by the screen printing method is treated at 230°C to obtain a uniform silver film. Accordingly, the silver can be also reduced by irradiation with an ultraviolet lamp. The resulting sample has a strong mechanical stability when bent and folded, with a resistivity of the order of $10^{-4}$ or $10^{-5}$.

2.4. Silver oxalate as a precursor

Dong Yue [22] used silver oxalate as a precursor, ethylamine as a ligand, ethanol and ethylene glycol as solvents to synthesize a particle-free conductive ink, and printed a silver conductive pattern on a PI substrate. The ink contains 27.6wt % silver, and the deposited thin film is heat treated at different temperatures and time ranges, and then analyzed according to its micro-morphology and resistivity. The silver film was found to cure at 170°C for 30 minutes and the resistivity was $8.4 \times 10^{-8}$ Ω.cm. The pattern resistivity printed on a 150°C. cured PI substrate is only $8.6 \times 10^{-8}$ Ω.cm with good adhesion.
In view of the low stability of the ink, which cannot be stored for a long time, Zope [23] developed a solid ink. Using silver oxalate as a precursor and ethylenediamine as a complexing agent, a solid complex can be obtained. When used, the complex is dissolved in distilled water to obtain a particle-free conductive ink. A new hybrid heat-light curing method was proposed in this paper, which greatly improved the electrical properties and adhesion of the substrate. Finally, the resistivity of the silver film was $4.26 \times 10^{-8} \Omega \cdot m$.

2.5. Silver tartrate as a precursor

Li Xiaodong [24] prepared a particle-free conductive ink by using silver tartrate as a precursor, 1, 2-diaminopropane as a complexing agent, and ethanol as a solvent. Each of the different substrates was coated with ink and reduced at 130°C for 5 minutes. The synthesized powders, conductive inks, and films were analyzed and the results showed that the decomposition temperature of the ink was much lower than the decomposition temperature of the precursor. Silver films cured on different substrates showed different morphology and particle size. Among them, the lowest resistivity is $6.7 \times 10^{-6} \Omega \cdot cm$. Conductive ink was printed on the substrate using a commercial inkjet printer and cured at 130°C for 5 minutes, resulting in a silver line width of about 100μm, a smooth surface, and a dense microstructure.

Dong Yue [25] prepared highly conductive silver inks that can be cured at low temperatures by screening different organic amines. Using silver tartrate as the precursor and ethanol as the solvent, compared 4 types of monoamines and 2 kinds of diamines, it was found that the type of amine has a significant influence on the thermal decomposition temperature, electrical properties, and microstructure of the ink. By adding 1, 2-diaminopropane ink, a highly conductive silver film having good flexibility stability and good adhesion was prepared.

2.6. Silver nitrate conductive ink

In another document, Sureeporn Uttiya [26] used silver nitrate as a precursor, and made the ink by adding only a silver nitrate solution in deionized water and adding a commercial detergent as a surfactant. After the ink is ink jet printed on the substrate, it needs to be reduced in a hydrogen atmosphere containing 5% argon, the reduction temperature is 190-210°C, and the measured resistance value is $3 \times 10^{-5} \Omega \cdot cm$ after reduction for 15 minutes. The benefit of this type of ink is simple formulation, but the reduction temperature is high and the reduction environment is harsh.

Jung-Tang Wu [27] used silver nitrate as a precursor in the study. 1-Methylamino-2-propanol was added to silver nitrate, and a conductive silver wire was prepared by inkjet printing on a flexible PET substrate at a lower sintering temperature (100°C). Using a mixture of solvents (ethanol and ethylene glycol), the morphology of the pattern surface and the formation of the coffee ring can be controlled. Using inkjet printing technology, the resulting silver film resistivity was $1.37 \times 10^{-5} \Omega \cdot cm$.

Stephan F. Jahn [28] also uses silver nitrate as the precursor, triethylamine as the complexing agent, and 2-[2-(2-methoxyethoxy) ethoxy] acetic acid as the solvent, configured as a the particle-free
conductive ink was found to have a reduction temperature of 100-250°C. If it is desired to obtain better conductivity under low-temperature reduction, it requires a longer reduction time (reduction time in the text is 5 to 60 minutes). Piezoelectric ink jet printing printed ink on the substrate, the measured resistivity was $9 \times 10^{-6} \, \Omega \cdot \text{cm}$. The resulting pattern was subjected to a tape test to prove that the ink has excellent adhesion properties.

2.7. Silver oxide conductive ink

![Figure 5. Structure of organic silver complexes [29].](image)

Liu, Z. C. a. Z. [29] studied the method for preparing silver films by laser direct write organometallic inks using a 1071nm continuous-wave, yb-doped fiber laser beam. The ink used herein was prepared by reacting silver oxide with ammonium carbamate in methanol. At a power of 0.1W laser, the organometallic silver decomposes. The silver conductors prepared under a laser power of 0.5W have a resistivity value approximately four times that of bulk silver. The resulting silver film has good adhesion.

![Figure 6. Mechanism of DEA Reducing Ink [30].](image)

In a study by Shih-Pin Chen [30], a simple and effective ink formulation was developed that sinters at low temperatures to produce a highly conductive silver film. This article proposes to use a "latent" reducing agent that is stable at room temperature but slightly heated to form a reducing material. Diethanolamine (DEA) is an autoxidation compound that is mixed with a solution of silver ammonia to form a transparent and stable solution at a mild temperature. The prepared ink is sprayed on the substrate and heated. DEA is found to decompose to generate formaldehyde when it is higher than 50°C., and spontaneously reacts with silver ions to form a silver thin film. A good adhesion silver film was obtained after heating at 75°C for 20 minutes, and its resistivity reached $6 \times 10^{-6} \, \Omega \cdot \text{cm}$. The ink has good storage stability at low temperatures, and no significant changes have occurred at 5°C for 8 days.

3. Summary and Prospect of Particle-free Conductive Ink

Through the investigation of the above literature, it can be seen that the particle-free conductive ink is currently facing the following problems: First, the reduction temperature of the precursor is still high, a lot of energy is wasted, and it is not suitable for fragile paper or fabric; The conductivity of the resulting silver film fluctuates greatly, and there is still a large gap compared to bulk silver; due to the low temperature treatment, correspondingly to the silver film for the same performance, a longer recovery
time is required; The most important is the general storage stability. Since the ink contains reducing substances, the silver particles will precipitate and settle as the storage time increases.

With the development of printed electronics, there will be more and more methods and methods of printing, and for conductive inks, it will continue to develop along with low-cost, environment-friendly, high-conductivity and low-temperature heat treatment, and further realize Printed circuit manufacturing is intelligent, diversified and efficient.

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