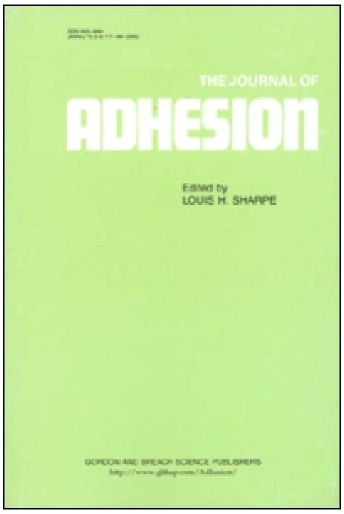

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Jana Kolbe[a]
[a] Fraunhofer-Institut fuer Fertigungstechnik und Angewandte Materialforschung, Bremen, Germany

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A Novel Electrically Conductive Adhesive for Use in Microelectronics and Microsystems by Ink Jet Technology

Jana Kolbe
Fraunhofer-Institut fuer Fertigungstechnik und Angewandte Materialforschung, Bremen, Germany

Ink jet is an accepted technology for dispensing small volumes of material (50–500 picolitres). Currently, traditional metal-filled conductive adhesives cannot be processed by ink jetting (owing to their relatively high viscosity and the size of filler material particles). The smallest droplet size achievable by traditional dispensing techniques is in the range of 150 μm, yielding proportionally larger adhesive dots on the substrate. Electrically conductive inks are available on the market with metal particles (gold or silver) <20 nm suspended in a solvent at 30–50 wt.%. After deposition, the solvent is eliminated and electrical conductivity is enabled by a high metal ratio in the residue. Some applications include a sintering step. These nano-filled inks do not offer an adhesive function. Work reported here presents materials with both functions, adhesive and conductive. This newly developed silver-filled adhesive has been applied successfully by piezo-ink jet and opens a new dimension in electrically conductive adhesives technology.

The present work demonstrates feasibility of an inkjettable, isotropically conductive adhesive in the form of a silver loaded resin with a two-step curing mechanism. In the first step, the adhesive is dispensed (jetted) and precured leaving a "dry" surface. The second step consists of assembly (wetting of the second part) and final curing.

Keywords: Electrically conductive adhesive; Ink jet application; Sedimentation; UV-curing

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Address correspondence to Jana Kolbe, IFAM, Weiner Strasse 12, D-28359 Bremen, Germany. E-mail: jk@ifam.fraunhofer.de

INTRODUCTION

Ink jet is a very versatile production method especially suited to product development and production up to intermediate lot sizes. The process involved is an application method for small volumes. The continuing trend towards miniaturization in microelectronics has been discussed by different authors with different point of views [1–3] and presents new challenges to adhesives technology with respect to the amount of adhesive to be applied. The current minimum droplet diameter attainable using standard dispensing technology is about 150 μm. This refers to the diameter of the droplet lying on the substrate. This depends on a number of factors such as the internal diameter of the needle and the surface tension of the adhesive and substrate. Under special boundary conditions, small diameters of 120 μm can also be realized—sometimes at the expense of the reproducibility of the droplet diameter. Regarding the dispensing, this is a contact application method. In contrast, there are also non-contact ink jet technologies. Non-contact application methods are advantageous if the substrate surface, onto which the adhesive has to be applied deviates from the two-dimensional plane.

Ink jet technology allows for glue dots down to $<30\,\mu m$ when used with non-filled adhesives. Numerous applications for this process are to be found in the assembly of components in surface mount technology (SMT). However, an inkjettable, conductive glue would also be of interest to the smart-label and radio frequency identification (RFID) industries.

So far there are no inkjettable, electrically conductive adhesives available. Commercially obtainable isotropically conductive adhesives (ICA) contain 70–80 wt.% silver flakes which provide the electrical conductivity. This high amount of filler is necessary in order to exceed the percolation threshold. Current ICAs cannot be applied by ink jet due to their high viscosity and relatively large silver particles.

Commercially available electrically conductive inks (Table 1) contain roughly 40–80 wt.% solvents, additives (e.g., dispersion stabilizers), and silver particles in the range of 10 nm. Solvents must be removed after deposition. In addition, some applications also require the silver particles to be sintered on the substrate at elevated temperatures in order to obtain the required electrical conductivity [4,5]. This can be achieved by heat treatment in an oven or by using a laser. Electrically conductive inks cannot be used as adhesives.

It was our goal to formulate an inkjettable, electrically conductive adhesive, to develop suitable silver particles, and optimize the ink jet for the use of such a highly filled adhesive.

TABLE 1 Electrically Conductive Inks Available in the Marketplace

Supplier	Product	Filler	Filler content wt.%	Viscosity mPa.s	Curing	Specific electrical resistance μΩ cm
ANP, Chungwon-kun, Korea	Goldjet DGH-(T)-50LT 25 C	Gold	49.62	2.8–3.0	30–60 min @ 250°C	Not available
	Silver Jet Inks DG******	Silver	45 to >50	8–12	30 min @ 150–300°C	26000–2.3
Cabot, Albuquerque, NM, USA	AG-IJ-G-100-S1	Silver	20	14.4	1–30 min @ 100–350°C	4–32
Harima, Kakogawa, Japan	NPS-J	Silver	57–62	5–10.0	60 min @ 210–220°C	3
	NPS-J-HTB	Silver	53–58	8–13.0	30–50 min @ 350–500°C	2–3
	NPS-G	Gold	46–52	5–10.0	60 min @ 230–250°C	7
Novacentrix, Austin, TX, USA	Metalon JS-011 Nanosilver Ink	Silver	20	1–5	100°C or using a xenon lamp: 300 microseconds	9.0–26

EXPERIMENTAL

The adhesive used is a resin of acrylate and methacylate monomers and initiators from the market. The composition is proprietary to IFAM.

The silver powder used in the formulation of the conductive adhesive was developed by Metalor Technologies SA (Neuchâtel, Switzerland). The chemical surface properties were fine-tuned to the adhesive's requirements by Metalor Technologies SA.

The shape of the particle, was monitored using a LEO 1530 Gemini electron microscope from Zeiss (Oberkochen, Germany).

The particle diameter was determined using a Coulter LS 130 particle size analyzer from Malvern Instruments (Worcestershire, England). The measurements were carried out in ethanol.

The rheological behaviour of the adhesive was determined with a Rheolyst AR 1000 from TA Instruments (New Castle, DE, USA) using parallel plates.

The contact resistance and the adhesive strength were determined from joints with SMD 1206 R100 from Conrad Elektronik (Hirschau, Germany). SMD 1206 is a resistance (actually, a varistor, 100 Ohm), SnPb terminated. The specific electrical resistance and the contact resistence were meassured with a Prema 6048 Integrating Digital Multimeter from Prema Präzisionselektronik GmbH (Mainz, Germany). The test structure for measuring the specific electrical resistance, the contact resistance, and the bond strength is shown in Fig. 1. The mesurement of the specific electrical resistance were carried out on an four-point measuring structure on an adhesive film of 30 μm thickness.

For measuring the bond strength the Bondtester 4000 from Dage (Aylesbury, England) was used. The measurements were carried out with 33.3 μm/s test speed.

All dosing (dispensing) experiments were carried out using Microdrop Technologies' microdosing system (Berlin, Germany). First, glass was used as substrate. Later we tested FR-4 (epoxy-glass) printed circuit boards (PCB), polyethylene terephthalate (PET film), and paper.

RESULTS AND DISCUSSION

Formulation of the Adhesive

Requirements on the Adhesive

Application *via* ink jet makes specific demands on the adhesive. The silver particles must not exceed a maximum size determined by the internal diameter of the nozzle used. The specifications defined a particle size of $\leq 5\,\mu m$. In these considerations it was assumed that the ratio of the particle diameter to the internal diameter of the nozzle

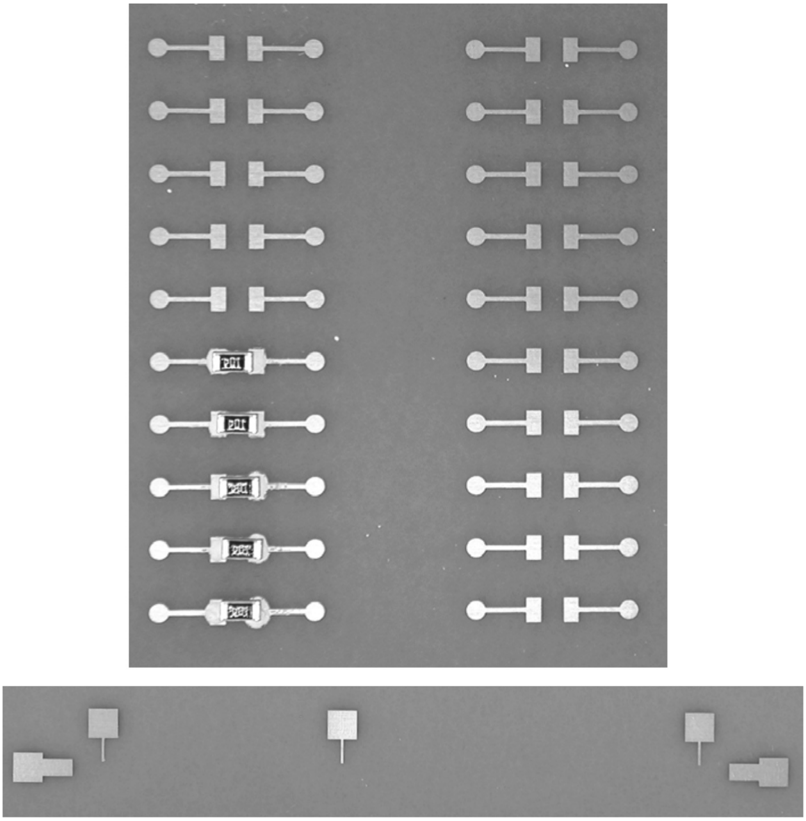

FIGURE 1 Test structure: above-copper pads on GRP (glass-fibre reinforced plastic) for measuring contact resistance and the bond strength: below—copper pads on GRP for measuring the specific electrical resistance.

may not exceed a critical value, so that the nozzle does not become blocked. The particle shape and the filler content also play an important role. The viscosity of the material should be $\leq$100 mPas in the handling temperature range. As adding the silver particles to the resin markedly increases the viscosity of the system, the unfilled resin must have a very low viscosity. At room temperature the adhesive should resist sedimentation for at least 8 hours, and preferably 24 hours. At the processing temperature, the system has to be stable to sedimentation for 1 hour.

A further requirement by the end user on the adhesive's properties was a two-stage curing mechanism. In the first curing step the adhesive surface is dried and remains meltable. In this state the product may be stored for several weeks. The second curing step involves

TABLE 2 Requirements for the Adhesive

Viscosity	≤100 mPas
Max. particle size	≤5 μm
Pot life at operating temperature	1 hour
Curing	1st step drying 2nd step thermal activation
Specific electrical resistance	10^{-4} Ωcm

gluing the components with the previously applied adhesive. By heating and applying pressure the adhesive is remelted and cured. Thus, the processing operation is similar to that required for soldering. A resistivity in the range of 10^{-4} Ωcm in the bulk material is called for. The first stage was implemented through UV-curing, the second stage *via* thermal curing (Table 2).

Filler

Figure 2 shows a scanning electron microscope image of the silver powder. It consists of spheroidal silver particles with a D_{10}-value of 4.2 μm, which means that 10% of the particles are larger than 4.2 μm. The D_{50}-value lies at 1.8 μm. Figure 3 shows the measurement results.

Two-step Curing Process

To enable the two-step curing process an acrylate-methacrylate-epoxy resin matrix was formulated and equipped with commercially

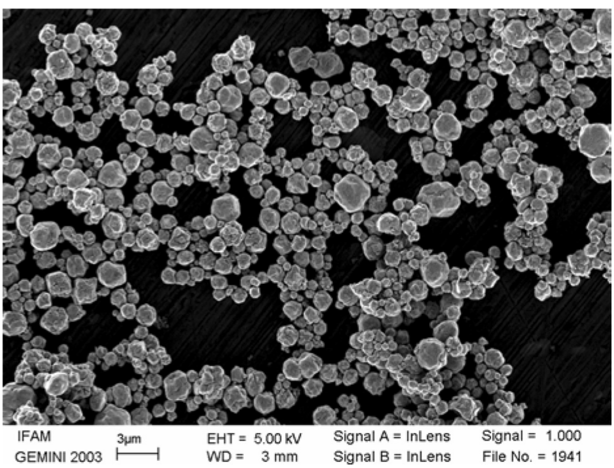

FIGURE 2 Scanning electron micrograph of the silver powder.

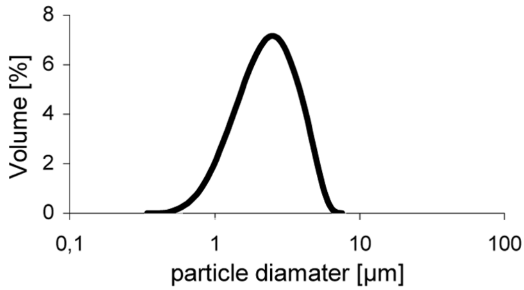

FIGURE 3 Particle diameter distribution of the silver powder.

available initiators for the UV and thermally activated reaction stages. In the first reaction stage, which is a UV induced polymerization, the double bonds of acrylate and methacrylate groups react to give a thermoplastic material with epoxy side groups (Fig. 4). In this state, the adhesive may be stored in a refrigerator for more than 4 weeks without losing its application-related properties. The UV curing process is a free radical reaction. Radical polymerizations are sensitive to oxygen. During the radical termination reaction, the simplest scenario involves two radicals recombining to form one molecule. An oxygen molecule possesses two free electrons and can also bond to the radicals that form. This reaction is considerably faster than the radical growth reaction, meaning that in the presence of oxygen the oxygen molecules become preferentially bonded to the radicals. The resulting peroxy radicals, in contrast, react slowly; compared with the radical growth reaction, the bonding of a monomer molecule is very slow. The mechanism of this inhibition by oxygen was first described by Schulz and Henrici [6]. That is why the UV curing step must be conducted in an oxygen free environment, for example in a nitrogen atmosphere.

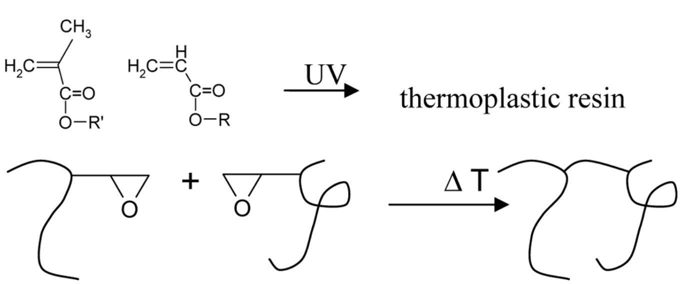

FIGURE 4 Two-step curing mechanism.

Although it is possible to carry out the UV curing process in the presence of oxygen, the UV reaction needs more time and the resulting polymer will no longer be thermoplastic as initial cross-links will have formed. It is to be expected that oxygen not only inhibits the polymerization but also results in an increased number of radical transfer reactions to polymer chains. These disrupt the wetting of the second component during thermal activation in the second curing stage and hamper adhesion.

UV curing the highly filled conductive adhesive was challenging, as parts of the matrix were hidden behind silver particles and, therefore, only received very little UV radiation *via* reflection from other particles. In order to achieve an acceptable level of conductivity, a filler percentage of 70wt.% was used.

In the second curing step, a heated stamp is used to position the component on the pre-applied adhesive at a temperature of 180°C and a pressure of 2 MPa for 10 seconds. Afterwards, the adhesive is post cured in an oven at an elevated temperature (*e.g.*, 130°C for 30 min).

Sedimentation Problems

One focus of attention was the reduction of sedimentation. Sedimentation causes problems during the application of the adhesive. Ink jet technology only applies the most minute amounts of adhesive. Most of the adhesive is stored in a small container from which a small amount is continually dispensed to the dosing apparatus. Sedimentation leads to a gradient of filler material in the storage container, accumulating in the lower and depleting in the upper region of the container. The adhesive is taken from the lower end of the storage container. A significant accumulation of silver particles may clog the dosing system. By applying the adhesive depleted of silver particles, the electrical conductivity of the cured resin is reduced. In addition, sedimentation may lead to the formation of filler particle agglomerates.

The rate of sedimentation of spheroidal particles is given by the Stokes equation [7]:

$$\left(\frac{ds}{dt}\right) = \frac{2r^2 g \Delta\rho}{9\eta},$$

where ds/dt-rate of sedimentation of spheroidal particles, r-radius of the particles, $\Delta\rho$-density difference between the resin and particles, g-gravitational constant, and-η-viscosity.

Formula 1—Stokes Equation

Factors which influence the rate of sedimentation are the density difference between the particles and medium the viscosity of the medium, and the particle radius.

Silver has a density of 10.5 g/cm^3, whilst the density of the resin is ca. 1 g/cm^3. This means that the particles exhibit a strong tendency to sediment. Decreasing the particle size and increasing the viscosity of the resin lead to lower rates of sedimentation. As the ink jet process requires a low viscosity, it cannot be adjusted at random. The viscosity of the formulated resin matrix is 3 mPas. It exhibits Newtonian flow characteristics. Particle size not only affects sedimentation rate but also the viscosity of the adhesive itself. If the particles are too small (1<μm), they will increase the adhesive's viscosity and it may no longer be possible to apply the adhesive using the ink jet process.

Pure silver is a ductile metal with highly reactive surfaces. In order to prevent the silver particles from sintering they receive a protective coating during production. If embedded in a resin, however, they may still agglomerate or even aggregate, a risk that grows with increasing sedimentation. This increases particle size which may lead to clogging of the dosing nozzle during application of the adhesive.

An adhesive less prone to sedimentation was formulated using suitable (proprietary) additives. Furthermore, the formation of filler agglomerations during dispersion and storage was reduced. When using these additives, a very sensitive balance is required. If the concentration of these additives is too high or the interaction with the silver particles becomes too strong, then the overall specific electrical resistance is significantly increased (Table 3).

Table 4 summarizes the properties of the optimized adhesive.

Ageing Behavior

Depending on the specific application, the long term durability of the adhesive bond is of interest. According to today's state of the art

TABLE 3 Electrical Resistance and Printability by Means of Ink Jet

Additive	Specific electrical resistance [Ωcm]	Ink jet application
–	2×10^{-4}	Not possible
1.5 wt.% A	$>3 \times 10^{7}$	Good
1 wt.% A	2×10^{-2}	Applicable
0.5 wt.% B	6×10^{-4}	Good

TABLE 4 Specifications of the Adhesive

Viscosity at 2005 s^{-1}, 23°C	30 mPas
Max. particle size	8 μm
Filler content	70 wt.%
Specific electrical resistance	6×10^{-4} Ωcm
Contact resistance (SMD 1206)	20 mΩ
Adhesive strength (SMD 1206)	19 N

technology this cannot be predicted satisfactorily. Therefore, testing procedures for accelerated degradation ("ageing"), *i.e.*, at elevated temperature and humidity, have been established—for microelectronics typically 85°C and 85% relative humidity. Such tests were also carried out with adhesive joints of SMD 1206 with printed circuit boards, etc. Specific electrical resistance, contact resistance, and mechanical bond strength were evaluated. The results are summarized in Table 5. The electrical resistivity of the adhesive was not significantly influenced by the ageing procedure. The mechanical bond strength even increased about 50%. This is quite positive although the reason for this higher bond strength has not yet been clarified. The contact resistance, however, increased up to unacceptable values after the aging procedure. As a reason for this effect, the corrosion of the copper leads of the PCB was suspected, because the bonding took place without any surface pre-treatment. In industrial applications there are several methods available to improve the corrosion behavior. We decided to pretreat the copper leads with benzotriazole as a corrosion inhibitor, which is a cost effective solution [8]. After storage at 85°C and 85% RH the increase of the contact resistance after ageing could be lowered significantly, although the contacts of the SMD were

TABLE 5 Ageing Behavior of SMD Interconnects

	Specific electrical resistance [Ωcm]	Bond strength [N]	Contact resistance [mΩ]
Initial state	6×10^{-4}	19	20
After 500 h 85°C/85% RH	5×10^{-4}	34	370
After 1000 h 85°C/85% RH	5×10^{-4}	29	1740
After 500 h 85°C/85% RH with corrosion protection of the copper	20	125	
After 1000 h 85°C/85% RH with corrosion protection of the copper		29	172

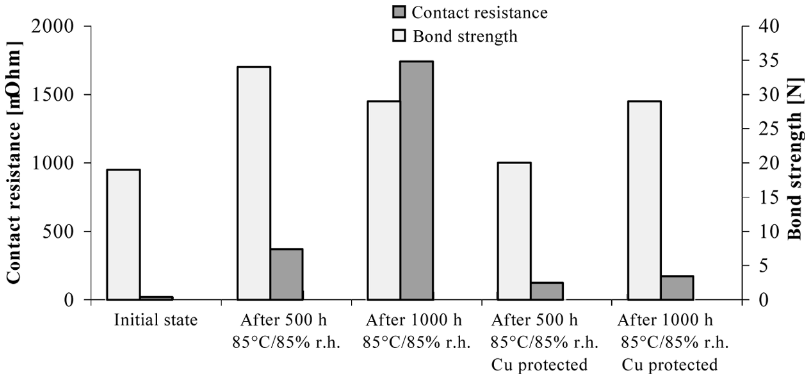

FIGURE 5 Ageing behavior of SMD interconnects.

not protected against corrosion (Fig. 5). Surely there is still a high potential for further optimizations, for example to have the corrosion inhibitor in the adhesive itself in order to save additional steps during production.

Printing Adhesives Via Ink Jet

The term ink jet covers a variety of technologies for non-contact application of liquids. A distinction is made between valve technology, pulse jet, and continuous jet. In valve technology, a valve which forces the liquid out of a nozzle under pressure is opened *via* an electronic control system. Continuous jet technology covers two techniques: binary continuous technology and printing by deflection. In both these printing techniques a continuous jet of liquid is atomized. At printing by deflection the resulting droplets are deflected by an electrostatic field according to the desired print pattern. The binary continuous technology works with multiple nozzles; the droplets not required for the printing patterx are deflected by an electrostatic field. Pulse jet technology also covers two techniques: the piezoelectric and the bubble jet techniques. The bubble jet technique is in widespread use in office printers. The area of work studied in this project is dispensing using the piezoelectric technique. This dispensing method uses a tapered glass capillary with a 30 to 100 μm nozzle diameter to supply the adhesive. The capillary is surrounded by a piezoelectric actuator which contracts when a voltage is applied and, thus, increases the pressure on the adhesive. As a result, liquid is squeezed out of the nozzle and forms a micro–drop. Typical printing parameters are shown in Table 6.

TABLE 6 Typical Printing Parameters

Voltage	100 V
Pulse width	35 μs
Frequency	100 Hz

The size of the droplet, which tends to lie in the range of 30–100 μm, depends not only on the properties of the adhesive, but also on the internal diameter of the nozzle. Liquids with viscosities up to 100 mPas may be processed using the Microdrop micro dosing system. The formulated conductive adhesive exhibits shear thinning flow properties. At low shear rates the adhesive is highly viscous, while increasing shear rates result in a sharp drop of viscosity (Fig. 6). When the shear rate decreases, the viscosity is immediately affected and it increases to the original value again. This is typical behavior for fluids which contain a high fraction of particles. This behavior is advantageous for the sedimentation properties of the adhesive. In the stock vessel on the unit the adhesive is at relative rest—the viscosity is high. This lowers the rate of sedimentation, as described by the Stokes equation. The shear rate is very high in the nozzle. According to the manufacturer, the shear rate in the nozzle during printing lies in the range of $10^5\,s^{-1}$. A low viscosity is required for the adhesive application. At a shear rate of $10^5\,s^{-1}$ the viscosity could not be measured by the rheometer because this high shear rate lies outside the specification of standard rotation rheometers. The adhesive developed for ink jet application has a viscosity of 30 mPas at a 2500 s^{-1} shear rate.

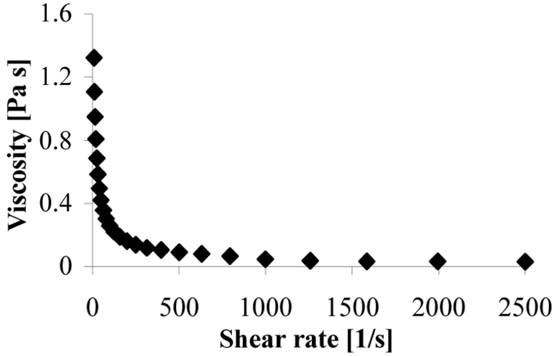

FIGURE 6 Characteristic flow properties of the formulated adhesive as a function of shear rate at 23°C.

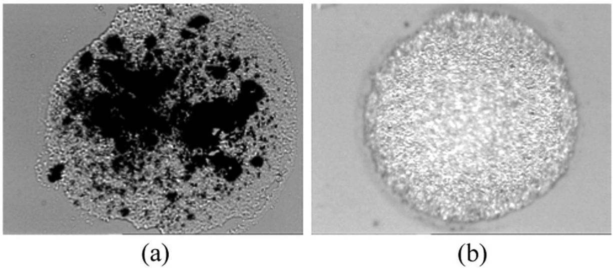

FIGURE 7 Micrograph of a printed droplet with agglomerated filler particles (left—droplet diameter 200 μm) and with a homogeneous filler particle distribution (right—droplet diameter 170 μm).

Initial printing tests confirmed that it is not possible to achieve consistent dosing without adequate actions to reduce agglomeration. Particles accumulated at the tip of the nozzle and disrupted accurate dosing. As a result, droplets developed an increasingly lateral path of flight which led to the formation of small additional droplets—called satellites. Microscopic analysis of the applied glue showed that filler particles had agglomerated (Fig. 7). The use of appropriate (proprietary) additives allowed settled filler particles to be re-dispersed by stirring. In the course of dosing tests pronounced catenoids formed between the capillary and the droplet; however, catenoids and drops merged into uniform drops during flight, thus minimizing satellites. This leads to droplets with homogeneous filler particle distributions.

At first a capillary with an inside diameter of 100 μm was used for printing on a glass substrate. In the next step a 75 μm capillary was chosen in order to reduce droplet size. With this setup droplets of 130 μm diameter were produced (Fig. 8).

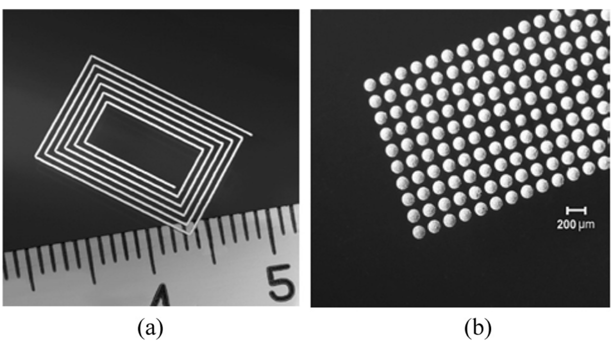

FIGURE 8 Ink jet printed antenna (scale in mm) and dots of adhesive.

Other substrates used in testing were FR-4 printed circuit boards, polyethylene terephthalate (PET film), and paper.

In order to reduce sedimentation further, Microdrop Technologies is developing a device in which the adhesive is continually pumped through the storage container and the supply tubes. The resulting constant flow reduces the sedimentation of the silver filler particles. This newly developed device is currently being tested.

CONCLUSION AND PERSPECTIVE

A silver-filled, electrically conductive adhesive was developed that can be applied *via* ink jet. The currently attainable droplet sizes are in the range of 130 µm but are set to be further reduced by using smaller and more advanced nozzle shapes. Future nozzles are to have inside diameters of 50 µm which should decrease the droplet size to 80 µm as a first step.

Furthermore, in addition to the conductive adhesive with a two-step curing process, a conducting, inkjettable glue is to be developed which only requires one step of thermally activated curing. This will open up new potential applications.

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