Inkjet printing of conductive and resistive coatings

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Coating of functional materials is the basis of many electronic device manufacturing processes. Screen printing, roll coating and other methods have been used for decades, permitting low cost, high production rates of Plastic Card Boards (PCBs), where conductive pathways are printed before components are integrated. Nowadays, the PCB industry in developed countries is suffering a revision of all manufacturing processes, to cope with severe market constraints: short runs and fast time-to-market. Inkjet technology has arrived to complement the traditional, analogic production, with new tools that makes possible to produce goods with great versatility.
In this work we will state the problem of inkjet printing functional materials in the frame of PCB manufacturing. The use of numerical methods to asset the formation of conductive pathlines using digital techniques will be presented. Also, the use of resistive and dielectric inks will be discussed.

1 Introduction

Inkjet printing has become in recent years the basis for revolutionary techniques in electronic device manufacturing. The industrial success obtained so far has raised a great expectation about “plastic electronics”. Several industries have been working for some years developing semiconductors, Thin film transistors and other devices printed directly onto a plastic substrate using inkjet technology. Although integration of components has reached the nanometer scale, there are several electronic devices that cannot be reduced, for example high power resistors, potentiometers, etc., where thermal dissipation and ergonomics makes this reduction undesirable. This products are mainly produced in an industrial scale following conventional coating techniques (screening, slot coating, flexographic roll coating). In this work we study the possibility of printing directly resistive and/or conductive coatings on polyester films, via inkjet printing.

In order to undestand the benefits behind inkjet printing of electronic devices, first we will discuss briefly the actual process of mass production of plastic card boards (PCBs). The process of PCB manufacturing, depending on the degree of accuracy and complexity of the pattern, is carried out by screen printing or flexographic roll coating, or etching of a previously coated conductive layer on a substrate. All the methods allows a high production rate at a relatively low cost. However, the initial costs and development stage from design to production are high, involving manufacturing of special tools, screens, rollers, etc. for each product.

For that reason, short runs and/or new designs frequently involve high costs which raise the price considerably. This is the case, for example, in the automobile industry, where new designs are being developed continuously and time-to-market is usually pushed down by OEM. Inkjet printing, on the other hand, since it is a fully digital process, is quite flexible, and provides a way to accomplish short runs and new designs faster and at a competitive price. Thanks to the development of new inks, and the improvement of industrial printheads, the introduction of this technology at an industrial scale can be done at a low risk.

One important aspect for the success of this process are the inks and its electrical properties once cured. Actual resistive inks consist of a highly loaded dispersion of graphite on an organic resin. Viscosities are high (about 25-35 kPa s) and several rheological properties such as thixotropy and yield stress behavior were observed. On the other hand, conductive inks are silver dispersions, which however share many rheological features with graphite dispersions. High viscosity, together with yield stress values are the main difficulties in order to get a proper

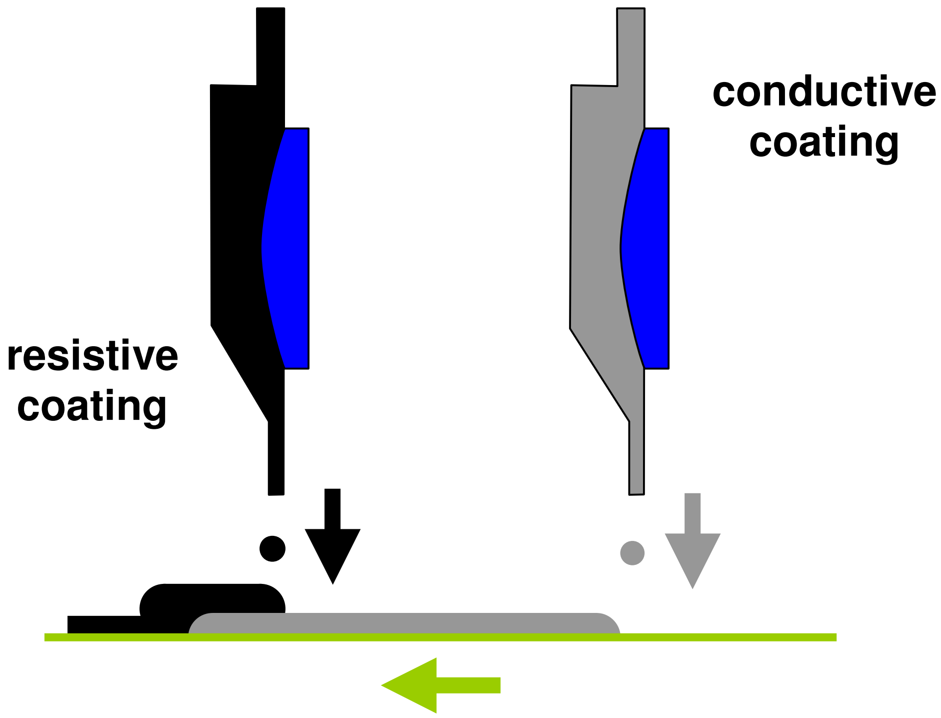

Figure 1: a typical DOD piezo inkjet device for electronic applications

deposition using inkjet technique, and new formulation are now being tested. For that reason the design of the hole and the pressure waveform generated by the electromechanical actuator must take into account this properties. A design approach based on rheological tests followed by CFD analysis has been developed, showing that hole size, pressure and wetting effects must be effectively chosen in order to improve resolution and homogeneity, and enhance drop frequency.

2 DOD Piezo technology

Among the different techniques for drop generation and deposition, the Drop-On-Demand (DOD) methods are the most suitable for printing patterned electronic circuitry. In particular, piezo actuators are the standard for inkjet printing in an industrial scale, due to its reliability. For that reason, we will focus our attention on this particular type of inkjet deposition system.

In a piezo DOD inkjet, ink is jetted trough a nozzle of about 30 μm diameter, driven by an acoustic wave generated in the fluid by a membrane attached to a piezoelectric crystal. Several manufacturers provide different modes of pulsing (shear modes, direct modes, parallel walls, etc). Schematically, a common inkjet nozzle is shown in figure 1. The mechanism of drop formation, detachment and further impingement on the substrate is rather complicated and would need some further discussion. However, several general aspects can be stated:

- Ink Viscosity should be under 10 cP
- Pigments should be evenly dispersed to avoid nozzle clogging
- Ink surface tension and nozzle wettability must guarantee the correct drop formation

In general, if these statements are fulfilled, functional materials will be correctly jetted onto any substrate. However, several problems may arise, and production may be compromised. Most problems are related to the ink: poor wetting on the PCB substrate and pigment settling. In fact, manufacturers in this field are waiting for the development of new fluids that comply with all this requirements.

3 Conductive and resistive coatings

The possibility of integrate inkjet technology in industrial fabrication of electronic devices can be achieved because of the improved reliability of the new generation of inkjet printheads. However, even when printhead technology was mature enough to accomplish production rates and specifications dictated by the industry, the formulation of conductive inks suitable for inkjet printing presents great difficulty, and it was only recently that these products are available.

Conductive inks are mainly printed by screen or flexographic processes. For that reason, they differ extraordinarily from an inkjet ink: screen printing inks are highly viscous, and flexographic inks usually have pigments whose sizes (and its flocculated aggregates) are well above the limit imposed by inkjet nozzle geometry. The new generation of printing inks are based on a totally new formulation that complies with viscosity limits imposed by the process, as well as solids size, with acceptable electrical properties. These are nanoscale silver particles, dispersed on low viscosity polymeric solution (usually acylate-based, UV curable). The rheology does not show significant differences with respect to regular inkjet inks, although deeper analysis is being carried out.

The main concern in the case of conductive liquids is to get electric pathways once solvent is removed and polymer is cured. The connectivity among silver particles is the responsible of the conductivity of the printed path. For that reason, flocculation and particle size play an important role on this property. The same happens on resistive inks, where silver is replaced by graphite aggregates. In both cases, the need to get into contact and, at the same time, to avoid flocculation, impose severe constraints to the ink formulator. One way to tackle this is to use de-flocculating agents which are removed during curing: this makes the ink more stable, and allows the formation of conductive paths once the ink is printed.

4 VOF simulation of the printing process

Inkjet printing process has been divided in three steps: drop formation in the nozzle, pattern formation on the substrate and drying/curing of the pattern previously formed. Since these are rather separated processes, where each one affects the next in a well-defined way, the study could be carried out in steps. The relationship between variables as well as the performance of the overall process has been determined using numerical methods. Simulation were carried out using a VOF scheme using FLUENT 6.1 software. On each case, user-defined procedures were implemented to take into account several features not contained in the commercial version of this software.

4.1 Drop ejection from the nozzle

The driving force of the drop ejection mechanism is an acoustic wave generated in the ink channel by a sudden contraction of a piezoelectric actuator. These crystals usually deliver pressure pulses of about 10^{-5} s, producing waves that travels through the nozzle, carrying ink to the nozzle tip. As the pulse stops, fluid is no longer pumped and drop detaches from the tip, driven by inertial forces: velocities can be of the order of 5-10 m/s at this stage, while volume drops are around 40-70 picoliters.

For the modelling of this particular process, only the nozzle tip will be considered, since pressure waves near the tip are roughly plane. Since the tip has symmetry of revolution, a 2D-axi model is accurate enough in this case. The geometry as well as the mesh used for the calculations is shown in figure 2. In order to track the interface more accurately, a dynamic adaption scheme was implemented. In the following table the parameters involved in the simulations are presented:

Table I. parameters for CFD modelling of the process

Nozzle diameter	35 µm
Firing time	20 – 50 µs
Pressure step	1 – 3 bar

Ink viscosity	10 mPa s
Ink Surface tension	30 mN/m

Pressure step at the inlet generates a mass-flow of ink that is ejected. Pressure pulse was optimised to obtain drops of definite volume between 40 and 70 pl (roughly 20 – 25 µm in diameter). On each case, velocity of the drops were calculated, in order to avoid slow or fast drops (velocity must lie around 5 m/s in order to improve image quality). Also, pulse were formulated to avoid satellite drops, a well known effect derived from the instability of the liquid neck formed during break-up. Usually these drops coalesce with the main drop before impact, but in some cases may lead to printing defects. The results obtained in this step serves as input for the second part of the simulation, where each drop ejected impact the surface and participates from the pattern forming process.

4.2 Pathline formation

The interaction between firing frequency and substrate velocity are the main effect during pattern formation. In particular, we will focus on attention on pathline formation, since this is the most crucial aspect to guarantee the right electrical conductance of the electronic circuit. While in graphic industry, inkjet is intended to generate well-defined colour pixels to enhance printing quality, the printing of electrical pathways requires an accurate degree of overlap of each pixel. Firing frequency, nozzle arrangement and drop/substrate velocities must be perfectly matched to achieve the right pattern on the surface.

Numerical simulation consisted in this case in a 3D mesh as shown in figure 3. Substrate moves in the x-direction at 0.2 m/s. Also, a contact angle of 30º is prescribed for the ink-air-substrate system. This corresponds to the case of a FR4 epoxi substrate, previously plasma-treated, in contact with a water-based conductive ink.

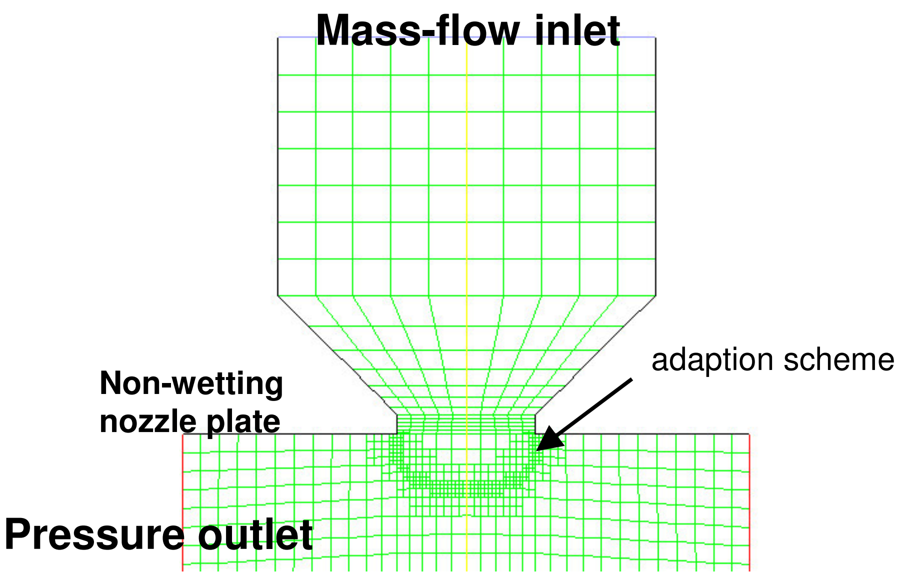

Figure 2: drop ejection simulation: nozzle mesh. It can be seen the interface-tracking adaption scheme.

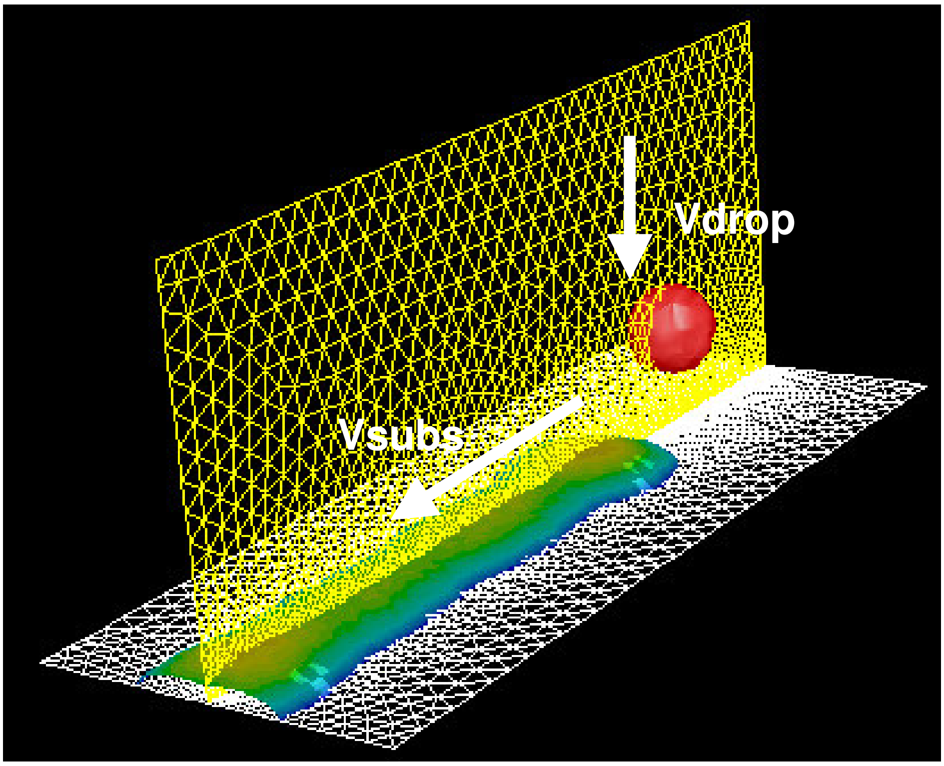

Figure 3: pathline formation scheme.

Drops are created near the surface (around 100 µm above substrate) with the radius and velocity calculated previously (sect. 4.1). Simulation then starts, following the drop fall, impingement and further advection over the moving substrate. The process repeats according to the firing frequency adopted, and a new drop is formed in the same place. The new drops impact the surface and join the previously formed liquid pattern. A sketch of such a process can be seen in figure 4.

One question that arises is the following: inkjet nozzles are 2 – 5 mm above substrate, Does drop velocity varies along this distance? Since Reynolds number is relatively low ($Re < 1$-10), Stokes formula is valid for prediction of terminal velocity. For spherical drops of 20 – 25 µm diameter, falling at a velocity of 5 m/s, air resistance effect is negligible on a distance of 2 – 5 mm. For that reason, the nominal velocity obtained previously is considered in this case.

4.3 Drying/curing

The final step allows the estimation of curing time for each design. Inks are waterborne, acrylate resins loaded with graphite or silver. Curing of such systems is a complicated function of UV radiation exposure, temperature and environmental variables. For that reason, numerical simulation makes possible to separate the different mechanisms acting on the printed pattern.

Considering initially the pathline resulting from previous section, a mass-transfer function is imposed to both phases, thus reducing liquid volume fraction at a constant rate. This evaporation rate is a function of liquid/gas properties as well as temperature and relative humidity, and it has been estimated from experimental data. The constant rate assumption is valid only at early stages of drying: more realistic models will be implemented soon, as more experimental data is available.

While in normal ink deposition curing and drying are controlled in order to enhance pixel quality (via UV pinning techniques, for example), in our case the result is completely different. Electric pathways are constructed during curing and for that reason the control of this process is much more important than in other printing processes. On the other hand, several question arises when electrical contacts between different inks are established (for example, between a printed resistor and a silver wire). Silver ink is first applied, then resistors are printed. Curing/drying between first and second application must be controlled, otherwise spurious impedances may arise making PCB card lie outside quality tolerances. The dependence of this effect with process parameters, as well as the optimum curing between each application is not yet well understood.

5 Results

In Figure 5 a representation of the drop ejection process is shown. As it can be seen, the pulse (represented here as a stepwise mass-flow) drives the ejection, which is modulated by capillary forces in the nozzle tip. Detachment of the drop from the tip is a complicated process that leads to satellite drop formation. Usually this small droplets travel faster than main drop, coalescing. However, if velocity is too fast, this may lead to dispersion of the printed pattern. On each case, there is a close relationship between drop size and final velocity, depending on the nozzle design, firing pulse profile and ink properties. However, the span is rather narrow, and in many cases variations in drop size and velocity are less than 10%.

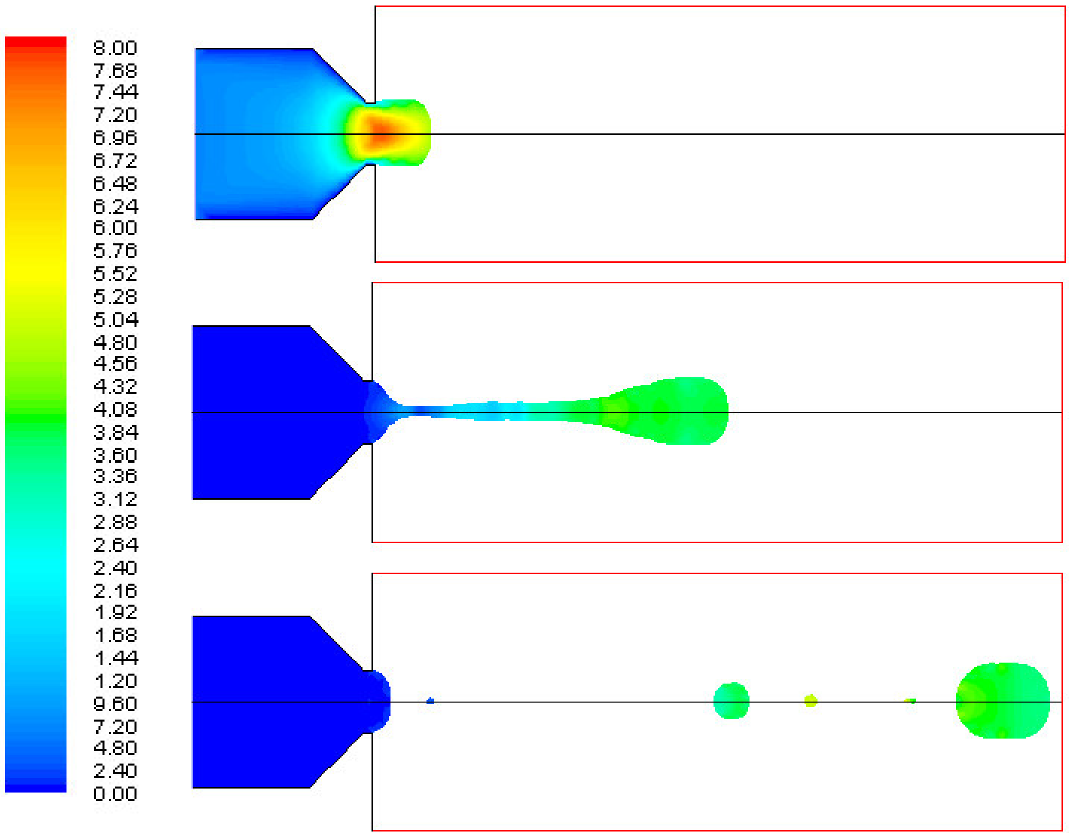

Figure 4: droplet ejection at 140, 180 and 240 µs. Color scale represents velocity magnitude (in m/s). Satellite drops travel slightly faster and eventually coalesce with main drop.

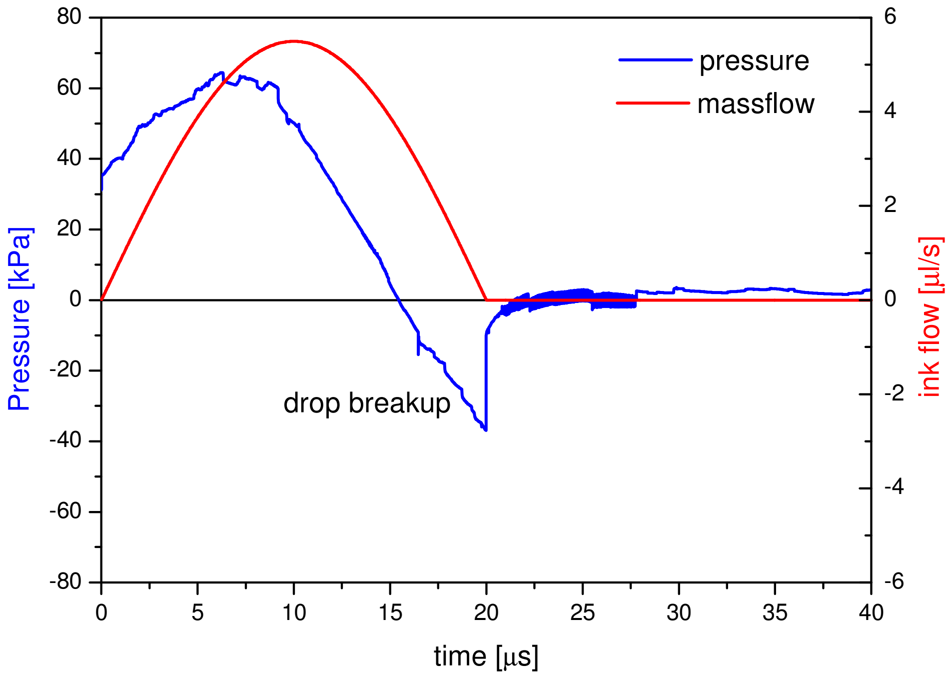

Figure 5: Pressure profile during firing.

Pressure generated during firing is shown in figure 5. Capillary forces arising on the nozzle are responsible for the pressure drop during detachment. Usually, meniscus control is desired in order to avoid air entrainment in the nozzle, which may cause serious harm to the printhead. For that reason, pressure in the chamber is forced below atmospheric pressure, by keeping an offset voltage on the piezo crystal between pulses. Thus, meniscus is pulled back slightly, providing a negative curvature and a much more stable position.

Pattern formation depends on many variables. Among them, firing frequency and drop size are tuned in order to achieve the right cross-section: This is of particular importance when printing resistors and other passive components, where linearity and ohmic values must keep a definite value. Numerical simulation in this case allowed the estimation of the operating window as well as the right set of parameters that print a given pathline. In figure 6, the prediction of cross-section as a function of firing frequency, for different drop sizes is presented.

6 Conclusions

The use of inkjet technology in printed electronics provides manufacturers with alternative tools to deal with new challenges that affects this industry: to reduce the time to market of new developments, and to find a way for short-run production. By now, this technology is mature enough to start mass production, although several problems must be solved to guarantee reliability: ink formulation and substrate treatment.

Conductive inks usually present a high viscosity since they are applied by screen printing and flexo roll coating. Inkjet inks are usually less viscous and metallic pigments are more difficult to stabilize. The higher price of such liquids is a drawback for future developments; however, an increase in the demand will surely drop the price significantly, making this technology more attractive.

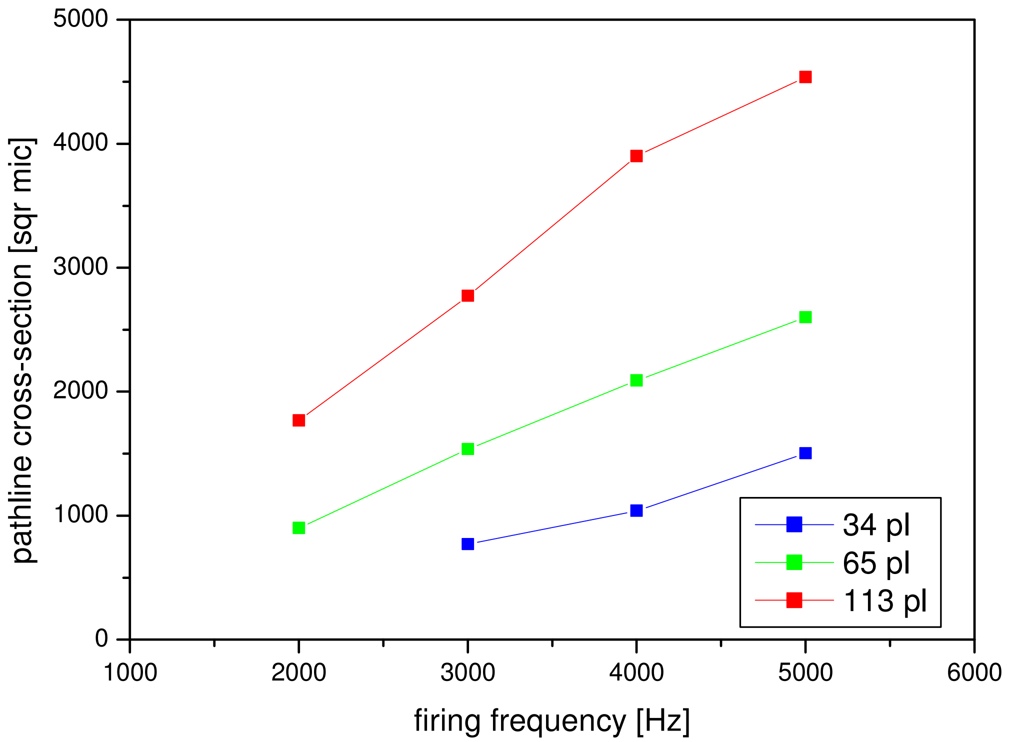

Figure 6: Pathline cross-section as a function of firing frequency and drop size. Cross section is responsible for important properties such as overall resistance and linearity.

One important aspect of inkjet printing of circuits is the possibility of printing several inks simultaneously: conductive paths, resistors, capacitors and inductors usually covers more than 90% of PCB surface. The possibility of integration of all passive components in a single printing device allows the development of brand new circuits, reducing weight and price, making it specially suitable for automotive parts. It is expected that this technology will integrate passive electronics on many plastic parts inside the car, providing designers with new tools that would change dramatically manufacturing processes.