Electrical Measurement of Ink Sedimentation

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Abstract

Characterization of inks, particularly sedimentation in particle inks, is an important challenge in inkjet printing. This paper proposes the approach of ink characterization by electrical measurements. A conductivity cell is used for the application of alternating current. This provides well-defined ink characteristics without changing ink properties. Thus, the method can be used not only in ink formulation but also for on-line monitoring during the printing process.

Two different ink compositions are investigated regarding impedance and phase angle. Silver inks, common as the conductive component in printed circuits and barium titanate inks. The latter inks comprise of an insulating (dielectric) material. The method is proved to be applicable here. Both compositions show low-pass filter characteristics. Accordingly, similar analysis methods are used. The low-pass frequency response allows for the implementation of the random walk method to obtain equivalent capacity and resistance.

From the measured values, accurate discrimination of the actual solid substance content is possible for both inks.

Introduction

Rapid advances in inkjet printing technologies revealed great potential in a wide area of applications in the last decade. Inkjet printing is a cost-efficient and flexible process, which can be used for rapid prototyping and the production of small lot sizes, e.g. of printed circuit boards [1].

One of the major challenges in inkjet printing of particle inks is long term stability of the ink. Especially when it comes to printing electrically functional materials, such as silver particles, the dispersed material frequently has a significantly higher density than the dispersion medium. Thus, sedimentation is likely to occur. In order to allow for long term stable printing processes, sedimentation has to be avoided. There are some methods that, in general, allow for the evaluation of sedimentation in particle inks.

Visual classification is one possible method. For instance, inks can be classified as exhibiting one of four typical modes [2]. These modes describe the distribution of clear liquid, cloudy liquid, suspension and sediment in a test tube over time. Measurements require a considerable amount of time when using silver nanoparticles, e.g. 10 days using commercially available silver inks of 2 and 5 vol% silver [3] or more than 35 days applying different surfactants with silver particles [4]. In addition, inks are not ready to use after sedimentation. Determining the height of the different layers or distinguishing them from one another is not always possible by mere observation. This is the case, for example, when using silver particles.

The difficulty of visual evaluation can be diminished by using a light source or x-rays measuring transmission and/or reflection [5]. Thus, even quantitative measurements can be conducted using the amount of radiation reaching a detector. However, these methods can suffer from a lack of transmission (light) or may come along with administrative efforts concerning radiation sources (x-ray).

When using the pipette method, small amounts of liquid are extracted from a predefined layer to measure their solid substance content using an Andreasen pipette. This method is time consuming and also renders the extracted ink unusable. Results obtained by these methods may differ due to their differing principles of measurement, thus, calibration is necessary for comparisons between methods [6, 7].

An established method for the evaluation of particle sizes by sedimentation that overcomes the disadvantage of long settling times is the centrifugal pipette method [8]. However, this method has to be used with sufficiently dilute samples and only a limited number of samples can be extracted per centrifugation.

All the methods discussed suffer from severe disadvantages. In fact, not even one of these methods can be used during printing. A reliable and easy to use alternative to these methods is the use of a conductivity cell. In its simplest form, this cell consists of two plate electrodes and is used to measure the liquids electrical conductivity. Conductivity cells are, for example, often used to determine the purity of water, where dissolved ions contribute to the liquids conductivity.

For the characterization of inkjet inks, the particular measurement is compared with a calibration curve to obtain the mean solid substance content of the ink placed between the electrodes. Different electric parameters are investigated concerning their suitability for the characterization of conductive and insulating inks.

Electrical measurements of ink sedimentation can be used for fast evaluation of inks in storage. However, the main advantage over the previously discussed methods is, that this method can easily be applied while printing.

Materials & methods

Ink preparation & non-electrical properties

Two different inks are investigated. First, a silver ink used for printing conductive elements like circuit lines or electrodes. Second, an insulating barium titanate ink used for printing dielectrics.

All variations of the silver ink are based on the same paste of 300 nm silver particles (Silver Powder #11000-10, Ferro GmbH, Germany, paste prepared at the Helmut Schmidt University) and butyl diglycol. Additionally, the paste comprises a small amount of ethyl cellulose for ink stabilization. All ingredients are manually mixed followed by three roll milling. The paste is then thinned to the desired solid substance content (SSC, if not otherwise stated, always given as ratio by volume instead of in percent) with butyl diglycol. The investigated SSC ranges from 10 to 40 wt%, i.e. the range suitable for inkjet printing. Suitable means, this SSC leads to inks with a viscosity of around 10 mPas (depending on ink temperature), which can be easily printed with printheads like the MD-K-140 (microdrop Technologies GmbH, Germany).

Silver inks of this composition have been, for example, used for printing multilayer capacitors on ceramic substrates [9] and through silicon vias in silicon wafers [10]. Thus, they have proven their applicability in a wide field of inkjet printing applications.

The barium titanate inks are prepared at the Karlsruhe Institute of Technology using a laboratry stirred media mill with zirconia grinding media (0.2 mm). The powder is dispersed in an organic solvent (butyl diglycol) with an alkyl phosphate as dispersant (DOLACOL D1001). SSC is 40 wt%, i.e. 11.7 vol%. Again, butyl diglycol is used for thining (SSC from 6.5 vol% to 2.5 vol%).

Similar barium titanate inks are used for printing of dielectric thick films in multilayer capacitors [11, 12].

Measuring device & data acquistion

The measuring device consists of two main parts. First, the LCR meter ST 2826 (Sourcetronic GmbH, Germany) and second, the conductivity cell LTA 1 (WTW Wissenschaftlich-Technische Werkstätten GmbH, Germany).

Using four-wire sensing, contact resistance and impedance contribution of the wiring are drastically reduced. However, there are minor residual contributions of the electrodes and their wires. The particular LCR meter was chosen because it allows for the acquisition of all relevant electric variables. In addition, DC voltage as well as AC voltage can be applied.

The conductivity cell is mounted on a micrometer screw, which can be used to accurately adjust the immersion depth of the electrodes. This is not necessary for a simple setup of the measuring device, but it may be useful for depth-dependent measurements. Besides, the micrometer screw provides an easy way to conduct reproducible and comparable measurements independent of filling level and flask shape.

The setup of the measuring device provides a small and cost-effective device, capable of providing highly accurate measurements. The apparatus can be easily adapted for any specific application, such as measurements of sedimentation while printing.

The electrical characteristics of the ink are not of interest by themselves but as means to an end, the evaluation of the particle distribution or concentration. Thus, no theoretical model that might fit all possible inks has to be developed. Data sets are chosen that are particularly promising for the characterization of the investigated inkjet inks, i.e. resistance/conductivity and capacity. However, other variables might turn out to be more appropriate for other ink compositions.

For a general evaluation of the applicability of the setup, the resistance and capacity of silver inks are measured at 1 V, 1000 Hz. In all presented measurements, temperature is controlled to be at room temperature (20 – 22 °C).

Subsequently, impedance and phase angle are recorded for a frequency range from 20 to 100000 Hz for silver inks and barium titanate inks.

Results & discussion

Silver ink

The measurements with a fixed frequency of 1000 Hz are carried out at controlled ink temperature. Deliberate variation of ink temperature (± 5 K from room temperature) shows no significant influence on the results in these measurements. Hence, strict temperature control should not be necessary for future measurements. Still, significantely raised temperatures (e.g. by dispersing) should be avoided to allow for comparable results. In addition, temperature influence might be significant for other ink compositions. Therefore, temperature should be controlled at least for the first measurements of a new ink composition. This is particularly important, when heat producing dispersion methods are used prior to measurements or heated ink is used in a printer.

Results of the conductivity measurements (converted from resistance) at 1 V, 1000 Hz are shown in ***Figure 1***. As expected, a larger amount of conductive silver particles in the inks solvent leads to a higher conductivity. However, the conductivity does not rise strictly linear with a higher SSC ($R^2 = 0.78$). As the very small error indicators (standard deviation) show, unexpected variation does not seem to result from large variances. Even though measurements of the same inks are taken over several days, they always give the same results.

Depending on ones definition of outlying values, coefficient of determination R^2 can be raised up to 0.96. However, the same results where obtained in reproductive experimentes with multiple samples. Thus, it can be said that in the case of the investigated silver inks conductivity does not seem to be a reliable predictor of SSC.

The silver inks capacity is shown in ***Figure 2***. Here, R^2 of the linear fit is almost as high as 0.99 while, overall, relative standard deviations are smaller than for the conductivity. This leads to a more reliable prediction of an inks SSC. A possible drawback of choosing the capacity over the conductivity of the silver ink for characterization is the smaller value range (by percentage).

A possible explanation for the higher R^2 of the capacity measurements can be found in the impedance

$$Z^{-1} = R^{-1} + (\mathrm{j}\, X_{\mathrm{C}})^{-1} \qquad (1)$$

where the reactance is

$$X_{\mathrm{C}} = -\frac{1}{\omega C} \qquad (2)$$

with ω representing the angular frequency. Eq. 1 assumes a parallel equivalent circuit for capacity C and resistor R which corresponds a low-pass filter in terms of the transfer function. If the assumption of a parallel equivalent circuit (eq. 1) is correct, there should be a plateau for low frequencies (dominant resistance, here $Z \approx R$) and a slope of 20 dB/decade for higher frequencies (above cutoff frequency) where ωC is dominant over R. Accordingly, for a comparable measurement of resistance/conductivity between inks and a linear fit of conductivity vs. SSC a frequency above the cutoff frequency of all inks should be chosen. 1000 Hz is above the cutoff frequency, as will be seen later.

The presented measurements at a fixed frequency of 1000 Hz seem promising for the electrical characterization of silver inks'

SSC. However, the limitation on only one frequency leaves a large amount of information unrevealed.

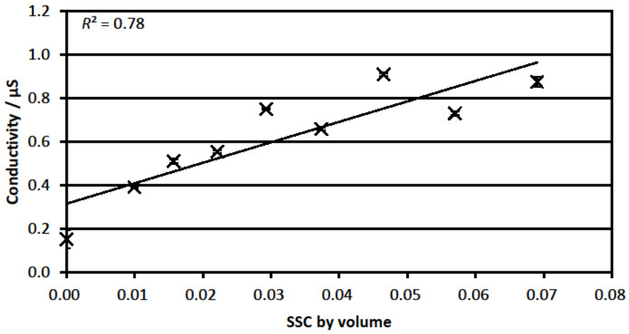

***Figure 1**. Linear fit to the measurements of conductivity vs. SSC by volume at 1 V, 1000 Hz*

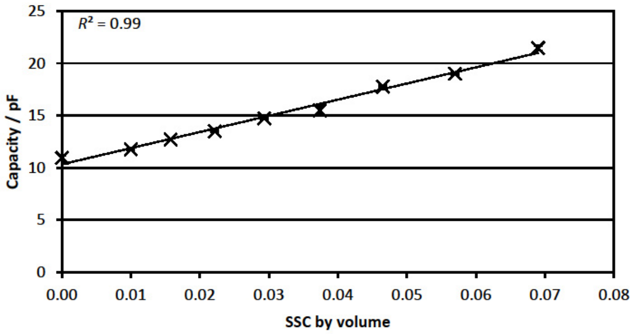

***Figure 2**. Linear fit to the measurements of capacity vs. SSC by volume at 1 V, 1000 Hz*

Electrical characterization in the frequency range of 20 to 100000 Hz is displayed in the usual 20 log(Z) scale and by the phase angle φ. This allows for an easy check of the assumption of a parallel equivalent circuit.

As expected, plateau and slope can be found in ***Figure 3***, i.e. the assumption of a parallel equivalent circuit is correct. Thus, calculation of R and C is possible by using eq. 1, e.g. utilizing the random walk method. As mentioned before, R can alternatively be read from low frequency values of the impedance Z. Values obtained by random walk are displayed in **Table 1**.

Table 1. Parameters of the equivalent circuit obtained by random walk method

SSC by volume	R / MΩ	C / pF
0.000	9.53	19.71
0.010	2.16	20.22
0.016	1.70	20.60
0.022	1.49	20.83
0.029	1.24	21.19
0.037	1.25	21.33
0.046	1.02	21.65
0.057	1.04	21.51
0.069	0.88	22.51

The accuracy of the random walk method is reduced by the very low amount of values at the plateau (about 2). This is reflected in the higher R^2 when plotting the capacity vs. SSC ($R^2 = 0.98$) in comparison to resistance vs. SSC ($R^2 = 0.82$). Here, the lower predictive value results from an underestimation of the resistance. The outlier for a SSC of 0.046 is not considered. However, other models than a linear correlation, e.g. logarithmic, between resistance and SSC can improve the resistances predictive value to a level comparable to that of the capacity ($R^2 = 0.96$).

One important information that can be obtained from the phase angle (***Figure 4***) is the cutoff frequency, i.e. where φ is 45°. For all investigated dilutions cutoff frequency is above 45° apart from the pure solvent where it is at about 750 Hz. This explains the low reliabilty of measurements at 1000 Hz. Readings of the cutoff frequency are quite rough here, as the frequency steps are quite large (500 Hz). Still, even then a linear correlation can be seen in cutoff frequency vs. SSC ($R^2 = 0.92$).

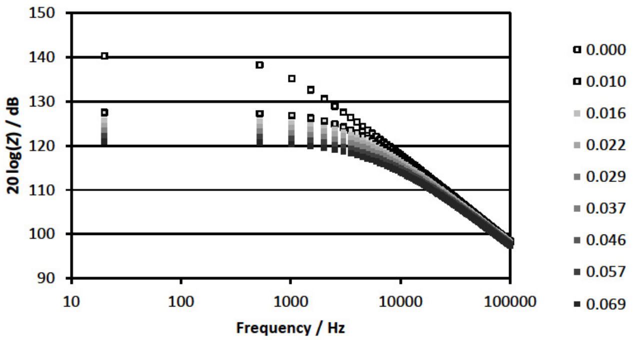

***Figure 3**. Impedance of silver inks over a wide frequency range. Legend shows SSC by volume*

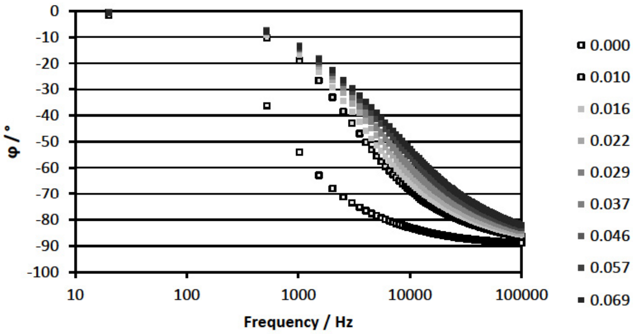

***Figure 4**. Phase angle of silver inks over a wide frequency range. Legend shows SSC by volume*

Barium titanate ink

The barium titanate inks are characterized using measurements of impedance Z and phase angle φ in the same way as for the silver inks, i.e. using a 20 log(Z) scale for the impedance and applying the random walk method. Measurement results are shown in ***Figures 5*** and ***6***. Data for pure solvent can be taken from the previous measurements (see SSC of 0.000 in ***Figures 3*** and ***4***) but are not displayed here, because the wide value range would decrease clarity in the figures.

A similar pattern to that found for silver inks emerges. Differences in total values obviously result from different ink compositions. For barium titanate inks, the capacity is in a similar range to that of silver inks, i.e. up to 22.98 pF for 11.7 vol% of solid substance. The resistance obtained by random walk, however, is considerably smaller (791 kΩ to 276 kΩ).

Appling a linear fit to the SSC, capacity, resistance and cutoff frequency give a coefficient of determination R^2 of around or above 0.9. Just as for silver inks, the model applied for the resistance should be logarithmic. This allows for an accurate electrical characterization of the investigated barium titanate inks in terms of their SSC.

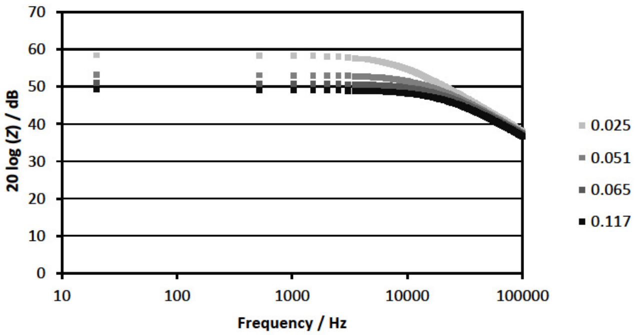

Figure 5*. Impedance of barium titanate inks over a wide frequency range. Legend shows SSC by volume*

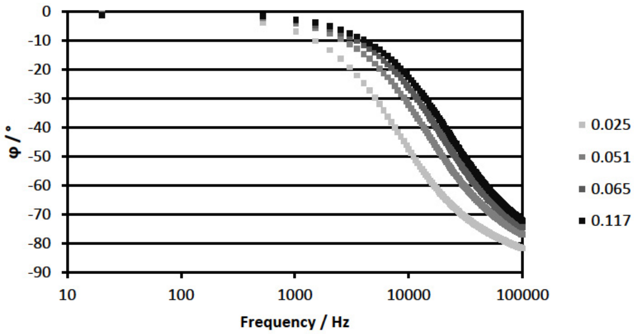

Figure 6*. Phase angle of barium titanate inks over a wide frequency range. Legend shows SSC by volume*

Conclusions

A simple setup for the electrical characterization of the sedimentation of inkjet inks was developed. Here, the frequency response of impedance and phase angle was chosen to prove the setups applicability. Regression analyses of several electrical variables yielded a coefficient of determination higher than 0.9 which is adequately high to use the results as calibration curves for the rating of unknown ink samples of a similar composition.

While using a fixed frequency of 1000 Hz, no shift in the measured values was detected over days (particle sedimentation was hindered by continuous stirring). Sedimentation in an unstirred ink reservoir or other changes of ink composition will still be a challenge for ink formulation, but now it can easily be detected with the presented setup. This offers the opportunity to characterize inkjet inks while printing without any destructive influence. Thereby, some cases of nozzle clogging can be avoided. Moreover, the SSC can be controlled during extensively long printing processes, whereby well-defined structures can be printed from start to finish.

Improved setups can include multiple stacked electrode pairs for space-resolved measurements. The advantage over one moving pair of electrodes would be the avoidance of turbulence. Thus, a fast and non-reactive measurement of the whole liquid column is possible.

Some ink formulations may be less well suited for the characterization by impedance and phase angle. However, the setup is not limited to measuring just these values. Adaptation is a mere question of adjusting the measuring device.

The ink characterization setup is a step towards more reliable industrial scale printing processes as it allows for fast intervention when necessary. Thus, production stops and deficient products or large variance in product characteristics can be reduced.

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