Pre-Treatment of Silver Particles as a Basis for Functional Toner

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Abstract

During the last decade large efforts were made to implement digital printing as a method to manufacture electronic circuits. The need for higher flexibility and efficiency than provided by the established production methods is the driving force in this development.

A very developed technology in digital printing is electrophotography ("laser printing"). Although it is a very common method in graphic applications, it is yet barely used in printed electronics. One of the reasons for avoiding electrophotography assumingly can be found in the basic principles of the process itself. Printing electronics necessarily involves processing conductive materials. In opposition, a toner, as used in electrophotography, must not be conductive to work in a laser printer.

This paper describes the challenge of using silver particles in the electrophotographic process, in order to print conductive silver lines as a basic layout for future circuits. A method to pre-treat silver particles in order to apply an insulating coating that dissolves during firing is presented. Additionally a testing method to evaluate the quality of the pre-treated particles is researched. Furthermore, functional toners were developed from these particles and compared to toners using non-pre-treated silver particles, concluding with the evaluation of the resulting laser-printed conductive silver lines.

Introduction

Although electrophotography, commonly known as laser printing, is a very important technology for graphic printing applications, it is a rarely used for functional printing. Only few approaches are documented, for instance in 3D printing [1]. Despite existing patents [2], no results of using electrophotography as a method for printed electronics are published yet, besides the ones created at HSU. Only a single approach is known to the authors, where elements of electrophotography are tested for their capability to print electronics, but without applying the whole process [3].

The main reason for not using electrophotography is that it is a huge challenge to print conductors with this technology. Circuit elements may include non-conductive materials. Nevertheless, whatever circuitry one wants to print, at the bottom line it is crucial to print a conductor somehow, which is contrary to the physics the electrophotographic process is based on.

In a laser printer, tribocharged toner powder gets developed onto a selectively discharged photoconductor. In a two-component system, as used in this study, the tribocharge is generated by stirring ferrite carrier particles with a polymer toner in a developer station. These charged particles get developed by creating a potential difference between the developer station and the discharged areas of the photoconductor [4].

Hence, a conductive toner would not work in the process just described. First, it can hardly be tribocharged with a ferrite carrier, and if so, its charge would flow away immediately to the surface of the toner bulk. Second, and far more important, a conductive toner would cause a current flow due to the already mentioned potential difference between developer station and photoconductor. Thus, short circuits would appear and shut down the process immediately. Furthermore, the photoconductor would be enduringly damaged at the spot where the short circuit occurs. Summarized, the main challenge is that the toner must not be conductive during the electrophotographic process, but must yield a conductive layout at the end.

At Helmut Schmidt University (HSU) in Hamburg, Germany, electrophotography is researched as a method to print conductive silver lines, in order to supplement or replace established screen printing as a production method for printed electronics. In cooperation with Zobrist Engineering in Switzerland, silver powder is processed into a toner that is printable in a laser printer prototype available at HSU. To form conductive lines, a firing process is implemented after printing, so that the organics, necessary to achieve toner properties, burn out and sintered silver lines remain. This paper documents the approaches taken towards the described challenges.

Preliminary studies

When trying to print conductive silver lines, the choice of particles is one of the first steps, as a basis for toner production. In established non-digital printing technologies for electronic circuitry, namely screen printing, mainly two sorts of silver particles are used: either a powder purely consisting of spherical particles, or of a mixture of spherical and flake-shaped particles. For toner production, the same approach is chosen by processing two off-the-shelf silver powders.

To characterize the particles of both powders, their size is measured using the ultrasonic spectrometer DT1200 from Dispersion Technology Inc. Particle size is determined from the attenuation data and it is indicated as the equivalent spherical diameter. Thus the flakes are described by their equivalent spherical diameter [5].

Silver A consists of a mixture of flakes and spheres with a total D_{50} diameter of 1.12 µm and a D_{90} of 2.73 µm. Second silver powder used, named Silver B in the following, consists of spherical particles with a D_{50} diameter of 1.12 µm and a D_{90} of 2.92 µm. So, both kinds of silver particles are in the same range regarding size.

The goal when preparing a silver toner based on these particles must be the complete coverage of the silver particles by an insulating polymer. Otherwise, the undesired effects mentioned in the introduction will occur. This is especially challenging when considering that the toner, as part of the regular production process, has to be grinded after extrusion to get toner-sized particles (mean diameter approx. 10 µm [4]). Here, grinding may cause silver particles to break through the polymer surface of the toner particles. Furthermore, conductive silver particles may loosen from the toner particles and get part of the developer mixture. Both effects are highly undesirable because the toner particles become conductive.

Especially the use of Silver A seems to promote these effects. This is disadvantageous when considering that the mixture of flakes and spheres promises high conductivity after firing due to the large area of contact between the particles. Assumingly, the flake shape of the particles leads to frequent breakthroughs of the toner surface. This effect is shown in the SEM picture displayed in **Figure 1**. A large amount of the lighter silver particles can found on the darker surface of the toner particles.

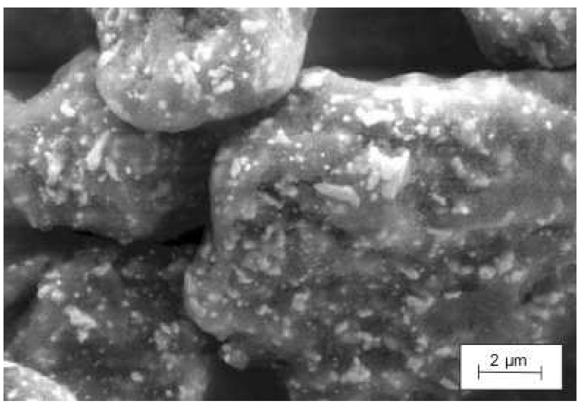

***Figure 1**. SEM image of toner particles containing Silver A*

Several approaches are made to process Silver A particles into a toner. The corresponding charge distributions of several toner/carrier mixtures are shown in **Figure 2**. Same as for all presented charge distributions in this paper, the EPPING q/d-meter is used for measurement [6].

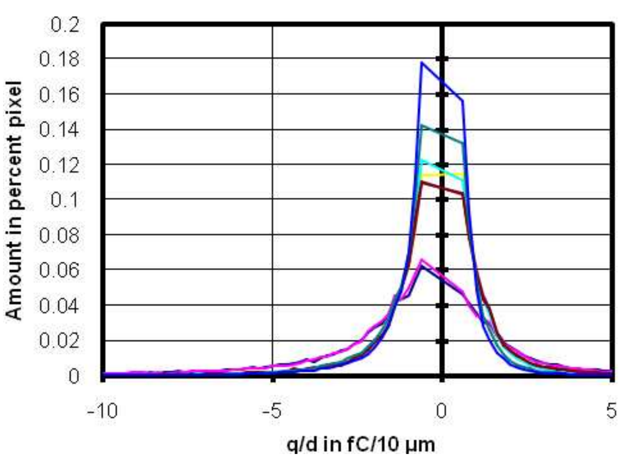

***Figure 2**. Charge distribution of Silver A based toner with a standard carrier*

As the figure shows, the toner's polarity is almost balanced between positively and negatively charged particles; amount of positively charged particles ranging between 35 and 47 %. This is undesired due to the fact that a printable toner should have as many particles as possible with the same polarity. For the printer prototype available for this study, negatively charged toner is necessary. The charging behavior cannot be pushed into a completely negative direction and therefore, no printable toner can be produced using untreated Silver A so far.

Silver B performs significantly better. The spherical particles assumingly show lower tendency to break through the surface. Better dispersion in the toner polymer leads to fewer particles on the toner's surface, as **Figure 3** shows.

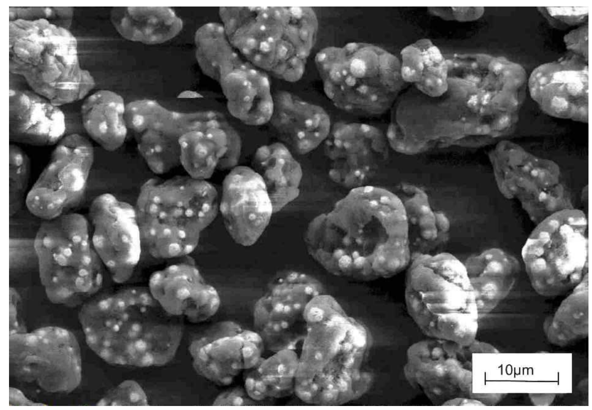

***Figure 3**. SEM image of C01 toner particles containing Silver B [7]*

Thus, an acceptable toner named C01 can be produced. This toner contains 68 wt% of silver and has a D_{50} diameter of 11.7 µm. Its charge distribution is displayed in **Figure 4**.

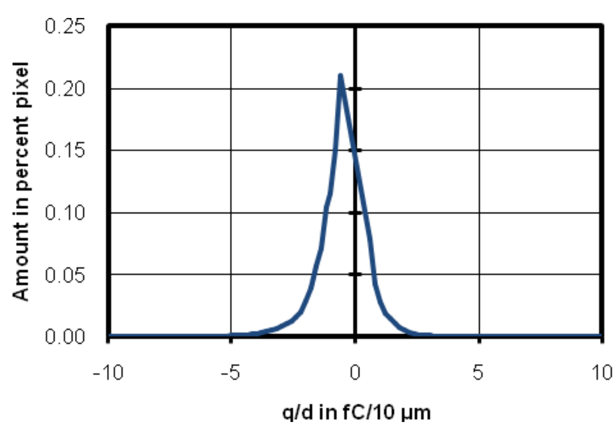

***Figure 4**. Charge distribution of Silver B based C01 toner with a standard carrier [7]*

However, still major drawbacks exist regarding C01 toner. Its mean q/d value is only -1.15 fC/10 µm and it contains about 18 % of positively charged particles, which is an improvement towards Silver-A-based toner, but still is not satisfying.

The toner can be used in the printer prototype at HSU, but its performance is not as good as necessary for the desired application. However, silver lines can be printed using C01, although the line quality is not very satisfying. Conductivity is only given on short tracks and line density is not sufficient at all. Nevertheless, the feasibility of printing silver lines could be proven and published [7].

Enhancing silver particles

During the described experiments to prepare a silver toner, results stringently led to the conclusion that the silver particles have to be coated before they are processed to a toner. As already mentioned before, the silver particles should be completely covered by the polymer. Prior results show that this is not sufficiently achieved during the present toner production process.

As a new approach, a method is developed to coat the particles before they enter toner preparation process. This coating method results in a paste, where silver particles, coated with polymer, are dissolved in a solvent. Afterwards the paste is dried and used as basis for the regular toner production process. Intention is to provide fully polymer-covered silver particles, in order to achieve improved toner properties after grinding. Thus, even if the particles break through the toner's surface or loosen themselves from the toner particles, they still remain non-conductive. Same as before, the polymer burns out during the firing process, and conductive silver lines can be achieved.

When experimenting with coating methods and parameters, one of the issues is determining the quality of the coating before starting toner production, which is time-consuming and expensive. Two methods were researched, both based on the electrical properties of the paste. First method measures resistance and capacity of the paste in a defined environment (volume of paste sample, distance of the electrodes). Second, the paste is dried and grinded to a powder, which then is pressed to a geometrically-defined pill. Afterwards, resistance and capacity of the pill is measured. To start with the outcome: Both methods do not yield very satisfying results and leave enough room for improvement, but nevertheless, they yield indications.

Regarding the measurements of the pastes, resistance increases and capacity decreases when polymer is added to the silver particles dispersed in the paste, as expected. Furthermore, the effect's magnifies when the coating process is applied to the particles. This yields a correlation between the electrical characteristic of the paste and the quality of coating. However, the amount of solvent in the paste also has a significant impact on both values. This has to be considered because the amount of solvent is not constant over the time due to evaporation. Thus, only indications can be extracted. To gain a significant correlation between the electrical characteristic of the paste and the quality of coating the method has to be improved

The pill measurement also only yields indications. Resistance increases with an increase of the amount of polymer in the pill. Capacity does not yet lead to any clear indications. Assumingly, too many parameters in pill production and measurement influence the results and therefore, further research is necessary.

Although both methods yield indications that the coating method works, they cannot be seen as a proof for the coating's success. Thus, the necessity of an in-process quality control method remains; if improvements of both methods do not yield sufficient results, other approaches have to be considered.

Toner based on coated silver

As a reliable method to evaluate the quality of the coating before toner production cannot be applied yet, the success of coating silver particles has to be judged by examining toners using such particles.

First, coated particles of Silver A were used to produce a silver toner. Although the particles did not work in any attempt to produce a toner before, this time production is successful. The resulting C02 toner contains 69 wt% of silver and has a D_{50} diameter of 10.5 µm. Its charge distribution is shown in **Figure 5**.

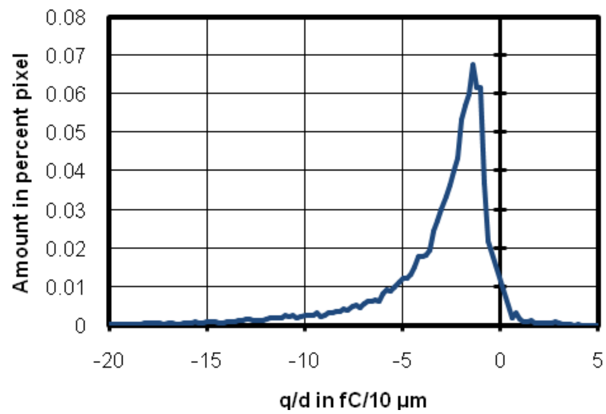

***Figure 5**. Charge distribution of C02 toner, based on coated Silver A particles, with a standard carrier [8]*

C02 has a mean q/d value of -3.6 fC/10 µm and it only contains about 2 % of positively charged particles. The fact that C02 works at all can be considered a quantum jump for electrophotography as a production method for electronic circuitry. The toner has decent charge and the amount of positive toner particles is in the range of common toners. Neither loosened silver particles, nor the breakthrough of the toner surface by silver particles seem to be severe issues any more. Especially when considering that Silver A was not applicable for silver toner before at all. A comparison between Figure 5 and Figure 2 underlines the magnitude of this development.

Thus, the effectiveness of the coating method is proven. Conductive silver lines with good conductivity and satisfying line density can be printed using C02. Their quality is significantly better that the one of lines printed using C01 [8].

Nevertheless, room for improvement still remains. During the printing trials, large traverse cracks occurred on silver lines printed on certain substrates. Also, conductive silver lines cannot yet be formed after a single printing cycle; multiple cycles have to be applied. Assumingly, the high density of silver leads to a bad charge-to-mass ratio [8].

Thus, an even more improved toner named C03 is developed. It is based on coated Silver B particles, in order to test their performance when coated. Also, its mixture is adapted to overcome the crack issue. Resulting C03 toner contains 67 wt% of silver and has a D_{50} diameter of 10.4 µm. Its charge distribution is displayed in **Figure 6**.

C03 has a mean q/d value of -5.0 fC/10 µm and it contains between 1.7 and 3.3 % of positively charged particles. These values not only exceed the ones of C01, but also are a little better that the ones already achieved with C02. A comparison between Figure 6, Figure 5 and Figure 4 shows the huge development in toner production.

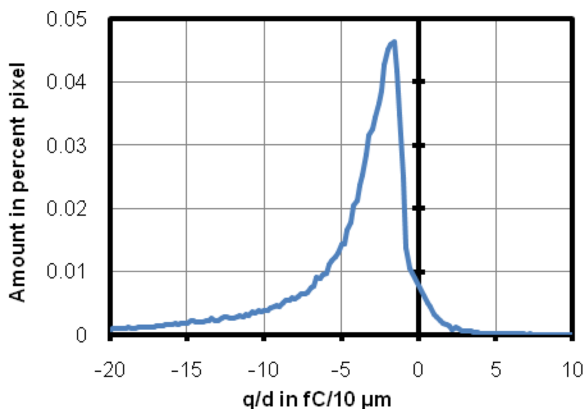

***Figure 6**. Charge distribution of C03 toner, based on coated Silver B particles, with a standard carrier*

The resulting silver lines when using C03 show a further increase in line density. Regarding conductivity, sheet resistances in the range of 2 mΩ can be achieved, which can be compared with competing technologies. The before mentioned crack issue is overcome [9].

Conclusions

The presented results show that coating of silver particles prior to regular toner production is the decisive step when printing conductive silver lines via electrophotography. Before, Silver A seemed to be completely inapplicable for toner production and Silver B only could be processed to a toner with insufficient properties. After applying the coating method developed at HSU, both sorts of particles can be processed into a toner with good properties regarding charge and printing performance. Thus, well-shaped conductive silver lines can be formed after firing and the effectiveness of the coating process is proven.

Despite the good results, the technology still yields many approaches for further improvement. Also C03 yielded a better performing toner than C02, it cannot be said clearly whether a flake/sphere mixture or pure spherical particles perform better regarding conductivity. The mentioned crack issue prevented evaluation of the resulting lines. Thus, a modified Silver A-based toner which forms lines without cracks has to be produced and tested.

Furthermore, both toners are not optimized yet. Actually, their purpose so far was to proof feasibility of printing silver lines in general and to check the possibilities of coated silver particles. So far, neither the coating process, nor the following toner production is optimized. Although, the coating process is in an early stage of development and leaves room for further improvement.

The goal of forming a conductive silver line after a single printing cycle remains. Thus, the charge-to-mass ratio of the toner has to be improved further. Nevertheless, the described results can be considered as a major breakthrough in printing conductors using electrophotography. Based on this success and considering the already identified approaches, chances are good to establish electrophotography as a production method in printed electronics.

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