Digital Printing of Phosphorescent Particles

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Abstract

Phosphorescent (afterglow) particles are commonly used for safety and security applications, utilizing their ability to glow even after the stimulating energy source is removed. Fields-of-application are marking of safety and rescue equipment, escape routes and exit doors. They work at worst environmental conditions such as a power breakdown or smoke. For these applications screen printing is the commonly used printing method. However, especially for small batch sizes or personalized solutions, digital printing methods are desirable. In this paper, two digital printing technologies are presented. Inkjet printing is a contact-free method that allows for printing on textured and/or sensitive substrates. Printing of particles with several micrometers diameter is possible under appropriate conditions. Here, the size of the particles is a limiting factor. Electrophotography, commonly known as laser printing, allows application of larger particles. However, this method is not contact-free and limited by the choice of possible substrates. Both methods compete with each other in printing velocity and scalability, but they also complement each other in the applicable particle size and substrate choice.

This paper investigates the possibility of printing phosphorescent particles, by using afterglow particles from Honeywell as an example. The Lumilux SN-F5 particles have a diameter of about 6 µm and are printed with both technologies.

Introduction

At the Institute for Automation Technology of Helmut Schmidt University (HSU) in Hamburg, Germany, digital printing methods are researched in order to supplement or replace screen printing as a production method for printed electronics, mainly in thick-film applications [1, 2].

After gaining a lot of experience in that field of activity, HSU researchers are looking for further screen printing applications in order to test their methods and techniques in new fields.

One of these fields is the production of safety and security equipment. There, phosphorescent (afterglow) particles are printed e.g. on signs for emergency exits or on products as safety marking. So far, no approach to digitally print these particles is known to the authors, so that they took the challenge of implementing a digital printing method for these applications.

At HSU, two digital printing methods are used: electrophotography, commonly known as laser-printing and ink-jet printing. To compare both methods, off-the-shelf Lumilux SN-F5 particles manufactured by Honeywell, are chosen and applied in order to explore the feasibility of digital printing of phosphorescent particles.

Inkjet printing

Inkjet printing is an established method for graphic applications. Over the last two decades, it was adapted to the deposition of functional inks as well. During this period, great strides have been made in the printing of particle loaded inks. Functional nano particles could be handled successful for almost ten years [3]. Inkjet printing of particles up to one micron is possible as well [1, 4]. In contrast, printing of particles bigger than one micron is a great challenge for ink composition and the printing process.

The larger and heavier the particles are, the faster they sediment. Therefore, it is necessary to take measures to prevent the sedimentation or at least to reduce its speed. The sedimentation velocity is a limiting factor for using a particle loaded ink in a printing system.

Another limiting parameter for the particle size is the used print head nozzle. Printable particles may have a maximum size of about five percent of the nozzle diameter [5]. The use of larger particles leads to instabilities in the drop generation and to nozzle clogging.

Used materials

Large particles or high film thicknesses are necessary to achieve a high light density by using afterglow particles. In the case of inkjet printing, the particles size is limited. For this reason, small phosphorescent particles are chosen for the ink formulation. The already mentioned Lumilux SN-F5 phosphorescent particles have a particle size of D_{50} of maximum 6.0 µm and an afterglow intensity of 90 mcd/m² after ten minutes (manufacturer's data).

The manufacture specifies the sedimentation analysis as the particle size measurement method. At HSU, a particle sizes D_{50} of 5.06 µm and 7.5 µm are measured using laser diffraction (Cilas 1064) respectively ultrasound analysis (DT1200).

The SN-F5 particles are not compatible with water based formulations. Thus, an organic solvent is used as dispersion medium. The chosen diethylene glycol monobutyl ether (DGBE) is an organic non-polar solvent with a density of 0.95 g/cm³ and a viscosity of 6.5 mPas at 20 °C.

Printing equipment

A self developed printing system with a commercial single nozzle print head (MicroDrop) is used. This print head is available with different nozzle diameters from 35 to 100 µm. Two nozzles with a diameter of 75 respectively 100 µm are used for the printing trails.

To achieve good results regarding drop generation, the print head needs an ink with a viscosity in the range from 10 to 20 mPas. Usually, the viscosity of an ink strongly depends on

temperature. Thus, the print head has an integrated heating which allows to modify the ink temperature and hence the viscosity when printing.

The printing system uses a planar motor for moving the substrate, while the print head keeps its position during printing. This configuration offers the advantage of variable and very high resolution because the planar motor has a positioning accuracy of one micron. Furthermore, the substrate holder can be heated and allows an improved drying process.

Ink preparation

The used particles are dispersed in the solvent by using a triple roll mill. This is the first essential step of a two-step ink preparation process. First, a paste with a high solid substance amount is made. The high amount of the solid phase is necessary to achieve optimal dispersion results. An optimal dispersion is given, if all agglomerates are broken and the particles are wetted by the solvent as good as possible [6].

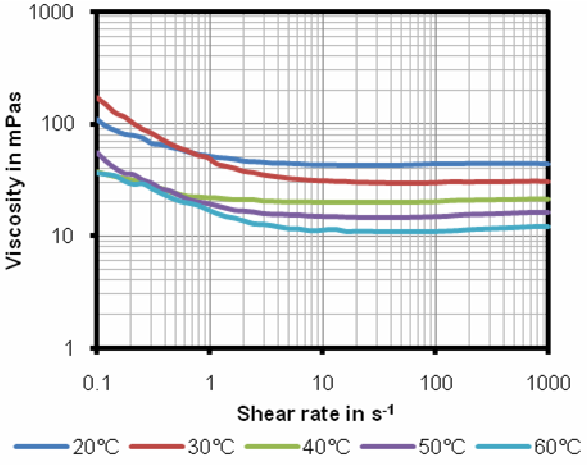

***Figure 1**. Rheological properties of the ink*

In the second step the paste is diluted to a printable ink. To dilute and homogenize the ink a dissolver or a sonication process is applied. Also, almost every solvent or solvent mixture can be used.

The ink preparation in two steps has the advantage that the ink formulation can be modified and optimized after the dispersion process. Also, the solvent used in the paste has only little influence on ink properties.

So, it is possible to choose the ink solvent depending on the corresponding substrate and the desired drying behavior. The dispersion process and the ink formulation can be optimized almost independently of each other. The required conditions are complete miscibility of the solvents and compatibility of solvents and particles.

Ink properties

The particles are sterically stabilized in the ink. With the used additives agglomeration can be prevented successfully. However, due to the large particle size, the sedimentation cannot be avoided completely. Nevertheless, the sedimentation velocity is reduced significantly. Additionally, mechanical stabilization is recommended to achieve a stabile printing process, for example by stirring.

The final ink includes 30 wt% of solid substance. Due to its high viscosity, the ink cannot be printed at room temperature. For the printing trails the ink temperature is increased to 40 °C.

The temperature-dependent viscosity is shown in **Figure 1**. Up to a shear rate of approximately 10 s^{-1} the ink shows shear thinning behavior. At higher shear rates the inks becomes almost Newtonian.

Inkjet printed structures

During the printing trails, graphical elements are printed on 1×1 and 2×2 $inch^2$ ceramic substrates. For evaluation of the luminance the entire surface of a 2×2 $inch^2$ substrate is covered by inkjet-printing. A high film thickness is necessary to achieve a high light density. The ink amount per area and therefore the film thickness can be increased by several parameters. First, the grip pattern (resolution) can be modified. Second, the used printing system allows the deposition of several drops with a single piezo pulse. Finally, the number of deposited layers can be varied.

In this trails single drops are deposited in an 85 µm grid and ten layers are printed in total.

Results

As expected the printing behavior confirms the assessment regarding the particle size and nozzle diameter mentioned above [5]. The 75 µm nozzle does not allow for a stable printing process. At low piezo voltages the drop generation is irregular and unreliable. At higher piezo voltages a reliable drop deposition is possible in general, but the drop shape is not acceptable. It becomes irregular and satellite drops occur. Using the 100 µm nozzle a reliable printing process can be achieved. Drop shape and drop generation are satisfying.

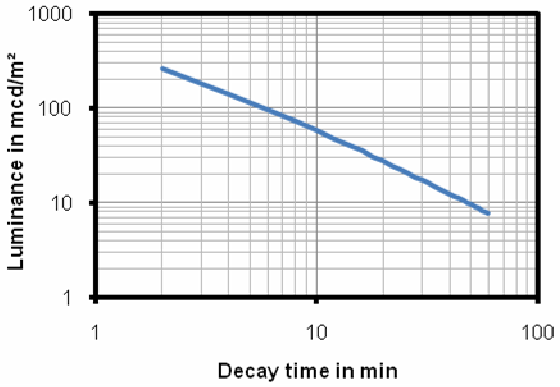

***Figure 2.** Luminance of inkjet-printed substrate; entire area of four square inch; ten layers*

A luminance measurement is done according to the DIN standard 67510-1. **Figure 2** shows the luminance over a certain decay time. Maximum luminance is 1335 mcd/m² at the beginning of the measurement. After ten minutes it decreases to 57.7 mcd/m².

According to the DIN standard 67510-4 a minimum value of 23 mcd/m² is required after 10 minutes for safety applications.

Electrophotography

While electrophotography is an established and highly developed technology for graphic printing applications, it still is rarely used in functional printing. The process is based on a photoconductor, on which a latent image is created by charging it via a corona and selectively discharging it via a light source (laser, LED). A toner powder, which is tribocharged in a developer station, adheres to the discharged area of the photoconductor, before it gets transferred and fused to a substrate, usually paper [7].

To use this method for printing phosphorescent particles, a toner based on the already mentioned SN-F5 particles is produced in cooperation with Zobrist Engineering in Switzerland. This toner is filled into a printer prototype existing at HSU. The printer is manufactured by CTG PrintTEC and is used at HSU for functional printing applications [2].

Printing Equipment

The printer prototype was developed especially regarding its robustness, its flexibility and its capabilities in functional printing applications. It uses an organic photoconductor (OPC) and an LED light source, creating a resolution of 600 dpi. The OPC requires negatively charged toner, which is charged in a two-component developer system.

Due to a special developed transfer roller, the OPC is not in direct contact with the substrate [8]. Hence, the printer is capable of printing onto soft as well as onto hard substrates. This is of relevance because in many security applications, phosphorescent particles are printed onto inflexible metal, glass or polymer signs. To transfer the particles, the substrates are charged via a corona, so that the transfer from the roller is performed via mechanical as well as electrical force. The transferred toner is fused via an infrared heater.

Toner production

A toner generally has to fulfill certain requirements. Especially a charge of approximately 20 µC/g should be achieved and particle size should be between 5 and 20 µm. Furthermore, it has to have good fluid capabilities, so that it does not agglomerate inside the developer station.

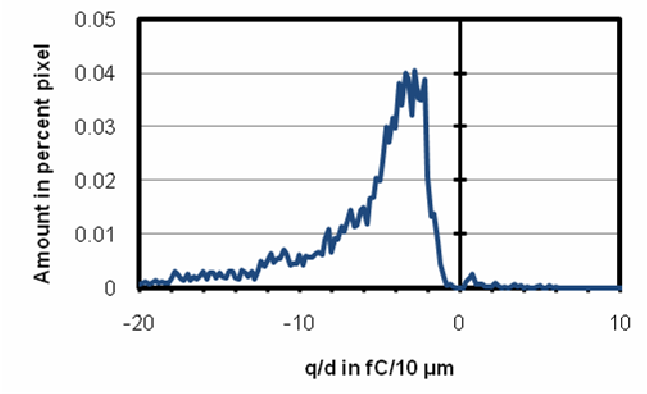

Figure 3. *Charge distribution of Lumix toner*

The already mentioned, size of SN-F5 particles size between 5.06 µm and 7.5 µm is, contrary to ink-jet, not a very challenging aspect. Actually, the particles are in an ideal range for toner production. More challenging is their charging behavior. When trying to charge pure SN-F5 particles, only low charges of 8 µC/g can be created, unfortunately only with an undesired positive polarity. This fact gets more important when considering that the concentration of phosphorescent particle in the toner should not go under 40 %, in order to achieve sufficient luminosity.

Nevertheless, the mentioned challenges are overcome by using well-selected additives and by using a special process technique in the extruder. So, a very homogenously, negatively charged toner is created that can be used in the presented printer. The charge distribution of the created toner named "Lumix", measured using the EPPING q/d-meter [9], is displayed in **Figure 3**. The mean q/d value is between -5.44 and -6.52 fC/10 µm and only about 1 % of positively charged particles occur.

Results

To evaluate the possibilities of the process, two major sets of tests are performed. One set examines the capability of printing onto multiple substrates, especially signs; the other one examines the luminance of the printed structures.

Generally, the toner is printable without any major drawbacks. No noticeable problems occur when using Lumix inside the printer prototype. The printed structures are well-shaped and only few satellites, implying wrong-polarity particles, are detected.

Printing on paper is reliable and the results seem to be comparable to regular pigmented toner. However, other substrates show a slightly interesting behavior.

Metal signs, in our case aluminum signs, are well to print on in general. The transfer to substrate can be created by electrically charging the signs with the corona; the metal seems to be charged easily. Fusing the particles with the infrared heater works not very well, assumingly due to the good heat conduction of the metal. However, the particles can be fused in an oven, at about 120 °C, without any problems. Furthermore, a hot transfer was possible, realized by pre-heating (also approx. 120 °C) the substrates before printing, so that transfer and fusing process are merged.

When printing on glass, the transfer via charge does not work very well. Obviously, no sufficient charge is creatable on its surface. However, on the other hand, hot transfer works pretty well.

Problems occur when trying to print on polymer signs. The ones used in this study do not charge well, so that an acceptable transfer is not performed. Furthermore, the polymer has a softening temperature of about 80 °C, so that neither hot transfer, nor any fusing works well with these materials.

In order to evaluate the luminance of the prints, also a test according to the DIN standard 67510-1 is performed. The results are presented in **Figure 4**, where two representative measurements are displayed. Five printing cycles are performed, on paper as well as on surface-treated aluminum.

On paper, a maximum luminance of 207.9 mcd/m² is reached at the beginning of the measurement. After ten minutes it decreases to 5.73 mcd/m². Aluminum prints reach 93.5 mcd/m² at the beginning and 3.02 mcd/m² after ten minutes.

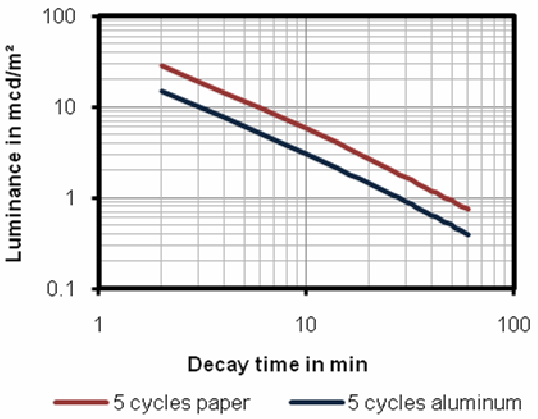

***Figure 2**. Luminance of laser-printed substrates*

When judging the aluminum, it has to be taken into consideration that the sign used in this test is silver colored, which is a major disadvantage towards a white background. However, the minimum value of 23 mcd/m² after 10 minutes according to the DIN 67510-4 standard cannot be fulfilled, yet.

Conclusion

The presented results show that it is possible to digitally print phosphorescent particles. Both methods are applicable and yield good results. The purpose of the presented study could be fulfilled in total and feasibility of both methods is proven. Due to the fact this is only a first approach, of course, new knowledge could be gained and further room for improvement can be determined.

Regarding ink-jet, the incompatibility of the particles with water is overcome by using an organic solvent. With the used solvent and additives an ink formulation is realized, which is printed successfully and has no negative influence on the functionality of the particles.

The sedimentation velocity of the particles could be decreased sufficiently. To ensure a reliable printing process mechanical stabilization is recommended additionally. In future, further improvements considering particle size, solvent and additives are possible. However, the luminance measurements already show remarkable results.

Regarding electrophotography, the luminance values are about one decade lower, but it has to be taken into consideration that only five printing cycles are performed and that other substrates are used.

Also, the performed study yields new approaches to improve the method. As mentioned before, the used particles, without any treatment, charge positively, but a negatively charged toner has to be produced due to the fact that this is required by the used printer. Assumingly, toner charge can be increased when using another printer that prints positive toner. So, the toner charge would benefit from the positive charge of the particles. Furthermore, in relation to other phosphorescent particles, relatively small particles are used. Bigger particles will yield better luminance, and contrary to ink-jet printing, particles are not as limited in size to work in the process.

Furthermore, the substrates are not yet prepared for electrophotographic printing either. A treated surface allowing higher charge or better background properties, a toner fitting to certain substrates and vice versa and respective modification of the printer would certainly improve the performance of the whole process and lead to higher luminance.

In summary, both technologies are capable of printing phosphorescent particles. Of course, the phosphorescent products on the market made by screen printing still perform significantly better than the ones produced with our new technologies. Nevertheless, when it comes to small batch series or personalized products, both technologies are capable of supplementing the established technology. Electrophotography offers capability of printing big particles in a high-speed, solvent-free process, applicable to flat substrates, while inkjet printing offers a very flexible, contact-free method to print smaller particles on all kinds of substrates, including those with a structured surface. The results at HSU show the feasibility of the processes and yield challenging topics for the future.

References

[1] W. Diel, M. Waßmer, K. Krüger, "Inkjet Printed MgO-Thickfilm-Layer with Embedded BST Pillars", Proceedings 7th CICMT, San Diego, (2011).

[2] D. Büttner et al, "Laser Printing of RFID Coils on Ceramic", Proceedings 7th CICMT, San Diego, (2011).

[3] S. B. Fuller, E. J. Wilhelm, J. M. Jacobson, "Ink-Jet Printed Nanoparticle Microelectromechanical Systems", Journal Of Microelectromechanical Systems, Vol. 11, Issue 1, pp. 54-60, (2002).

[4] W. Diel, M. Waßmer, K. Krüger, H. Naghib-Zadhe, T. Rabe, „Einfluss unterschiedlicher Dielektrika bei der Realisierung von Dickschichtkondensatoren im Tintenstrahldruck", IMAPS Deutschland, München, (2009).

[5] X. Li, "Ink-jet Patterning of Functional Materials", Report in Top Master Programme in Nanoscience, Zernike Institute for Advanced Materials, University of Groningen, (2007).

[6] M. Waßmer, W. Diel, K. Krüger, "Inkjet printing of post-fired thick-film capacitors", Proceedings 5th CICMT, Denver, (2009).

[7] M. Hoffmann-Falk, "Digital Printing", Océ Printing Systems, Poing, (2006).

[8] W. Weinberg, P. Auchter-Krummel, D. Jung, "Device for Applying Decors and/or Characters on Glass, Glass Ceramics and Ceramic Products", International Patent # WO 00/25182, May 4th, (2000).

[9] A. Küttner, R. H. Epping, "Theory and Practice of a Small Toner-Charge-Spectrometer", NIP 14, Toronto, (1998).

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