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Merge Technologies for Multifunctional Lightweight Structures

ADAPTED PARTICLE-FREE SILVER INK FOR THE MANUFACTURING OF THIN CONDUCTIVE PATTERN BY GRAVURE PRINTING AND NIR-SINTERING

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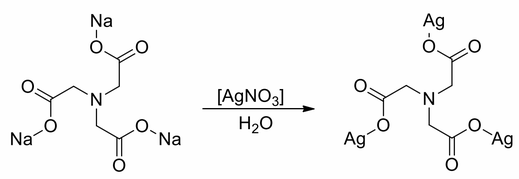
Introduction

Silver(I) carboxylates are suitable precursors to produce thin, highly pure and dense silver layers of high conductivity on diverse substrate materials which is of importance for micro- and nanoelectronic industries[1]. Nevertheless, for most flexible substances to be metallized, the thermal conversion of silver(I) complexes to silver is a challenge because of the limited thermal stability of the appropriate polymeric substrates[2,3]. Gravure printing is a key additive material deposition technology for printed electronics[4]. The process is flexible in the use of inks and is able to manufacture different layer thicknesses by changing the dipping volume of the engraved cells in the printing cylinder. Also precursors can be converted conciliatory, due to the use of controlled radiation.

Experimental and Results

Synthesis and Properties



1 **2**

Scheme 1: Synthesis of $[(AgO_2CCH_2)_3N]$.

The synthesis of colorless $[N(CH_2CO_2Ag)_3]$ includes the reaction of nitrilotriacetic acid trisodium salt with three equivalents of $[AgNO_3]$ in water at ambient temperature and with exclusion of light, due to the light sensitivity of the respective silver(I) compound. It is advisable to consecutively wash the respective silver carboxylate with water and diethyl ether to obtain a pure product.

Compound **2** was characterized by elemental analysis (calculated for $C_6H_6Ag_3NO_6$ (511.72 g/mol) [%]: C, 14.08; H, 1.18; N, 2.74. Found: C, 13.89; H, 1.00; N, 2.72) and infrared spectroscopy ((KBr) [cm^{-1}]: v 1588 (s), 1405 (s), 1332 (m), 1260 (m), 1146 (w), 1019 (w), 991 (w)).

The thermal behaviour of $[(AgO_2CCH_2)_3N]$ was studied by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The TG- and DSC-traces are depicted in *Fig. 1*. Experiments were carried out with a gas flow of 40 mL/min argon, 20 mL/min oxygen and a heating rate of 10 K/min. The thermal decomposition takes place at an onset temperature of 147 °C and a weight loss of 38.4 % to give silver as confirmed by X-ray powder diffraction (= XRPD) studies as shown in *Fig. 2*. The resulting residue shows a further weight loss of 1.1 % within 150 to 450 °C, indicating the removal of oxidizable impurities within the silver layer. The amount of residue (m_{exp} = 60.5 %, 500 °C) in the TG experiment is in acordance to the theoretical amount (m_{theo} = 63.2 %) of silver present in the complex. Hence, complex **2** reveals a spontaneous decomposition at low temperatures.

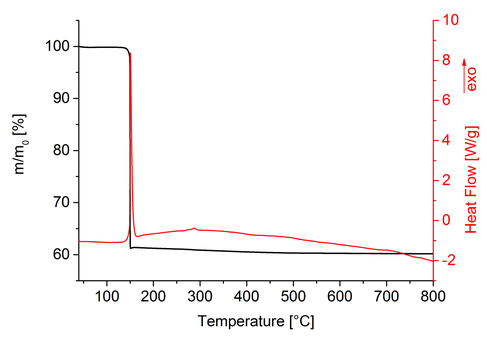


*Fig. 1: TG (black) and DSC (red) traces of **2** (heating rate 10 K/min, argon flow rate of 40 mL/min and oxygen flow rate of 20 mL/min).*

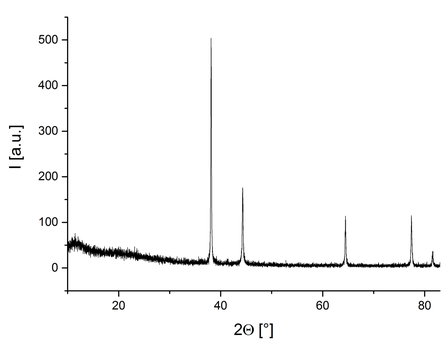


Fig. 2: XRPD-traces after heat treatment of **2** at *160°C.*

Printing

The ink from precursor **2** was prepared with 1.2-diaminopropane (ω = 59 %), the viscosity can be set-up by adding 50 weight percent of ethylene glycol.

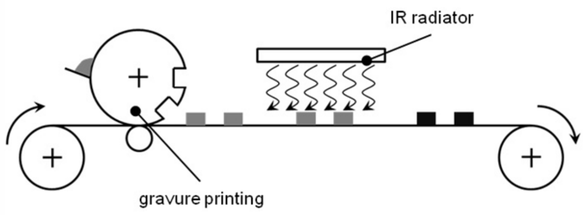


Fig. 3: Manufacturing of functional lightweight structures by R2R gravure printing and back injection molding[4].

The process steps to manufacture roll-to-roll gravure printed silver patterns which are cured by infrared sintering and applied into back-injection-molded functional lightweight structures are as depicted in *Fig. 3*.

The presented patterns are deposited with a hybrid roll-to-roll laboratory gravure printing equipment on 100 µm thick, flexible polyethylene terephthalate (= PET) films with a web velocity of 6 m/min. To transform the printed precursor ink to conductive silver patterns a special designed IR emitter system for printed electronics was used.

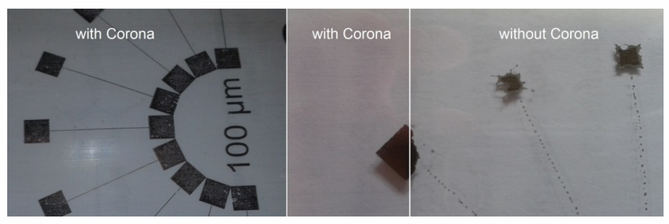


Fig. 4: Printing images of produced silver patterns with (left) and without (right) Corona pretreatement.

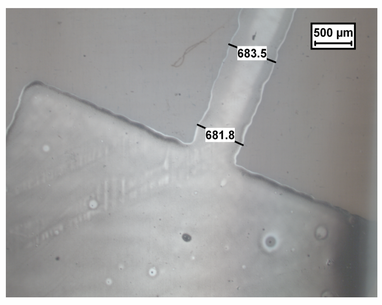


Fig. 5: Printing image of a single silver pattern.

Silver thin films on PET substrates reveal insufficient wetting. To optimize the wettability of polymer substrates it is a common technique to apply an inline Corona pretreatment of the surface of the polymer film. In the experiments the Corona pretreatment was done directly after unwinding the substrate with an energy of 0.82 kW at a printing speed of 6 m/min. The effect of pretreating is shown in *Fig. 4.* Due to substrate pretreatment a consistently good print image is available as depicted in *Fig. 5.*

Conclusion

The simple and cost efficient synthesis and thermal behavior of $[N(CH_2CO_2Ag)_3]$ is reported. Inks therefrom where printed with a hybrid roll-to-roll laboratory gravure printing equipment with a web velocity of 6 m/min on 100 µm thick, flexible PET, revealing good printing images due to Corona pretreatment. Therefore, this system enables mass production of conductive silver patterns at high speed and with good reproducibility.

References

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This work was performed within the Federal Cluster of Excellence EXC 1075 “MERGE Technologies for Multifunctional Lightweight Structures” and supported by the German Research Foundation (DFG). Financial support is gratefully acknowledged. We also thank L. Mertens and Prof. Dr. M. Mehring for XRPD studies.

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