Initial Steps to Develop Piezoelectric Inkjet Ink Containing Stimuli-responsive Pigments

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Abstract
Stimuli-responsive inks can appear in a 1-bit binary state - in two binary modes - by defining an upper and a lower limit as an active (1) or inactive (0) mode. They are also known as smart materials, which can report - by color changing - different environmental influences such as water/moisture, temperature, UV-light, pH, etc. Based on this behavior, smart materials are able to store information inside an intelligent dot code in form of zeros and ones (e.g. an analog relay). Thus, a sensor can be created, which works without any energy supply and which can be cheaply printed by means of inkjet printers.

The first step of the feasibility analysis was to examine, how stimuli-responsive inks for screen-printing can be modified to develop switchable inks for piezoelectric inkjet. Second step was to examine the printability of the developed inks. A piezoelectric inkjet printer was used to realize first printings. It was done to observe how technical parameters could influence the functionality of the printed smart materials. An intelligent dot matrix code could display where environmental influences can damage certain products such as seeds, food, electronics, pharmaceuticals and more.

In this paper, the compound characteristics of the stimuli-responsive inks and first research results of the developed smart materials will be compared.

Introduction

Smart materials or stimuli-responsive inks change their absorption spectrum through light (photochromism), temperature (thermochromism), pH (acid-base indicator), water (hydrochromism), etc. (Harvey, 2006). After receiving a certain stimulus, these stimuli-responsive inks can change their color, their index of refraction, and their volume (Bilgin & Backhaus, 2017, a; Harvey, 2006). Stimuli-responsive inks can be developed in many ways and can cover a wide spectrum of different chemical molecules, compounds or functionalities. One of these are chromophores, they are color bearing, often covalently unsaturated groups of conjugated π-bond systems (Herbst & Hunger, 1995). They impart color to a compound and they are responsible for absorption in UV (100380 nm) or visible/VIS (380790 nm) region (Latscha & Kazmeier, 2017). An increasing number of the conjugated double bonds induces an absorption shift (bathochromic shift) to a visible region (Cranwell et. al. 2017). Another option to develop smart materials is microencapsulation. The core (ink) of a microcapsule is surrounded by a shell (coating) with functional properties, e.g. paraffin wax (melts by heat), galantine (melts by water), polyvinyl alcohol (melts by water), etc. Some microcapsules can be charged electrically to change their color, e.g. e-inks in e-papers. Another compound is spiropyran. The reversible closure properties of the spiropyran becomes induced by heat or light colored (Hirshberg & Fischer, 1954).

The functionality of stimuli-responsive inks are usable to report environmental influences by switching between minimum two binary modes (from an inactive (0) mode into an active (1) mode), without any energy supply. Various stimuli-responsive dyes or pigments can be embedded into base-inks, to make them printable for different printing techniques. Through printing different sensitive dots in form of a variable dot-matrix-code, it is possible to store different dynamic states next to static information. Printed on a label, it can be applied to any product, e.g. house facades (to check the pH for mouldiness), electronics, seeds, cosmetics, etc. Thus, an intelligent code is able to communicate with the Internet of Things by the use of customary smart devices (e.g. smartphones, tablet, etc.), which can scan the intelligent code with an integrated CCD-camera, send current data to the server and get analysed data e.g. products' history. The aim of this research was to develop switchable inkjet inks, by the modification process of switchable screen-printing inks. Furthermore, characteristic behaviour of the switchable inkjet ink was to be examined and analysed.

Materials and Methods

Past investigations were realized with screen-printing and flexo-printing inks. A semiautomatic screen printer (SPS-Uniprint) was used to print all specimens in various layer thicknesses, by the use of different polyester screens. Because of this fundamental research, their behavior, properties, functionality and the influence of technical parameters (e.g. full tone, halftone dots, etc.) could be determined (Bilgin & Backhaus. 2017, b). In the following research, all experiments were done with a piezoelectric inkjet printer.

Instruments

All specimens were printed by a piezoelectric inkjet (Epson WorkForce WF-3620). Technical parameters: Print Head: PrecisionCore™; Thin Film Piezo element: 1/1000mm; Minimum Droplet Size: 2.8 pl (1.5 – 32.5 picoliters); Nozzle Configuration: 800 Nozzles Black (K), 256 Nozzles per Color (CMY); Printing Resolution: 4,800 x 2,400 DPI.

Measurements of characteristic remission curves and CIEL*a*b values of the stimuli-responsive inks were measured by a spectral-densitometer (TECHKON SpektroDens). Technical parameters: polarizing filter: off; type of light: D50, 2° standard observer; diameter of measuring orifice: 3 mm.

Rheological properties (viscous flow behavior) were measured by a rotational rheometer (Physica MCR 101) through a corresponding cone and plate measurement system (CP50-1); diameter: 49,966 mm; cone angle: 1°. The surface tension was analyzed with the bubble pressure method (SITA pro line t15).

Standardization

Possible deviations were recorded in logs - to ensure the reproducibility of this experiment. The temperature and humidity during the entire research were controlled with the help of an air-condition system. The temperature was continuously 20 ° C (± 1 ° C) and the relative humidity was 55% (±1%).

Test Chart

Experiments are based on the following test chart (Fig.1). This test chart shows a section for logs e.g. temperatures, date, time, ink, etc. - in the upper range and different solid colors (CMYK) - in the lower range. Stimuli-responsive inks will represent these solid colors: Cyan represents the hydrochromic ink; magenta: not defined, yellow represents a photochromic ink and black stands for static information e.g. text, symbols.

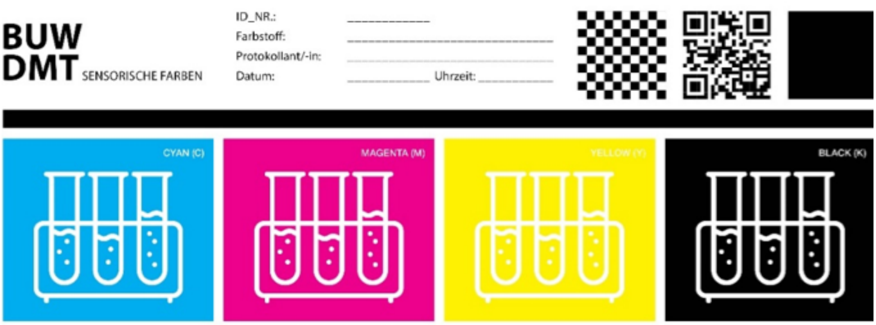

Figure 1: Simplified test chart CMYK

Materials

Substrates	Inapa tecno, oxygen pure high-white recycled paper, Format: 210 x 297 mm (A4), Grammage: 80 g/m^2
Inks	Photochromic ink (skyrad) • Color: transparent → dark blue • Viscosity 0.8000 Pa·s at 20 °C Hydrochromic ink (LCR Hallcrest) • Color: black → grey-transparent • Viscosity: 0.36000 Pa·s at 20 °C Epson piezoelectric inkjet ink • Color: black • Viscosity: 0.0050 Pa·s at 20 °C
Additives	Isopropyl alcohol (propan-2-ol / isopropanol) • Viscosity: 0.0022 Pa·s at 20 °C Vinyl acetate • Viscosity: 0.0041 Pa·s at 20 °C
Equipment (Filtration)	Millex-SV (SLSV025LS) • Pore Size: 5.0 µm • Maximum Inlet Pressure: 5.2 bar (75 psi) • Hold-up Volume: < 0.1 mL • Filtration Area: 3.9 cm^2 • Material: Hydrophilic Polyvinylidene Fluoride (PVDF)

Table 1: Materials

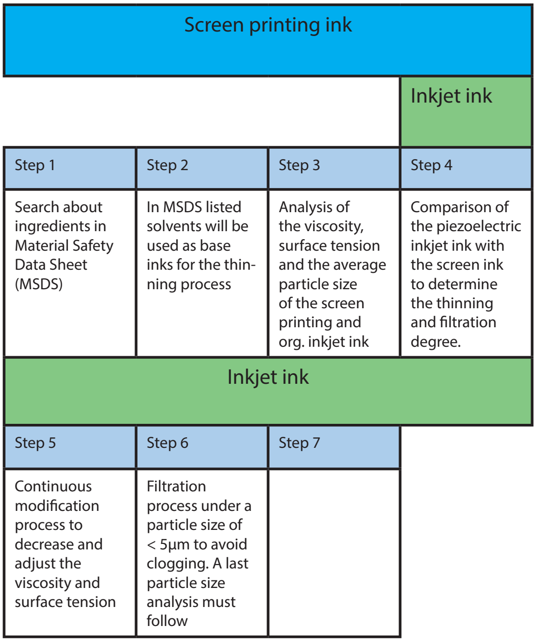

Figure 2: Modification process to develop a piezoelectric inkjet ink

Results and discussion

Method 1: Developing Switchable Inkjet Inks

In the following, the possibility to develop switchable inkjet inks from solvent- and pigment based screen-printing inks will be investigated. A simple approach for the feasibility analysis was pursued - a full characterization will follow. The resulting inks were printed on a laboratory scale (Fig.2). Its modification process bases on eight steps and will be realized with methods of filtration and thinning, under observance of the physical inkjet parameters such as viscosity, surface tension and particle size (Zapka, 2018).

In the first step, the material safety data sheet (MSDS) of a screen-printing ink will be examined for additives and information about pigments or dyestuffs. In the second step, the solvents in the MSDS will be used for the thinning process. In the third step, the three parameters: viscosity, surface tension and the particle size of both inks (original inkjet ink and screen-printing ink) - will be analyzed to determine the actual parameters and the target parameters. In the fourth step, both inks will be compared to determine the thinning and filtrations degree. In the fifth step, the decrease and adjustment of the viscosity and surface tension will be analyzed. The viscosity of an inkjet ink is typically in a range from 0.001 to 0.05 Pa·s (Zapka, 2018). In this experiment the Epson inkjet ink has a viscosity at an average of 0.0050 Pa·s at 20 °C and isopropyl alcohol has a viscosity at an average of 0.0022 Pa·s at 20 °C. The sixth step contains a filtration process. The particle size must match with the diameter of the nozzles (print head) – a stepwise filtration process can control the particle size, often ≤ 5 µm. Harmful factors such as agglomerating must be avoided through additives (ibid.). Additionally, a last particle size control is necessary, to assure the required particle size of the modified ink. A negative aspect of the filtration process is that many functional particles (> 5µm) get lost. Finally, a test print can be done to validate the correct functionality of the developed inks. The following samples are based on the developed switchable inks.

Method 2: Printability of stimuli-responsive inks

Stimuli-responsive inks appear in minimum two binary modes – by defining an upper and a lower limit – by changing their color from an inactive (0) to an active (1) mode. In Figure 3, all matrix codes were printed completely with stimuli-responsive inks. The progress of the reaction can take place in a reversible or irreversible form. Reversible inks return to their initial state if a certain stimulus is removed or another stimulus (e.g. heat or a particular wavelength) induces a switch back e.g. spiropyran. Irreversible inks switch in their new state and cannot switch back - a kind of chemical counterfeit functionality is given. In Figure 3, different stimuli-responsive inks that were printed by an inkjet printer and a screen printer can be seen.

The hydrochromic (response to water) and photochromic (response to UV light) inkjet inks (described in method 1) were printed by using two different printing techniques in order to examine its color switching functionality, its reaction progresses and to identify possible binary states. The upper range shows their original states and the lower range shows their states after stimulus. Color values (Fig.3) were measured according to CIEL*a*b and RGB in a greyscale mode to detect the progress of color switching. L* describes the luminance of a color with values from 0 (black) to 100 (white) and RGB in a greyscale mode describes the contrast differences with values from black (0,0,0) to white (255,255,255). The screen-printed (SP) and inkjet-printed (IP) hydrochromic ink show a direct contrast difference between its states before/inactive (SP L*:7 and IP L*:2) and after activation (SP L*:58 and IP L*:50) by a water drop. The contrast difference of the photochromic ink can also quantifiable between its states before (SP L*:60 and IP L*:80) and after activation (SP L*:40 and IP L*:60) by UV-light. Therefore, it is possible to define limitations (e.g. an upper limit and a lower limit) in form of binary states (1-bit: 0 or 1). The CCD-camera of a smart device can quantify dynamic (switchable) and static dots of an intelligent code under control of different light conditions. The switchable dots (magenta highlighted in Figure 3) can be integrated into a dot matrix code by elimination or modifying the error correction.

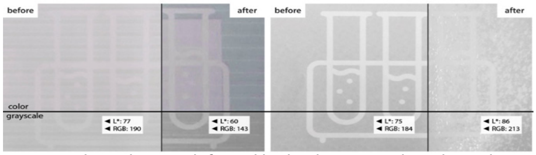

Figure 4: Photochromic (left) and hydrochromic (right) inkjet ink printed surface

Figure 4 displays the color switching functionality of the photochromic inkjet ink before and after an exposure (UV) duration of about 20 minutes and the switching functionality of the hydrochromic inkjet ink before and after an activation with water (simulation of raindrops). Moreover, the color was reduced to the maximum dilutable concentration of 25% - without losing its functionality - compared to the photochromic and hydrochromic inkjet ink in figure 3.

Method 3: Characteristics and Behavior

In the following, the characteristic wavelength parts of the modified hydrochr-omic and photochromic inkjet inks will be presented to reveal information about its color switching behavior. Especially the contrast and color difference of the both inks, before and after activation, is to be analyzed. Its comparison with the CIEL*a*b and RGB values for a binarisation process are of interest, to localize causing color changing ranges of the wavelength.

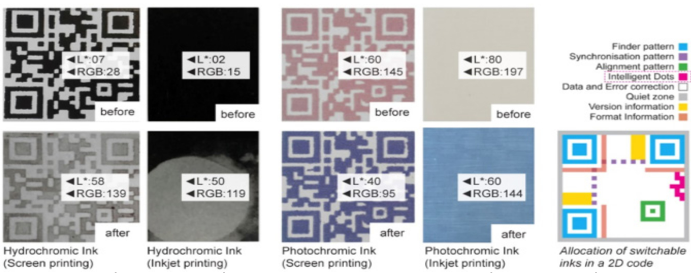

Figure 3: Stimuli-responsive dyes pre/inactive (upper range) and post/active (lower range)

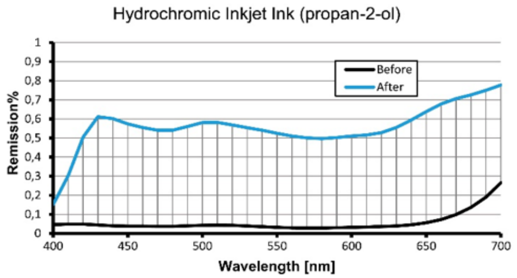

Figure 5: Spectral analysis pattern of the hydrochromic inkjet ink

The degree of remission of the thinned hydrochromic ink (Fig.5) decreases after contamination with water from almost 0.05 % to almost 0.6%; its black color shifts to grey-transparent. The reaction process of the hydrochromic inkjet ink is constant from 400 to 650 nm. The reaction process of the photochromic ink (Fig.6) begins at 450 to 700 nm. The differences are positive at 500 to 700 nm.

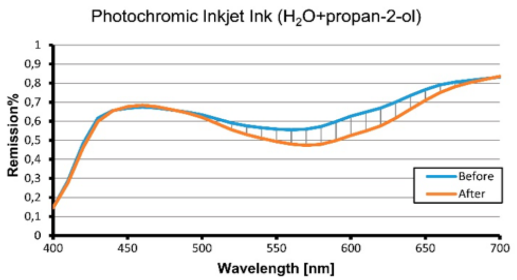

Figure 6: Spectral analysis pattern of the photochromic inkjet ink

Additionally, the rheological flow behavior of the modified stimuli-responsive inks was analyzed (Fig.7). Here especially the viscosity of the original screen-printing ink and the modified inkjet inks will be compared to display the process of thinning. The target piezoelectric inkjet inks show a Newtonian behavior with a low viscosity. In comparison, screen-printing inks show a higher viscosity and a non-Newtonian behavior (shear thinning). They are optimized to flow when the squeegee shears it (viscosity decreases over the shear time). The hydrochromic ink has a nearly shear thinning behavior, between shear rates from 2 s-1 to 20 s-1 and a viscosity about 0.46 Pa·s. It shows a nearly Newtonian behavior and behaves viscoelastically above 40 s-1. Possible viscosity deviations during the printing process should be considered. This is necessary to prevent performance problems.

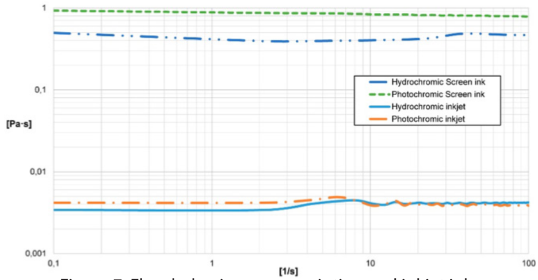

Figure 7: Flow behavior screen-printing and inkjet inks

The photochromic screen-printing ink shows mostly a small constant progression, with a viscosity at an average of 0.81 Pa·s. The viscosity of the original piezoelectric inkjet printer ink is in average at 0.0050 Pa·s at 20 °C – the target thinning value.

The material safety data sheet (MSDS) lists the solvents of the hydrochromic screen-printing ink – the solvents can be used for the thinning process. The listed materials: isopropanol alcohol (20 % – 30 %), with a viscosity of 0.0022 Pa·s at 20 °C and vinyl acetate (10 % – 20 %), with a viscosity of 0.0004 Pa·s at 20 °C. The thinning process was carried out through isopropanol. After the thinning process, the viscosity of the hydrochromic screen-printing ink could be reduced from 0.46 Pa·s to 0.01 Pa·s. The photochromic screen-printing ink was thinned through water and isopropanol alcohol from 0.81 Pa·s to 0.004 Pa·s.

At last, the surface tension of the developed switchable inkjet inks is shown in Figure 8. The surface tension of both inkjet inks were examined with the bubble pressure method (SITA pro line t15), since it is related with the drop formation.

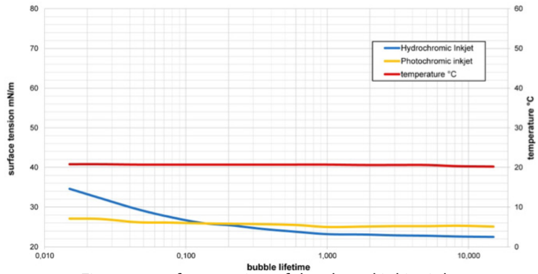

Figure 8: surface tension of developed inkjet inks

The surface tension of the hydrochromic inkjet ink was around σ = 25.76 mN/m and photochromic inkjet ink around σ = 25.72 mN/m, both at about 21°C. The surface tension working range is around 25 to 50 mN/m (Magdassi, 2010).

Conclusions

The development process from screen-printing inks to printable inkjet inks could be completed under the control of the physical inkjet parameters such as viscosity, surface tension and particle size. Harmful particles could be filtered to get suitable particle sizes ≤ 5µm. Its surface tension was also controlled and is in a stable region from about $\sigma = 23$ mN/m at around 20 °C. The last parameter to control was the viscous flow behavior of the inkjet ink. The viscosity of the hydrochromic ink could be reduced from 0.46 to 0.01 Pa·s and additionally the viscosity of the photochromic ink could be reduced from 0.81 to 0.004 Pa·s. Both developed switchable inkjet inks were printed with an Epson WorkForce WF-3620. The printed samples were measured to get RGB and CIEL*a*b values. Although larger pigment particles were removed during the filtration process, enough smaller colorant particles remained in the ink to ensure functionality. Its digital transformation from the measured greyscale RGB and L* values was successful.

Here, especially the color switching behavior (contrast difference) could be translated into binary information to visualize deviations caused by environmental influences. The next step will be the development of the intelligent code and the corresponding analysis of the data and their storage on a webserver.

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