JPMTR 123 | 1901
DOI 10.14622/JPMTR-1901
UDC 621.798-027-035.67

Research paper
Received: 2019-01-09
Accepted: 2019-06-24

Smart packaging by the application of sensitive dyes

Mustafa Bilgin and Johannes Backhaus

Bergische Universität Wuppertal,
Rainer-Gruenter-Straße 21, 42119 Wuppertal, Germany

bilgin@uni-wuppertal.de
jbackhaus@uni-wuppertal.de

Abstract

Smart packages can communicate with their users or other clients via the Internet of Things. By means of sensitive dyes implemented in an intelligent code, the code is able to report the history of critical environmental influences on the package and accordingly on the packed goods during the entire transport path. So all steps from manufacturing to delivery can be traced without any energy supply. Moreover, these intelligent codes are composed of different sensitive dyes in the form of dots. Each smart dot can change its colour from an inactive state into active states, in the form of colour gradations. Thus, a critical value of colour gradation can be defined as limitations that set the sensitive dot's state from inactive [0] to active [1]. Hence, static consumer or product information and dynamic information about environmental influences – e.g. water/moisture, temperature, UV-light, pressure, acids, etc., can be stored in one entire code. The use of various sensitive dyes also adds a significant anti-counterfeiting feature and a chemical fingerprint. The intelligent code can be cost-efficiently printed as a printable sensor. Furthermore, the intelligent code can be read and analysed by usual smart devices, e.g. smartphone, tablet, etc. – linked to a specific web server where the code can be compared with its original state, to indicate critical deviations. The foreground of this paper is the application of sensitive dyes (sensitive dyes are as well named as smart materials) in order to get information for comprehensive research. First, the printability of the sensitive dyes is examined as well as their reaction process and behaviour depending on technical parameters, e.g. viscosity. Second, their reaction processes and reaction times in dependence on different layer thicknesses based on various polyester screens and the remissions of the printed samples are analysed. Third, the characteristic wavelength changing of the sensitive dyes is shown, which will allow further investigations by a smartphone.

Keywords: smart materials, intelligent code, thermochromism, hydrochromism, photochromism

1. Introduction

Chromophores are the colour-bearing groups of molecules. They impart colour to a compound. They are often in organic solutions, where they have covalently unsaturated groups of conjugated π-bond systems, which are responsible for absorption in UV (100 nm to 380 nm) or visible/VIS (380 nm to 790 nm) spectral region (Latscha, Kazmaier and Klein, 2017). The chromophore structure of benzene (with a spectral bandwidth at 255 nm) is colourless, beyond visible wavelengths (Hesse, Meier and Zeeh, 2008). Many natural dyes like β-carotene (460 nm) in carrots and lycopene with a visible spectral bandwidth at 473 nm to 503 nm (Figure 1) in tomatoes have a large system of conjugated π-double bonds, which consist of alternating single and double bonds (Latscha, Kazmaier and Klein, 2017).

Some molecules have a small number of conjugated double bonds, which absorb non-visible radiation within a band of short-wavelength. If the number (n + 1) of conjugated double bonds of these molecules increases,

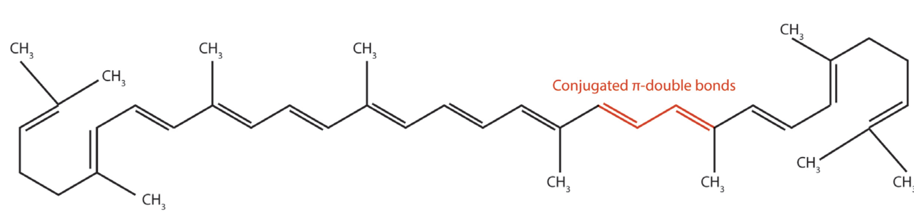


Figure 1: Lycopene

the absorption shifts to longer-wavelengths of VIS (Cranwell, Harwood and Moody, 2017). The particular energy of a wavelength defines the colour (Brown and Holme, 2015). Because of the absorption in the UV-VIS, the reflected light of the chromophore structures appears in a complementary colour (Herbst and Hunger, 1995). The intensity of colour increases by the number of delocalized electrons, shifts by absorption to longer wavelengths (bathochromic shifts) and needs lower frequency/energy. The gap between highest occupied molecular orbital – HOMO and lowest unoccupied molecular orbital – LUMO (HOMO–LUMO) energy is small (Engel and Reid, 2006). Shifting to shorter wavelengths (hypsochromic shifts) needs higher frequency/energy, because the gap between HOMO–LUMO is larger (Kalsi, 2005). Sensitive dyes change their absorption spectrum by light (photochromism), temperature (thermochromism), pH (acid-base/halochromism), water/humidity (hydrochromism), etc. – particular influences (stimuli) of the environment makes the dyes respond (Herbst and Hunger, 1995). During a stimulus-induced shift, these sensitive dyes change their colour, their index of refraction, and their volume (Bilgin and Backhaus, 2017a; Harvey, 2006). A well-known organic compound is spiropyran. Induced by heating and light irradiation it becomes coloured (Hunger, 2003). Hirshberg and Fischer (1954) observed the photochromic reaction of the spiropyran as the first ones in 1952. Hirshberg's vision was a photochemical memory model on the base of spiropyran: "Use of the phenomenon as a memory in a 'computer' as a 'high-speed memory' " (Hirshberg, 1956). This idea of a 'memory' can be extended through the use of printed autonomous sensors on a chemical basis, which records external influences. The use of sensitive dyes as printable sensors is a new field of application.

1.1 Smart packaging

With the Internet of Things (IoT), everything becomes smart and is connected to each other in an autonomous network to accomplish preassigned tasks (Ashton, 2009). For example, an object (e.g. a package) which is equipped with add-ons becomes intelligent when it includes an energy supply, printed electronics, sensors, integrated displays, audio input/output, communication technologies, programming code and more. There are various terminologies like smart, active and intelligent packages, with different definitions (Schaefer and Cheung, 2018):

1. Smart packaging: technologies with integrated functionalities, which can be chemical, electrical or kinetic.

2. Active packaging: subsidiary constituents enhance the performance of the package system, e.g. package material can absorb moisture, oxygen or it can eliminate bacterial contaminations.

3. Intelligent packaging: appearance is observed to detect temperature or humidity deviations.

There are many efficient and effective product applications of smart packages that can provide customers with information about conditions of the product, e.g. in the fields of medicine, pharmaceuticals, food, cosmetic, and more.

1.2 2D/3D code

Compared with smart packages, intelligent codes have a couple of benefits. One of these is the printability of sensors by using different sensitive inks. Another benefit is the cost-efficient printing of different sensitive dots inside a dot matrix code like an invented system of a QR code, (Denso ADC, n.d.; Hara, 2006; International Organization for Standardization, 2015). Moreover, by printing sensitive dots in different layer thicknesses, information about the intensity and duration of contamination (3D coding) can be displayed (Bilgin and Backhaus, 2017b). In this way, a modified QR code can contain both static and dynamic information if the code is extended for dynamic dots. For this application of dynamic dots, irreversible inks (sensitive dyes) are required, which change their colour from one state to another without changing back. By the definition of an upper and lower threshold, the states (inactive [0] or active [1]) of each sensitive dot can be defined.

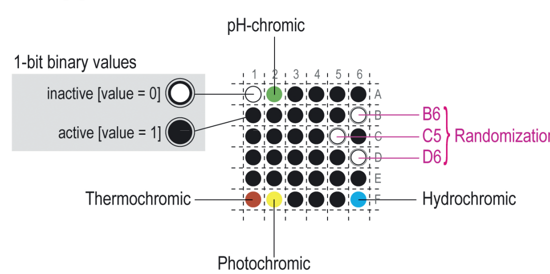


Figure 2: 1-bit binary values and randomized positions in a matrix

Furthermore, randomized allocation of the sensitive dots (Figure 2) can secure the code and gives it anti-counterfeited properties. Additionally, clusters of equal dots, which are at risk of partial contamination of one single cluster can be prevented (Bilgin and Backhaus, 2017a). Thus, static consumer or product information and dynamic information about environmental deviations, e.g. water/moisture, temperature, UV-light, pressure, acids, etc., can be stored inside an intelligent code.

1.3 Hardware and software

Smart devices such as smartphones, tablets, smart glasses, etc. are very popular in common use. They all are equipped with various helpful sensors. An impor-

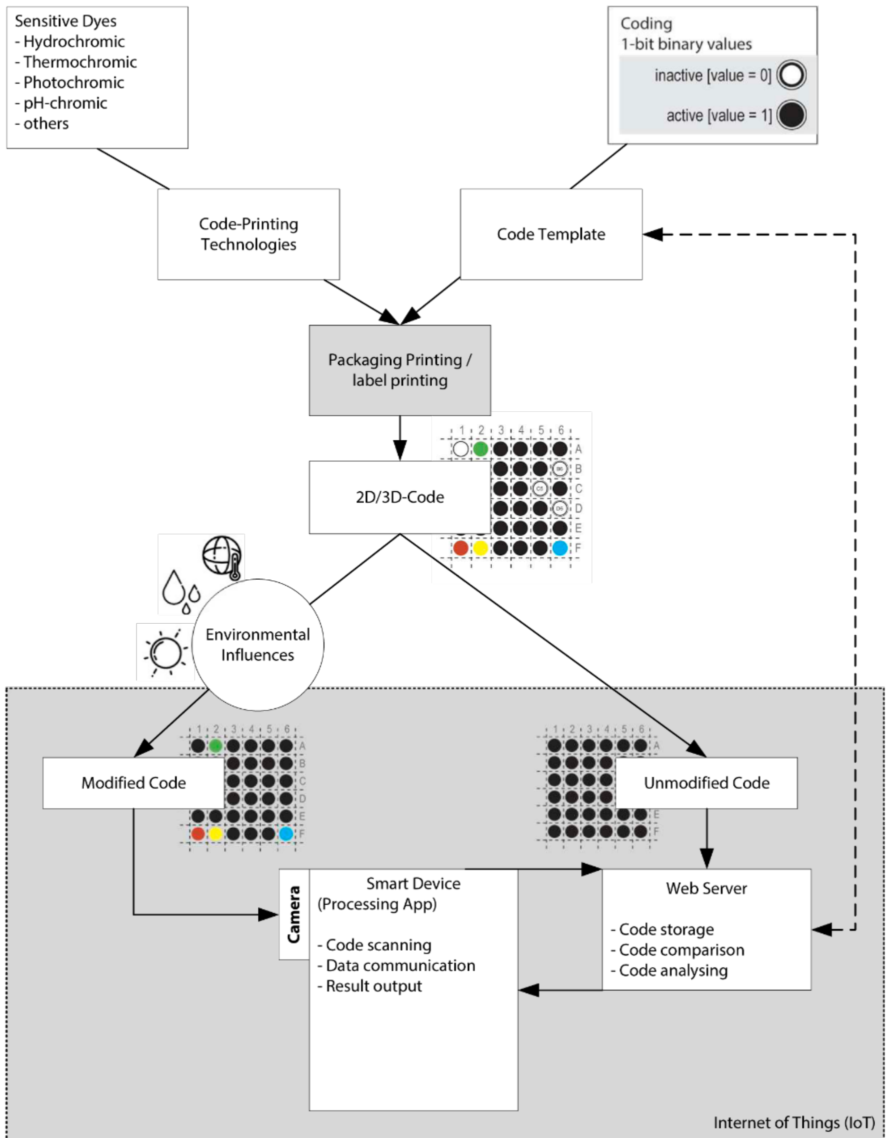


Figure 3: General concept of IoT based history tracing for packages

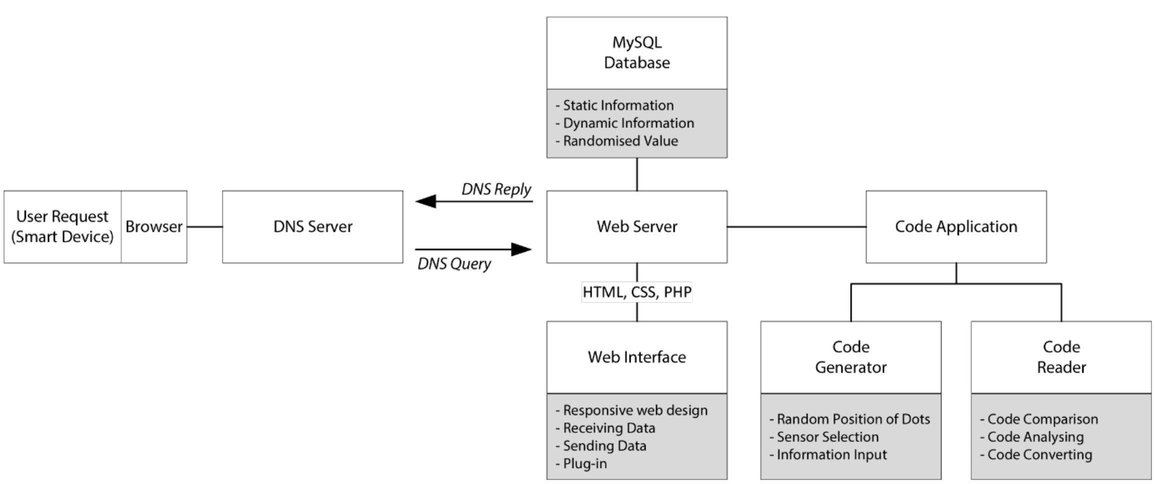


Figure 4: Software concept

tant component of smart devices is the CCD or CMOS image sensor. By means of the sensor, data (e.g. data of a QR code or intelligent code) can be read out and send bi-directionally via browser to a website on a secure web-server (Figure 3). Encrypted data exchange operates via web-server by a MySQL-database (Figure 4). The current state of the code will be transmitted and the package's history can be received via comparison with primary data. The server's web interface can be accessed by the web-browser via TCP/IP. Applications (Apps) are not necessary, because the browser directly accesses the web server via a web interface and domain address. The web interface based on HTML, CSS and PHP can be aligned by a responsive web-design to each screen resolution – independently of any hardware.

The aim of the work is to develop an overall concept for IoT-based history tracking for packages based on intelligent codes and sensitive dyes. Thus, the functionality (reaction process, viscosity and their characteristic wavelength for optical detection) and printability (screen-printed samples) of sensitive dyes were investigated for their future suitability as sensors inside intelligent codes in order to print self-developed sensitive colours. Firstly, the printability of various sensitive inks was investigated, in particular how process parameters of screen printing, such as different screens, can influence the sensitivity of sensitive inks. It was also determined, whether process parameters can influence the physiochemical properties of the dyes. Secondly, the reaction processes of the printed samples before and after contamination were analysed. Here, the coherence between different layer thicknesses and the individual reaction duration is reported. Third, the characteristic changes at distinct wavelengths (before and after contamination) of the various sensitive dyes were analysed, to detect material-specific limitations of their contrast after a colour change.

Currently, inkjet inks for laboratory application are under development (Bilgin and Backhaus, 2018). The inkjet inks are not included in the research covered in this paper.

2. Methods and materials

2.1 Equipment and instruments

All specimens were printed on a semiautomatic screen printer (SPS-Uniprint), by using different polyester mesh with thread counts: 140/cm, 100/cm, 71/cm, 54/cm; mesh angle: 45°; squeegee angle: 13.5°; printing speed: 116 mm/s; snap-off (distance between screen and substrate): 1.5 mm.

Rheological properties (viscous flow behaviour) of the smart materials were analysed by a rotational rheometer (Anton Paar Physica MCR 101) through a corresponding cone and plate measurement system (CP50-1); diameter: 50 mm; cone angle: 1°.

Technical printing results such as different layer thicknesses, volumes, surface structures, etc. were analysed by a confocal microscope (Keyence 3D Laser Scanning Confocal Microscope).

The colour changing behaviour (before and after an activation) of the smart materials were measured by a spectral-densitometer (TECHKON SpektroDens), in order to analyse their characteristical remission curves (spectral density). Technical parameters: polarising filter: off; illuminant: D50, 2° standard observer; measuring aperture: 3 mm.

Intelligent codes were captured through a reflex camera from Nikon (D7100); image sensor: 23.5 mm × 15.6 mm; the total number of pixels: 24.71 million pixels; file format NEF (RAW): 12 or 14 bit, lossless compressed; objective: AF-S 24/1,4G ED Nikkor.

Possible deviations were recorded in protocols to ensure the reproducibility of this experiment. The temperature and humidity throughout the research were controlled by an air conditioning system. The temperature was continuously 20 °C (±1 °C) and the relative humidity 55 % (±1 %). Measurement data are based on ten measurement repetitions.

Table 1: Material overview

Substrate	Multicolor Mirabell™, Chromo-duplex-carton with white and double-faced front and a grey pigmented back, from Papyrus Deutschland GmbH & Co. KG, with thickness: 0.340 mm, grammage: 250 g/m², suitable for screen, offset, and flexo printing
Inks (solvent-based)	Hydrochromic ink (LCR Hallcrest): black → transparent Thermochromic ink (Smarol): white → black Photochromic ink (Skyrad): transparent (light rosé) → dark blue
Additives for screen printing	Thinner: Ce-Jet® 090 (7101M000002) Retarder: VZ 2 (7102M000002)
Screen photo emulsion	FOTECOAT 1833 Stencil thickness below mesh: 6–7 µm

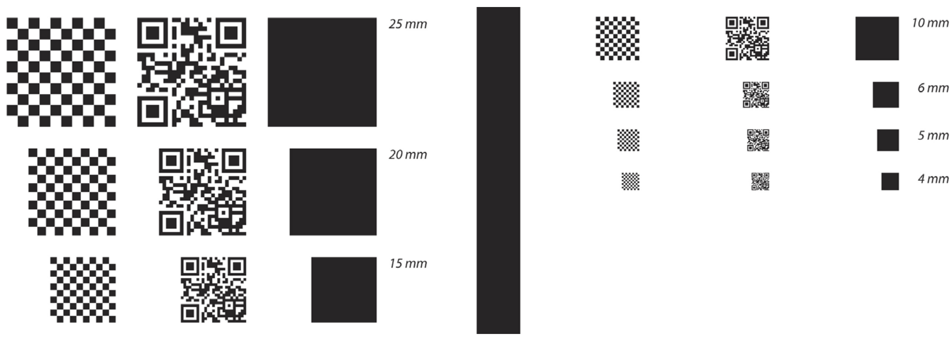


Figure 5: Test chart with different sizes of dots, dot distances, code fields and and other elements

2.2 Materials

The Table 1 lists the materials used in experimental setting. A uniform substrate was used throughout the study to analyse the reactivity of the sensitive materials under comparable conditions. The chemical characteristics of the sensitive materials were inquired, but no information about the functional components could be obtained. Thus, it can only be said that the dyes were embedded in a complex solvent. Therefore, in the future we will have to use materials we have developed ourselves. The additives are used for rheological investigations and the photo emulsion was used for making the stencil. Irreversible inks based on sensitive dyes are available for some printing technologies, e.g. flexo and screen printing. Because of this reason, general material tests were realised with screen-printed specimen.

2.3 Test chart

All experiments utilise one test chart shown in Figure 5. The test chart (DIN A3, 29.7 cm × 42.0 cm) consisted of different QR codes (Denso ADC, 1994; International Organization for Standardization, 2015) with different sizes of dots, fields and dot distances. The dots change their colour irreversibly by a particular influence. An intelligent code can be realized by means of dots printed by using different sensitive dyes. By means of the 'intelligent' dots, different environmental influences can permanently be detected and displayed on the test chart.

3. Results

3.1 Characteristic spectral reflectance

Before a smart device can reliably identify colour changes, it is necessary to analyse the behaviour of the sensitive dye by spectrophotometric methods. Especially the characteristic spectral reflectance bands are of importance. In Figure 6, remission curves are shown. The hydrochromic and thermochromic dyes show directly opposed reflections at all wavelengths. The contrast differences at these both inks are high enough to detect their current state. Thermochromic dye changes from white to black. On the contrary, the hydrochromic dye changes its colour from black to transparent. The change of the photochromic dye can be identified at two bands of the wavelength. On the one hand, the remission increases after a UV exposure at 450 nm to 475 nm (blue) and on the other hand, the remission decreases at 550 nm to 600 nm (yellow).

3.2 Difference in contrast of printed sensitive dyes

Entire QR-codes were printed with sensitive inks to analyse their colour-changing functionality and to reduce colour information to discrete binary information.

Figure 7 shows the screen-prints of different sensitive inks before (upper row) and after external influences (lower row). At these specimens, the contrast difference

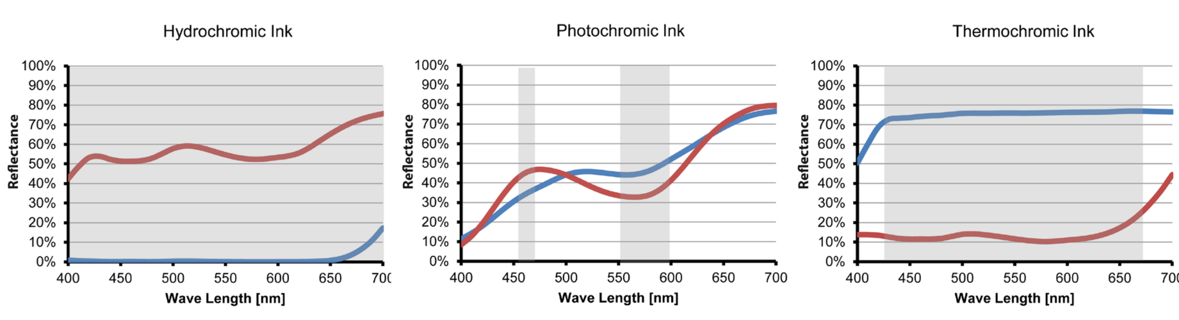


Figure 6: Remission curves and characteristic spectral bands of the sensitive inks; characteristic wavelengths that identify colour changes of sensitive dyes are grey marked

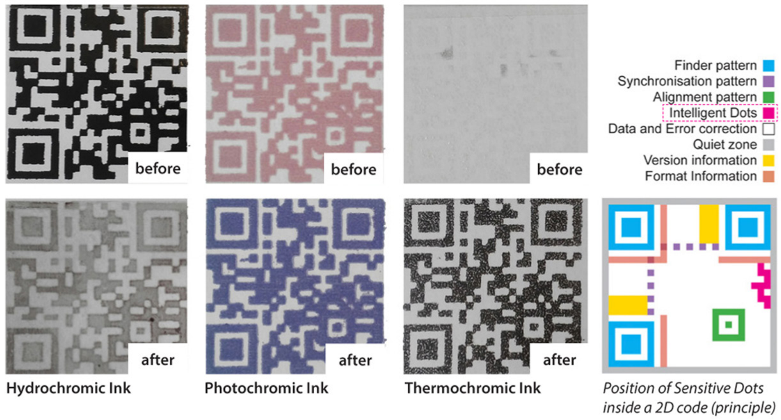


Figure 7: Sensitive dyes before / inactive (upper row) and after / active (lower row)

between all sensitive dyes after activation is high enough to be described by means of the CIE $L^*a^*b^*$ and the colour difference ΔE^*_{ab} (Table 2). Because an image capturing by means of a CMOS-camera could be error-prone, the transformation of the colour information would not be obvious if the colour contrast is not high enough.

Table 2: Measuremen[illegible]ive dye surfaces

	Hydrochromic before / after		Photochromic before / after		Thermochromic before / after	
R	24	135	173	87	184	69
G	24	136	133	88	184	68
B	24	132	137	132	184	67
L^*	10	57	62	36	75	28
a^*	0	−1	21	9	0	1
b^*	0	2	7	−27	0	1
ΔE^*_{ab}	48.3		35.4		45.9	

3.3 Flow behaviour

In this experiment, the flow behaviour of the inks with sensitive dyes was analysed (Figure 8). At shear rates higher than 1 s^{-1} (processing speed) they show a quasi-Newtonian flow behaviour.

The flow behaviour of the hydrochromic ink is shear thinning, between the shear rates from 2 s^{-1} to 20 s^{-1}. It exhibits in a Newtonian behaviour in observed intervals of shear rates 0.1 s^{-1} to 8.0 s^{-1}. Especially, the drying process of the ink is to examine. During the experiments with the hydrochromic ink, the screen several times clogged at low printing speed (116 mm/s). This maybe results from evaporating off the inks solvents. In order to prevent clogging, an alcohol-based screen-printing retarder (VZ 2) was added (20 volume percent). This addition of retarder reduced the ink's viscosity at about 0.3 Pa·s. The photochromic ink shows a slight shear thinning behaviour. The thermochromic ink exhibits a nearly Newtonian behaviour.

3.4 Reaction process

It was examined how technical parameters, e.g. full tone areas printed in various layer thicknesses can influence the behaviour of the thermochromic, hydrochromic and photochromic sensitive inks. The thermochromic ink was printed with a mesh thread count of 100/cm (theoretical ink volume: 21.1 cm^3/m^2). It reacts with different intensity to different levels of heat (Figure 9). The activation process of the ther-

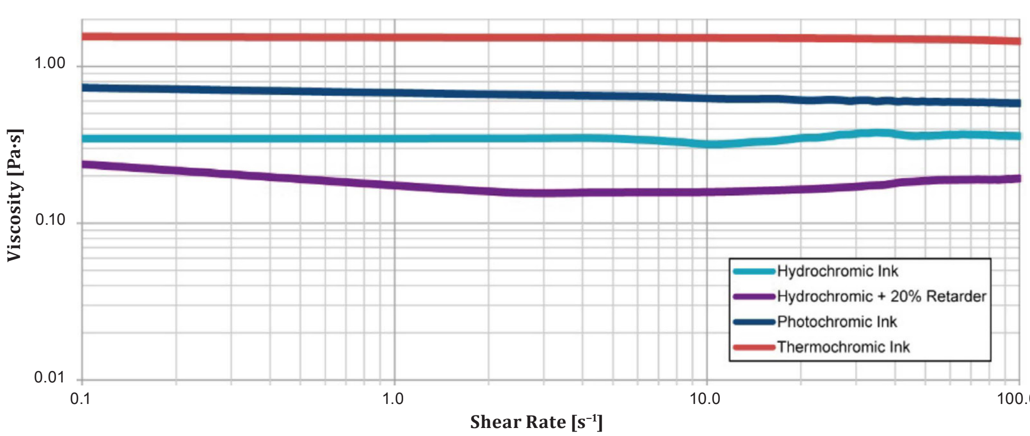


Figure 8: Viscosity of sensitive inks for screenprinting at 25 °C

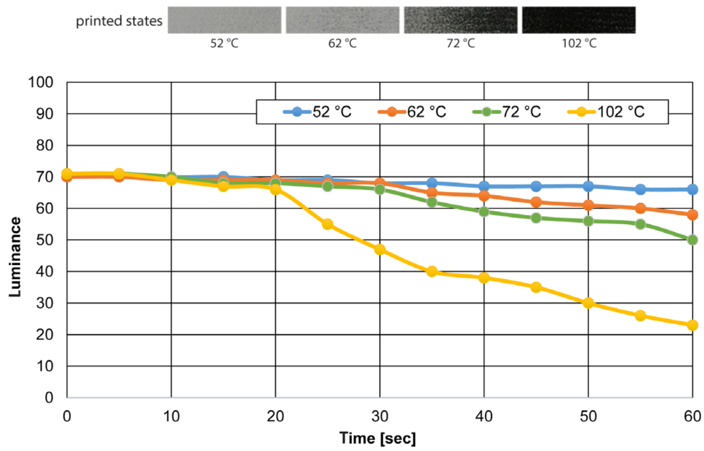
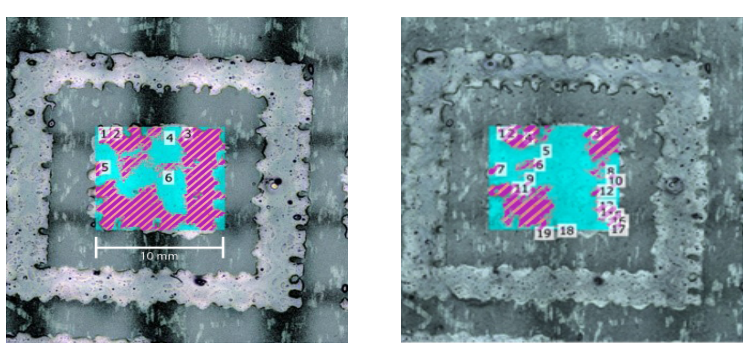


Figure 9: Luminance (L) as a function of heating (thermochromic ink)*

mochromic ink was carried out with a heating plate, which has a control precision of ±2 °C. The reaction process was recorded on video (Nikon D7100) in a preliminary study to define the reaction transitions of the thermochromic ink, presented in Figure 9, so that the measurements could be performed in the next step. After each activation step, the thermochromic ink surface was measured with a spectral densitometer. Up to 52 °C, the dye almost does not change. Above 52 °C, colour changes to black, the faster the higher the surrounding temperature is. The luminance (L^*) can be an indicator of the intensity (temperature and duration) of heat treatment. Depending on different temperature levels and treatment duration, the same L^* values can be reached. The recorded L^* values can give conclusions about the influence of the temperature in comparison with the reference. For example, the following statements can be given: the activated fields have different L^* values at different temperature ranges (normal states: 52 °C, 62 °C; activated states: 72 °C, 102 °C). Thus, exclusion can be made indirectly over the respective colour changes of the field over the degree of the heat impact. For example, the manipulation of a glued package closure, which was exposed to a certain temperature, can be visually represented.

Hydrochromic ink reacts to the presence of water or moisture and changes its colour from black to grey-transparent. In particular, it has been observed that the morphology of the printed dots changes due to water treatment. Investigations by means of a confocal laser microscope show smoothing effects of the surface and reduction of the volume. The surface of a printed dot (Figure 10) shows several peaks (high areas: magenta-dashed, Figure 10a) before water treatment. Treatment by water reduces a part of the peaks from 60 % to 30 % of the dot's area (Figure 10b). Simultaneously, the volume of the dot shrinks for about 45 %. Maybe the layer thickness of the printed dots is influenced by the reaction behaviour of the transferred hydrochromic ink.

The environmental influence of water (e.g. raindrops, humidity) can be verified through the hydrochromic ink. There is a complete colour change from black to transparent grey. Grayscale tones cannot be represented by hydrochromic ink, which indicates that it is not suitable for giving more accurate information about the degree of water influence. In particular, it would be necessary to use a hydrochromic ink, which presents moisture effects in different gradations, in



a) *b)*

Figure 10: Roughness peaks of a hydrochromic surface of dry sample (a), and after treatment with water (b) (Bilgin and Backhaus, 2017a)

order to provide information on the degree of exposure to moisture. This is currently being investigated in the development of improved hydrochromic ink.

The photochromic ink is a photosensitive compound. It changes its colour irreversibly from one state to another state, if it is induced with UV-light of particular wavelengths. Figure 11 shows printed photochromic samples (mesh thread count: 100/cm), exposed to direct daylight in a clear sky for one hour. In order to avoid changes in the lighting as far as possible, a sunny day without clouds was chosen (2017-07-21, 51° 14’ 22.9’’ N, 7° 09’ 34.6’’ E). The photos were captured every 10 s (360 pictures per hour) with a reflex camera (Nikon D7100) by the use of a stencil, which was moved and exposed every ten seconds. The samples were subsequently measured with a spectral densitometer, to analyse the grades of colour change in correlation to time. The activation process was based on continuous exposure of each square patch in the photochromic surface.

Besides the measurement by a spectral densitometer, the exposed samples (Figure 11) were captured by the Nikon D7100 camera. The images were taken in RAW format and opened in the Adobe Photoshop application (Adobe RGB, 1998) to determine the coordinates of the CIELAB colour space and the RGB values. It is possible to allocate the respective colour values from RBG or CIE $L^*a^*b^*$ to retrieve information about the intensity of changes caused by UV-light. Every photochromic sample at each stage of colouring has a specific colour value in RGB and CIE $L^*a^*b^*$. After exposing to daylight, the colour changes from a yellow colour to a yellow-blue colour at the first 30 min and becomes a very blue colour at about 60 min. This method of transferring colour impressions into characteristic values allows objectifying the results. This way the grade of colour changes or exceeding of limits etc. can be described by colour values. On the base of measuring this different colour values, a critical threshold can be defined. If this threshold is passed, warnings can be displayed.

This can be illustrated by the following example:

By dividing the measured values into three limit values, a traffic light system can be used to provide information about the respective influence of the light treatment. By sample measurements at initial state at 0 min: RGB: 208, 182, 166 / L^* = 80 (‘everything okay’); after 30 min: RGB: 182, 172, 165 / L^* = 72 (‘critical change warning’) and after 60 min: RGB: 83, 105, 154 / L^* = 44 (‘critical change’), it is possible to evaluate the range of a possible exceeding of the exposure to light. The references from Table 3 can be taken as a basis for imple-

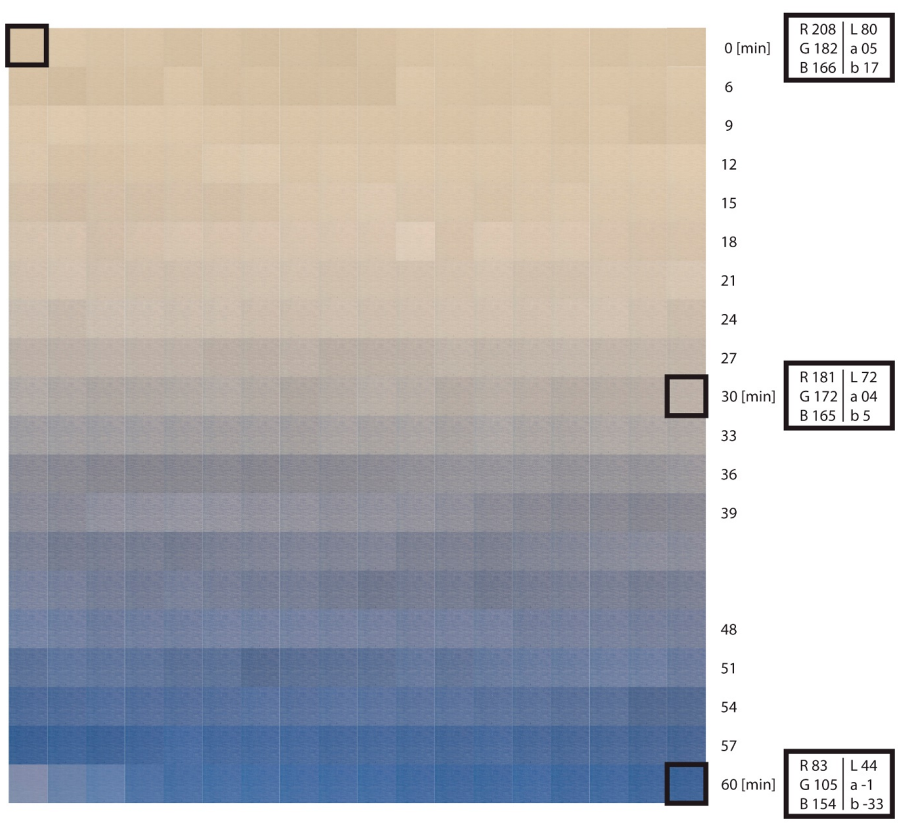


Figure 11: Photochromic samples exposed to sunlight

Table 3: Measurement data of photochromic surfaces; three fields from Figure 11 are grey marked

Min. of UV exposure	0	3	6	9	12	15	18	21	24	27	30	33	36	39	42	45	48	51	54	57	60
R	208	210	214	209	218	216	211	209	202	188	181	168	148	147	141	120	28	113	96	88	83
G	182	195	200	193	204	201	196	196	190	178	172	163	146	146	143	125	132	124	110	105	105
B	166	166	174	167	178	178	173	179	174	168	165	160	157	151	156	145	157	156	147	149	154
L^*	80	80	82	80	84	83	81	81	79	74	72	68	62	61	60	53	56	52	46	44	44
a^*	5	4	4	5	4	5	5	4	4	4	4	2	3	1	1	1	2	0	0	0	−1
b^*	17	18	16	17	16	15	15	11	11	7	5	3	−6	−3	−8	−12	−15	−20	−24	−29	−33
ΔE^*_{ab}	0.0	8.6	8.6	7.0	9.6	8.0	6.8	6.5	5.8	7.6	9.6	13.8	22.9	21.3	25.2	32.9	48.8	38.3	44.4	48.8	48.1

menting statistical classifications. All ΔE^*_{ab} values were calculated from colour values of the sample in the initial state and after treatment.

Mainly UV-A radiation (315 nm to 400 nm) influences the photochromic specimen. The spectral analysis of the 'Federal Office for Radiation Protection – BfS' (BfS, n.d.) shows that UV-B (280 nm to 315 nm) has a very low influence because these wavelengths are regularly filtered by the atmosphere.

4. Conclusions

Irreversible sensitive dyes can be applied to a substrate as a component of printing inks. Treatment with heat, moisture or light causes dyes to change, e.g. their colours or their volume, respectively. This can be measured and – also gradually – described by means of colour values, e.g. shifting of the colour shade, expressed in CIE $L^*a^*b^*$ values or by a change of the layer thicknesses. Integrated into a matrix code, e.g. QR code, the sensitive dyes can provide information about the exposure of the substrate or package to changes in the environment. Modern smart devices are able to capture current colour information and to transfer the information to a web server for evaluation. Calculations, based on the comparison of initial color values with the current information after treatment provide numerical evaluation of the deviations.

The flow behaviour of the inks with sensitive dyes was analysed, whereby statements could be made regarding their specific characteristics and suitability for use in the printing process. The viscosity was measured to analyse the processability of the sensitive screen-printing inks, which were modified in further investigation. The functionalities of the sensitive dyes were examined with regard to their reactivity. The colour shift between at least two transitions was investigated. Thus, it was found that the hydrochromic ink can detect a direct influence of water, but there is no detection of a continuous influence of moisture.

Colour shift allows statements about the condition of the respective sensor. There are differences between the different photochromic, hydrochromic and thermochromic sensitive inks, expressed as the changes contrast of the colouring, the gradual colour shift and the measurement of the individual phases of the respective colour gradation.

Against this background, three priorities can be deduced for further R & D work:

- Development of inkjet inks with irreversible sensitive dyes for easier production of the codes in single step operation in comparison to screen-printing technique.
- Development of an application for measurement, transmission, and evaluation of the colour information by means of smart device and web server in the Internet of Things.
- Development of robust, data-based models for the reliable description and comparison of information retrieved as changes of sensitive dyes.

References

Ashton, K., 2009. That 'Internet of Things' thing: in the real world, things matter more than ideas. *RFID Journal* [online] 22 June. Available at: <www.rfidjournal.com /articles/view?4986> [Accessed 09 January 2019].

BfS, n.d. *UV-Strahlung*. [online] Bundesamt für Strahlenschutz. Available at: <http://www.bfs.de/DE/themen/opt/uv/uv_node.html> [Accessed 27 July 2017].

Bilgin, M. and Backhaus, J., 2017a. Smart packages by means of intelligent odes. In: P. Gane, ed. *Advances in Printing and Media Technology: Proceedings of the 44th International Research Conference of iarigai.* Fribourg, Switzerland, September 2017. Darmstadt, Germany: iarigai, pp. 89–96.

Bilgin, M. and Backhaus, J., 2017b. Intelligent codes by controlled responsiveness to external stimuli. In: *Printing Future Days: 7th International Scientific Conference on Print and Media Technology.* 4–6 October 2017. Chemnitz, Germany, 04–06 October. Berlin, Germany: VWB – Verlag für Wissenschaft und Bildung, pp. 85–90.

Bilgin, M. and Backhaus, J., 2018. Development of a unidirectional switchable photochromic ink for smart packaging. In: P. Gane, ed. *Advances in Printing and Media Technology: Proceedings of the 45th International Research Conference of iarigai.* Warsaw, Poland, October 2018. Darmstadt, Germany: iarigai, pp. 55–63.

Brown, L.S. and Holme, T., 2015. *Chemistry for Engineering Students*. 3rd ed. Stamford, USA: Cengage Learning, p. 149, p. 176.

Cranwell, P.B., Harwood, L.M. and Moody, C.J., 2017. *Experimental Organic Chemistry*. 3rd ed. Hoboken, USA: Wiley, p. 226.

Denso ADC., 2014. QR code 20th anniversary. [video online]. Available at: <https://www.youtube.com/watch?v=f6sCS1OUJ9A> [Accessed 9 January 2019].

Engel, T. and Reid, P., 2006. *Physikalische Chemie*. München, Deutschland: Pearson Education, p. 404.

Hara, M., Denso Wave Incorporation. 2006. *Method for displaying and reading information code for commercial transaction*. U.S. Pat. 6,997,384 B2.

Harvey, J.A., 2006. Smart materials. In: M. Kutz, ed. *Mechanical engineers' handbook: materials and mechanical design*. 3rd ed. Hoboken, USA: Wiley, p. 418.

Herbst, W. and Hunger, K., 1995. *Industrielle Organische Pigmente*. Weinheim, Deutschland: Wiley-VCH.

Hesse, M., Meier, H. and Zeeh, B., 2008. *Spectroscopic methods in organic chemistry*. 2nd ed. Stuttgart, Germany: Georg Thieme, p. 17.

Hirshberg, Y. and Fischer, E., 1954. Photochromism and reversible multiple internal transitions in some spiropyrans at low temperatures. Part I. *Journal of the Chemical Society*, 0, pp. 297–303. https://doi.org/10.1039/JR9540000297.

Hirshberg, Y., 1956. Reversible formation and eradication of colors by irradiation at low temperatures. A photochemical memory model. *Journal of the American Chemical Society,* 78(10), pp. 2304–2312. https://doi.org/10.1021/ja01591a075.

Hunger, K. ed., 2003. *Industrial dyes: chemistry, properties, applications*. Weinheim, Germany: WILEY-VCH, p. 544.

International Organization for Standardization, 2015. *ISO/IEC-18004:2015 Information technology: Automatic identification and data capture techniques: QR Code bar code symbiology specification*. Geneva: ISO.

Kalsi, P.S., 2005. *Spectroscopy of organic compounds*. 6th ed. New Delhi, India: New Age International Publisher, p. 62.

Latscha, H.P., Kazmaier, U. and Klein, H.A., 2017. *Organische Chemie, Chemie-Basiswissen II*. Heidelberg, Berlin, Germany: Springer Spektrum, p. 540.

Schaefer, D. and Cheung, W.M., 2018. Smart packaging: opportunities and challenges. In: L. Wang, T. Kjellberg, X.V. Wang and W. Ji, eds. *51st CIRP Conference on Manufacturing Systems*. Stockholm, Sweden, 16–18 May 2018. Amsterdam, The Netherlands: Elsevier B.V., pp. 1022–1027.