

READABILITY OF 2D CODES CONSIDERING THE ACTIVATION TEMPERATURE OF THERMOCHROMIC PRINTING INKS IN SMART TAGS

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Abstract: Many advantages and applications of 2D codes and functional printing inks have led to the development of Smart Tags. Interactive 2D codes provide the ability to store a large number of various information on a relatively small area and are easy to use. Combined with temperature sensitive thermochromic inks, 2D codes can provide a possibility for making Smart Tags, which could be used in smart packaging applications. In this study, Smart Tag is a temperature – dependent system sensitive to surrounding temperature, which provides information in the form of 2D codes and hidden messages. By combining the information provided by the Smart Tag, it is possible to monitor the temperature conditions of a particular product, create anti – counterfeit elements, and high – temperature warning systems. In this paper, 2D codes will be printed using thermochromic (TC) inks with different activation temperatures (T_A) in screen printing technique. Printed 2D codes will be exposed to the defined temperature range around T_A , to determine readability of the codes by mobile code scanning. Colorimetric properties of TC inks will also be measured within the defined temperature range. The aim of this paper is to determine which temperature range of a particular TC ink provides readability of 2D codes. The results could help in design and development of 2D code - Smart Tags using functional inks. These kinds of Smart Tags could provide higher level of consumer protection, temperature monitoring of pharmaceutical and cosmetics products, as well as burn – hazard warning systems.

Key words: 2D codes, thermochromic inks, Smart Tag

1. INTRODUCTION

The development of 2D symbology was motivated by the need to place more information in a relatively small area. 2D codes can encode numeric, alphanumeric, binary, and Kanji characters, but also website URLs, documents, and multimedia files (Rizwan, 2016). QR (Quick Response) 2D codes are quickly and easily decoded using smartphones, thus providing a link to a digital media and additional information (Hakola & Linna, 2005). 2D codes can be printed on many different types of substrates, using regular printing inks and process. Error correction feature ensures readability of QR codes even if the code is damaged, distorted, or dirty, by up to 30% (Rizwan, 2016).

2D codes can be combined with environmentally sensing materials for a cost-effective tag that can be attached to product packages (Hakola, Vehmas & Smolander, 2021). This kind of functional Smart Tags can be printed with commercially available thermochromic (TC) printing inks, which changes its coloration according to surrounding temperature (Jakovljević et al., 2017). 2D codes printed with this type of functional inks creates temperature-sensing system in which the results of code-scanning dynamically change, depending on temperature conditions of a certain product. The specifications of mentioned functional materials must be well known and adjusted in detail, for usable and useful applications. Smart Tags based on QR codes and TC inks can provide information which is dynamically approached and can be combined with hidden messages. These types of Smart Tags can be used in intelligent packaging designed for food, pharmaceuticals, and cosmetics products. By combining the dynamic information provided by the Smart Tag, it is possible to monitor the temperature conditions of a particular product, create anti-counterfeit elements, and high-temperature warning systems.

This research aims to determine which temperature range of a particular TC ink provides readability of 2D codes. The complete function of this application is possible only if all the elements that affect the functional properties of Smart Tag system are examined and adjusted in detail. The results of this research could help in better understanding of 2D code-Smart Tags using functional inks and influence in future improvement of this system. These kinds of Smart Tags could provide higher level of consumer protection, temperature monitoring of pharmaceutical and cosmetics products, as well as burn-hazard warning systems.

2. MATERIALS AND METHODS

2.1. Materials

In this research, 2D codes were printed using reversible thermochromic (TC) inks with different activation temperatures (T_A); blue, $T_A=15^\circ\text{C}$ – denoted as TC 15; black, $T_A=31^\circ\text{C}$ – denoted as TC 31, and red $T_A=47^\circ\text{C}$ – denoted as TC 47. All three TC inks are water-based and change from colored to uncolored state at the defined activation temperature. TC inks were mixed with binder (50:50) provided by the producer (SFXC, United Kingdom), to prepare useful screen-printing ink formulation.

2D QR codes were printed on four types of uncoated paper substrates: N 160 – Navigator, 160 g/m²; FC 250 – Favini Crush, 250 g/m²; EPR 80 - Evercopy plus, recycled, 80 g/m²; and PRW 70 - Paperzone Reciclingpapier Weissegrad, 70 g/m². EPR 80 and PRV 70 are both specified as recycled papers, while N 160 does not contain recycled fibers. FC 250 is labeled as eco-friendly paper, made by replacing 15 % of virgin tree pulp with by-products from citrus fruits. Selected paper substates differ in their composition, basic, surface, and optical properties.

2.2. Printing process

Before the printing process, TC inks were mixed with binder and the printing paper substrates were conditioned at a temperature of $24 \pm 1^\circ\text{C}$ and 50-55 % relative humidity. Two types of designs were prepared for the printing process. For printing solid images, a full-tone square image was prepared and for printing 2D codes, a digitally created 2D code was transferred to the film. The films were used for exposure of the printing plates using the standard plate-making procedure [5]. Two types of printing plates were used. A printing plate with a mesh density of 43 lines cm⁻¹ (SEFAR® PET 1500 43/110-80 PW) was made for printing a solid image and a plate with a mesh density of 77 lines cm⁻¹ (SEFAR® PET 1500 77/195-55 PW) was made for printing 2D QR codes. The prints were made with a manual screen printing machine by Bochonow (Drucktisch 2000 50/70) and the printed samples were air-dried for 48 h at a temperature of $25 \pm 2^\circ\text{C}$ after the printing process.

2.3. Measuring methods

Optical properties of paper substrates were measured using Techkon (Techkon GmbH, Germany); opacity and whiteness were measured. Caliper was determined with a micrometer DGTB001 Thickness Gauge (Enrico Toniolo, S.r.l., Milano, Italy). Microscopic images of paper samples were performed by means of an Olympus BX51 microscope (Tokyo, Japan).

Surface roughness of paper substrates was measured to determine the differences in the surface structures of observed papers. An electromechanical stylus instrument MarSurf PS 10 (Mahr GmbH, Germany) was used for measurement. The diameter of the stylus was 2 μm and the measuring force was 0.00075 N. The measurement was performed ten times on each sample in the fiber direction and in the opposite direction, and the results of a mean value were presented. The roughness parameters determined and used in this research are compliant to the standards for geometric product specifications (ISO 4287: 1997). Three roughness parameters were defined: R_a - average surface roughness; R_z (ISO) - mean height of unevenness in ten points, numerically the difference in mean height between the five highest peaks and the five lowest peaks within the reference length; R_{max} - maximum roughness height (ISO 4288: 1996).

Temperature-dependent optical properties of TC prints were measured 5 $^\circ\text{C}$ below and 5 $^\circ\text{C}$ above the activation temperature of each TC ink. Spectral reflectance of the samples was measured between 400 and 800 nm, in 1 nm steps, using fibre – based USB 2000+ portable spectrometer (Ocean Optics, USA) with 30 mm wide integrating sphere (ISP-30-6-R), (8° :di) measuring geometry and a 6 mm sampling port diameter. Ocean View 2.0.7. software by Ocean Optics was used to calculate the CIELAB L^* , a^* and b^* values taking into account the D50 illuminant and 2° standard observer. The printed samples were temperature controlled using the surface of a water block (Ek Water Blocks; EKWB d.o.o., Slovenia) (Jakovljević et al., 2017; Kulčaret al., 2010; Mahović Poljaček et al., 2021).

2D codes printed with TC inks were exposed to the defined temperature range around T_A , to determine readability of the codes by mobile code scanning. The mobile app used for code scanning were: QR & Barcode Scanner (QR & BS), QR skener (QR) and Qr Barcode Scanner (QR BS).

3. RESULTS AND DISCUSSION

3.1. Characterization of paper substates

The results of measured caliper, bulk, opacity, and whiteness of all paper substates are shown in Table 1. FC 250 has the highest caliper of all samples, followed by N 160 and EPR 80, while PRW 70 results in the lowest value. These results are consistent with the values of basis weight for all samples. Substrate PRW 70 has the highest bulk of 1.351 cm³/g, which means it has the lowest density. Substrates FC 250 and EPR 80 have the bulk values of 1.3 cm³/g in the middle, while N 160 has the lowest bulk of 1.063 cm³/g. Sample FC 250 has the highest opacity of 99.6 %, followed by N 160 – 97.58 % and PRW 70 – 97.02 %. EPR 80 has the lowest opacity of 93.22 %. The results of whiteness show very high result for N 160 – 151.35 %, which indicates the presence of optical brighteners. EPR 80 results in whiteness of 90.62 %, PRW 70 61.11 %, and FC 250 35.43 %.

Table 1: The results of measured caliper, bulk, opacity, and whiteness of paper substrates

Paper substrate	Caliper (μm)	Bulk (cm ³ /g)	Opacity (%)	Whiteness (%)
N 160	170	1.063	97.58	151.35
FC 250	325	1.3	99.6	35.43
EPR 80	104	1.3	93.22	90.62
PRW 70	94	1.351	97.02	61.11

Figure 1 presents microscopic images of paper substrates N 160, FC 250, EPR 80 and PRW 70 under magnification of 5×. The surface of the paper substrate N 160 presented in Figure 1a is uniform, homogeneous, the fibers are thin and evenly distributed over the surface, without any visual irregularities. Figure 1b presents a FC 250 substrate. One can see that the structure of the paper is inhomogeneous, the particles of the organic residues are visible and interspersed with primary cellulose fibers. One can see that recycled papers (Figures 1c and 1d) have similar surface structure with intertwined fibers arranged in different directions forming a complex surface morphology. The particles of recycled material is slightly larger in size (up to 50 μm) on PRW 70 paper in comparison to EPR 80 but they are evenly distributed in the surface structure of the both papers.

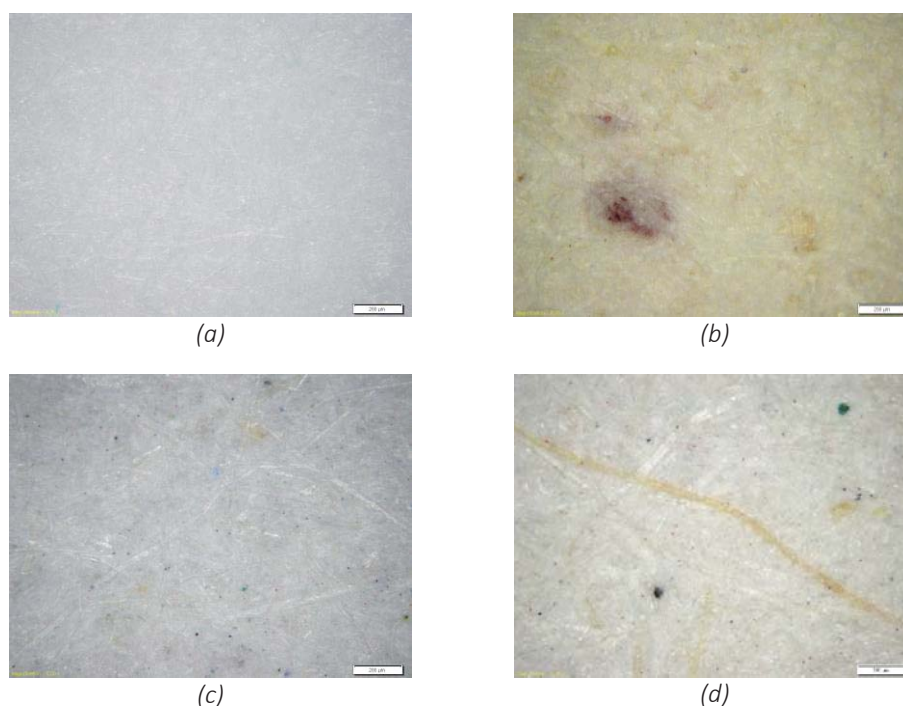


Figure 1: Microscopic images of the paper substrates: N 160 (a), FC 250 (b), EPR 80 (c) and PRW 70 (d) (mag. 5×)

Table 2 presents the results of measured R_a , R_z and R_{max} roughness parameters. It is visible that all three parameters have the highest values on paper FC 250 which means that FC 250 has the roughest surface structure. Substrate with the smallest surface roughness is paper N 160; recycled papers (EPR 80 and PRW 70) have similar roughness values. One can see that paper PRW 70 has average surface roughness slightly smaller than EPR 80 paper. These results correspond to the microscopic images of the papers, where the differences in the surface structure of the paper substrates are clearly visible.

Table 2: Roughness parameters measured on paper substrates.

Paper substrate	Roughness parameters (μm)					
	R_a	SD	R_z	SD	R_{max}	SD
N 160	1.552	0.109	10.472	1.004	13.323	2.371
FC 250	3.122	0.103	18.549	1.201	23.740	2.487
EPR 80	2.714	0.309	15.842	1.476	18.905	1.922
PRW 70	2.088	0.182	13.220	1.338	18.609	1.744

Spectral reflectance of substrates used in this research differ from each other, mainly because of the optical properties of paper, such as whiteness, brightness, and opacity, but also because of the presence of optical brighteners. The latter is most likely the reason for the highest reflectance spectra of N 160 substrate, especially between 420 and 520 nm (Figure 2). Substrate PRW 70 has the lowest reflectance spectra, which could be related to the lowest density of the paper. Sample EPR 80 has very similar trend as PRW 70, higher by about 10 % in reflectance between 420 and 500 nm. The specific yellowish tone of the FC 250 substrate results in spectral reflectance which partially follows the curve of the substrate N 160, between 555 and 800 nm.

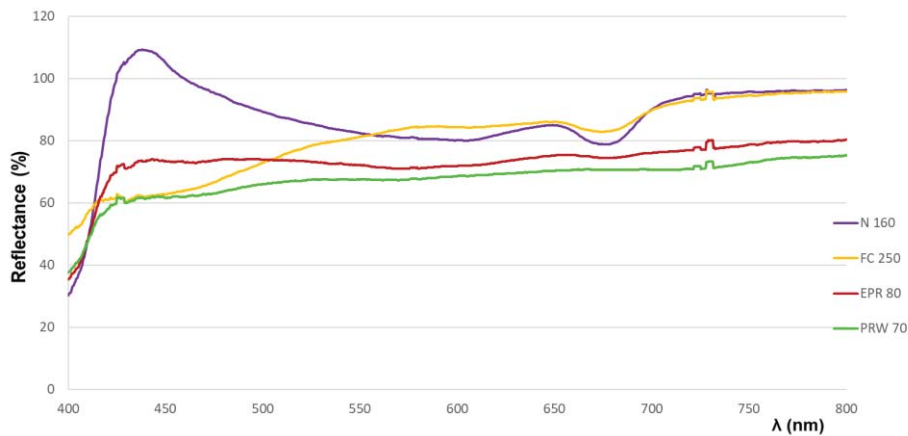


Figure 2: Spectral reflectance of substrates used in the research

3.2. Spectral reflectance of prints

The results of reflectance spectra of printed TC inks on all paper substrates are shown in Figures 3 – 5. In each individual diagram, each reflection spectrum is measured at the defined temperature, at temperature range from 5 °C below, and 5 °C above T_A of each TC ink. The reflection spectra of the printed samples measured at T_A are marked red in each diagram. The results show similar trend of the measured samples as the temperature rises, resulting in higher reflection spectrums and increasing lightness. These dynamic changes of the TC ink affect the readability of QR codes printed with them, which is explained in the section 3.5.

Spectral reflectance of TC 15 printed on all paper substrates (Figure 3) show greater mutual distinction between the samples measured at lower temperatures – 10, 11 and 12 °C, while other temperatures result in rather narrow area of measured reflectance spectra, overlapping with T_A of the samples for all substrates. Similar effect can be noticed for TC 31 printed on EPR 80 and PRW 70 (Figure 4c and 4d), where reflection spectrum of the samples measured at 26, 27 and 28 °C are more separated from the rest of the samples, overlapping the narrow range. Samples printed with TC 31 on N 160 and FC 250 show relatively even distribution of reflection spectra, but T_A is almost completely overlapping with adjacent

temperatures. The clearest mutual differences between the samples measured inside defined temperature range are shown in Figure 5, for the samples printed with TC 47, with the minor exception of the substrate EPR 80. These results are closely related to the readability of QR codes printed with TC inks, which is explained in the next section.

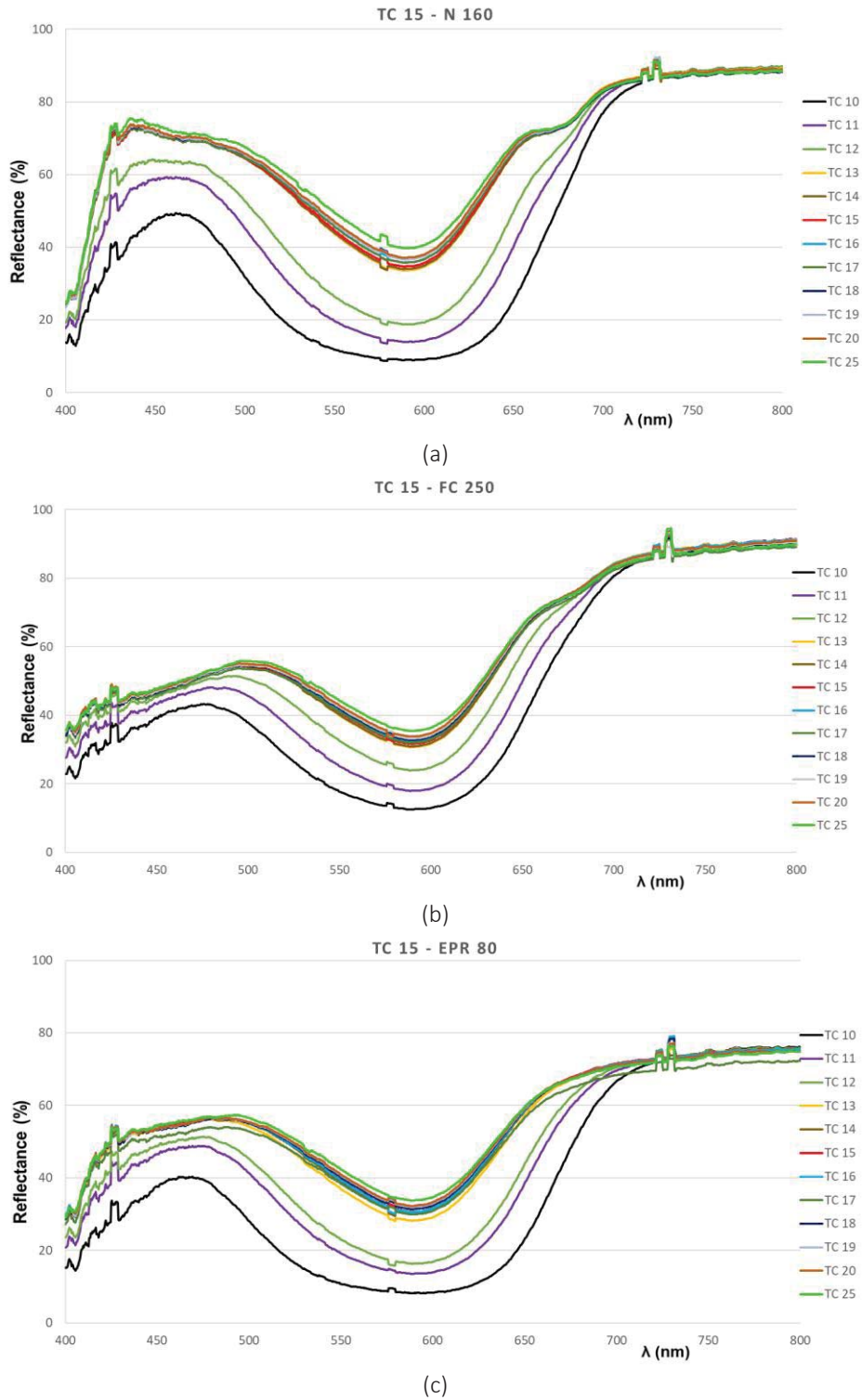


Figure 3 (part 1): Spectral reflectance of TC 15 ink printed on substrate N 160 (a), FC 250 (b), EPR 80 (c), and PRW 70 (d)

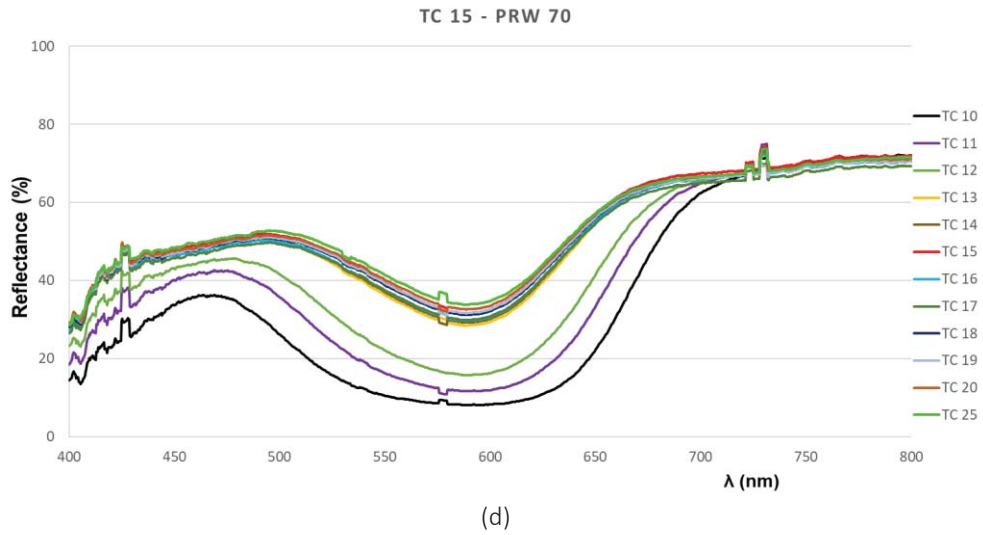


Figure 3 (part 2): Spectral reflectance of TC 15 ink printed on substrate N 160 (a), FC 250 (b), EPR 80 (c), and PRW 70 (d)

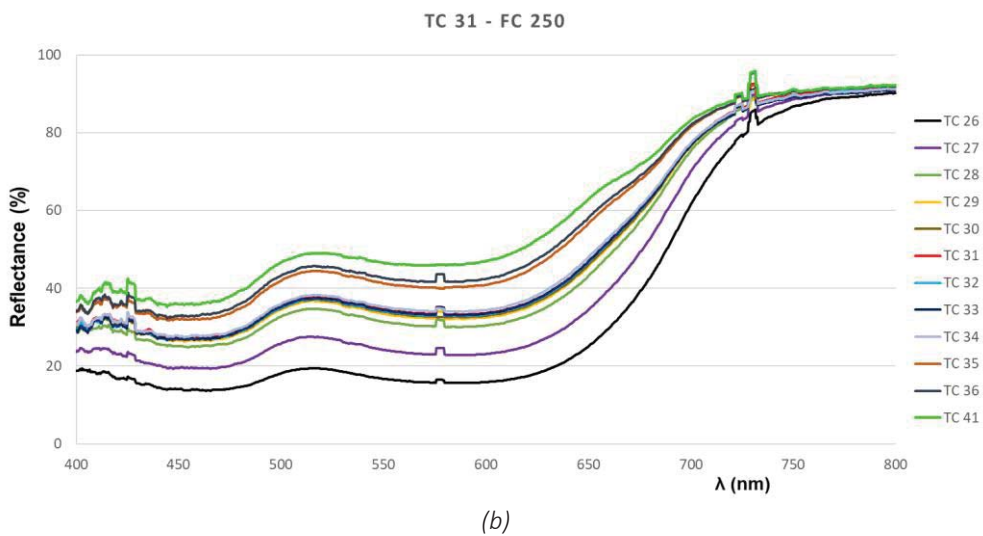
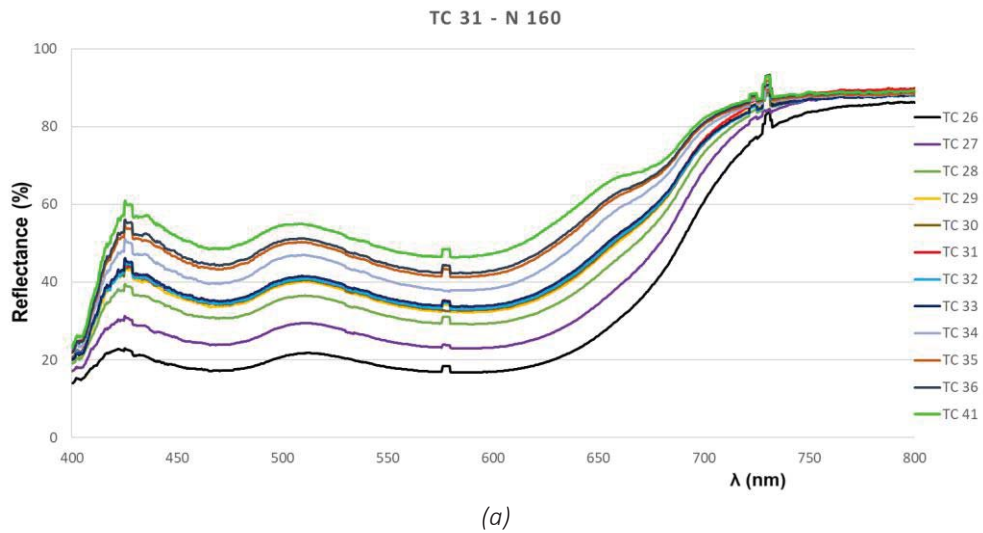
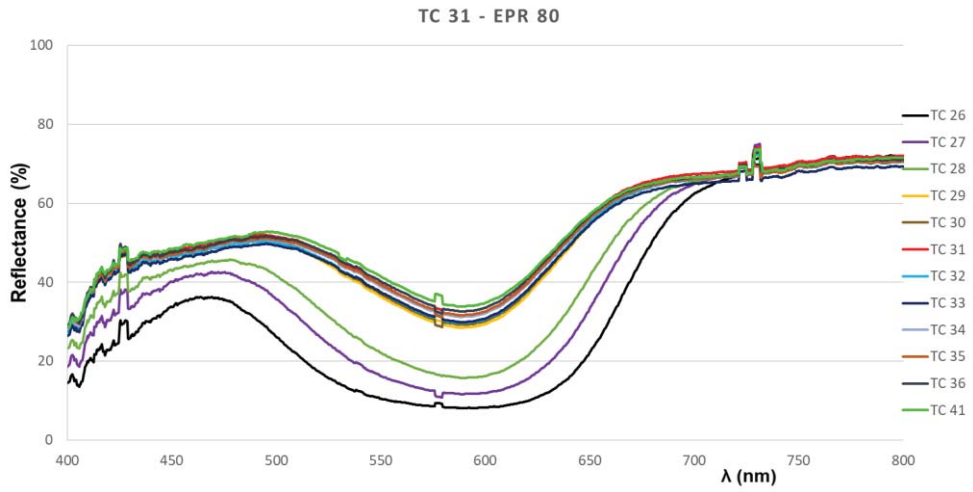
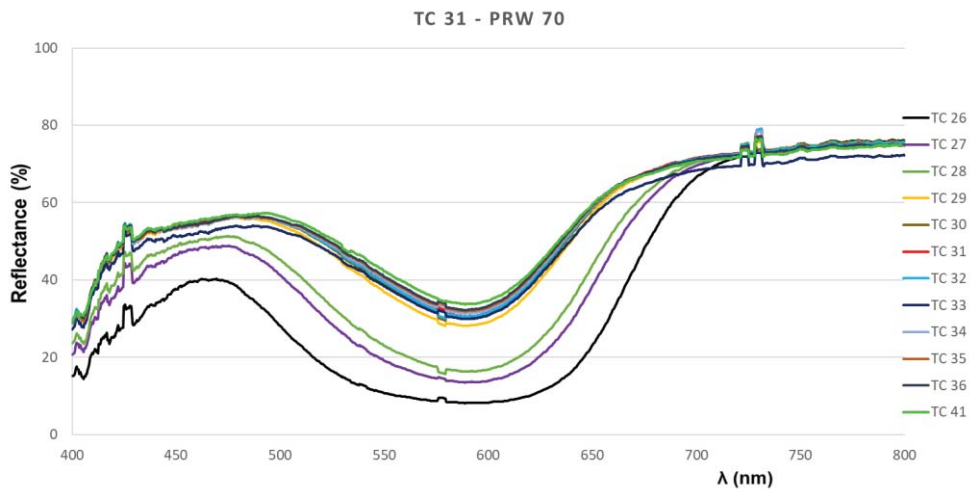


Figure 4 (part 1): Spectral reflectance of TC 31 ink printed on substrate N 160 (a), FC 250 (b), EPR 80 (c), and PRW 70 (d)

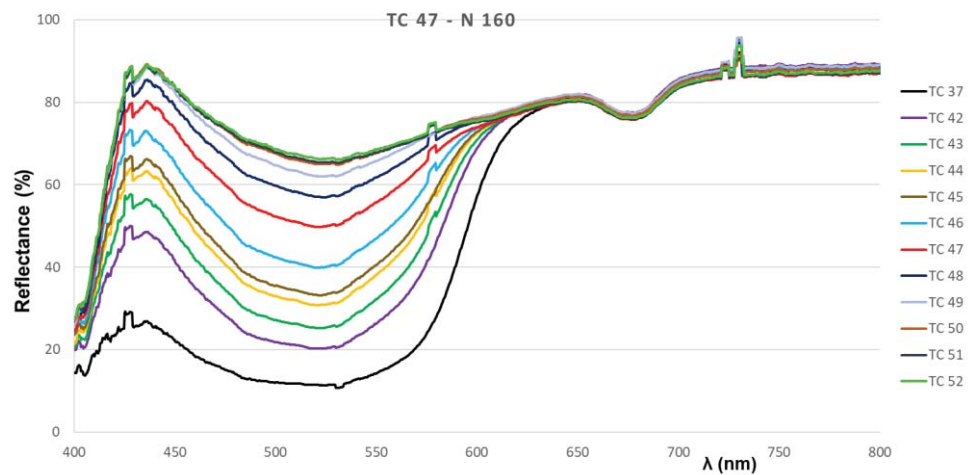


(c)



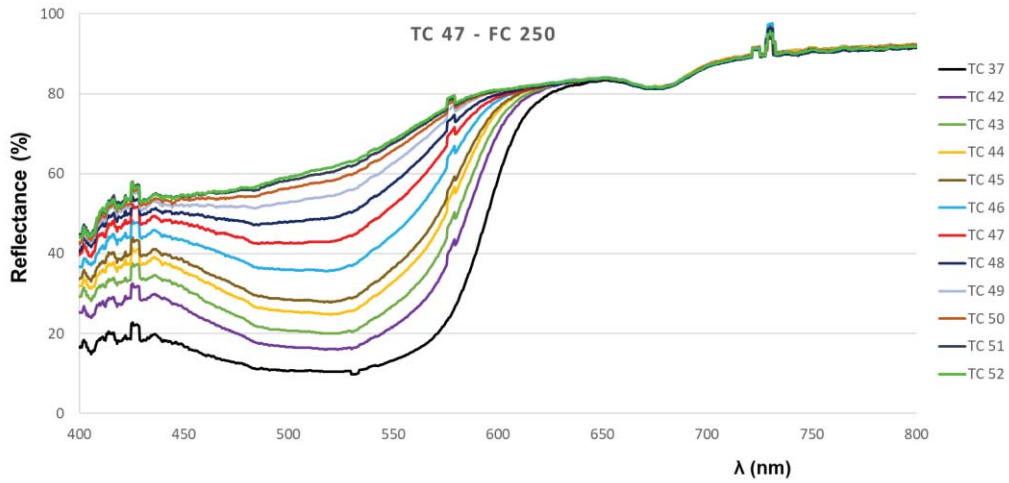
(d)

Figure 4 (part 2): Spectral reflectance of TC 31 ink printed on substrate N 160 (a), FC 250 (b), EPR 80 (c), and PRW 70 (d)

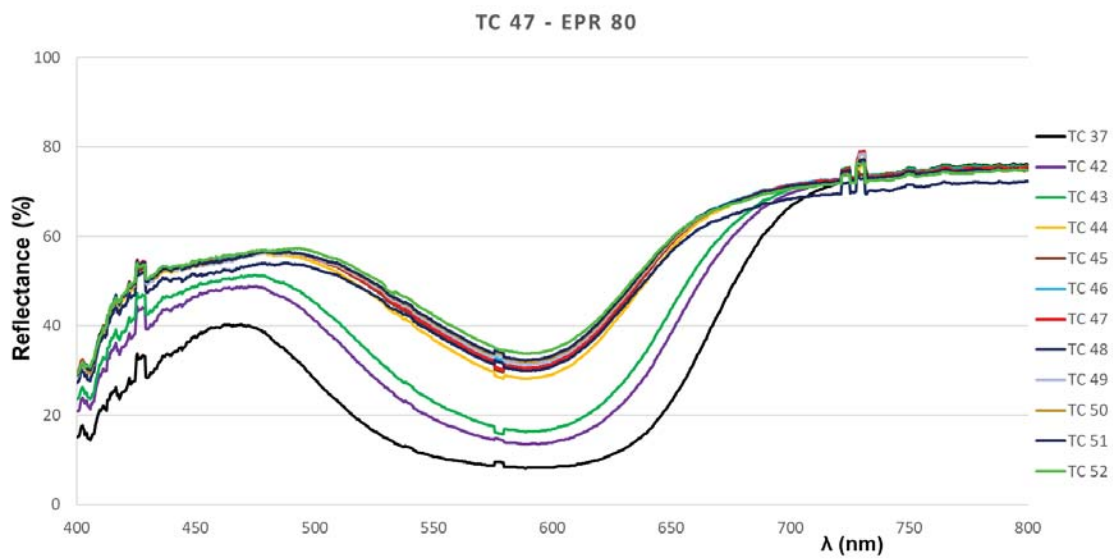


(a)

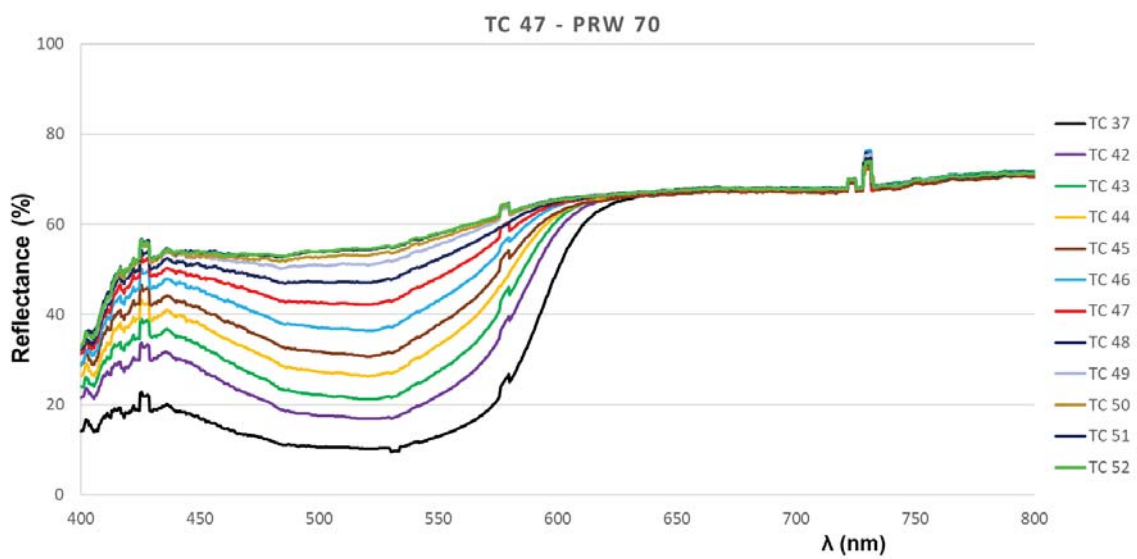
Figure 5 (part 1): Spectral reflectance of TC 47 ink printed on substrate N 160 (a), FC 250 (b), EPR 80 (c), and PRW 70 (d)



(b)



(c)



(d)

Figure 5 (part 2): Spectral reflectance of TC 47 ink printed on substrate N 160 (a), FC 250 (b), EPR 80 (c), and PRW 70 (d)

3.5. Readability of 2D codes at the defined temperatures

The results of readability of 2D codes at the defined temperatures are shown in Table 3 – 5. The readability of the QR codes printed with TC inks on all four paper substrates was checked using three different commercially available 2D code scanners/readers. The readability of printed QR codes at the T_A of each TC ink is marked in light blue. The producer of the TC ink defines T_A as the temperature at which TC inks changes their coloration from colored to uncolored state. This means the readability of the printed QR codes should be compromised at this temperature. However, the samples printed with TC 15 show inconsistency in readability of QR codes, considering the type of mobile reader and used substrate (Table 3). The codes are readable at T_A in the case of all used substrates when QR skener (QR) is used, despite the fact the TC ink should fade at this point, i.e., become translucent. Inside the defined temperature range, every single QR code is readable if QR skener is used. The results of code scanning with QR & Barcode Scanner (QR & BS) and Qr Barcode Scanner (QR BS) show loss of readability from 11 or 12 °C to the upper limit of temperature range at 20 °C. Ideally, printed QR codes should be readable at the temperatures below T_A , and gradually lose their tone and function with the rising temperature, i.e. become unreadable.

Table 3: Readability of 2D codes printed with TC 15 ink on different paper printing substrates

		T(°C)										
		10	11	12	13	14	15 (T_A)	16	17	18	19	20
N 160	QR code scanner											
	QR & BS	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗
	QR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR BS	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗
FC 250	QR & BS	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗
	QR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR BS	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗
EPR 80	QR & BS	✓	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗
	QR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR BS	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗
PRW 70	QR & BS	✓	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗
	QR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR BS	✓*	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗

Samples printed with TC 31 (Table 4) show a complete absence of functional properties of TC ink inside the defined temperature range. Besides a few isolated samples, all QR codes show complete readability on all printing substrates, making temperature monitoring according to inks specifications impossible. Most of the samples printed with TC 47 (Table 5) resulted in unreadable codes, even on temperatures below T_A . The exception from these results are samples printed on N 160 and EPR 80, where QR codes are readable at temperatures between 42 and 47 °C, and unreadable above T_A . Substrate PRW 70 resulted in readability only on temperatures of 43, 44 and 45 °C. These results are also followed by the photographs of QR codes printed with TC inks, at the defined temperatures (Figure 6 – 8) on substrate EPR 80.

Table 4: Readability of 2D codes printed with TC 31 ink on different paper printing substrates

		T(°C)										
N 160	QR code scanner	26	27	28	29	30	31 (T _A)	32	33	34	35	36
	QR & BS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR BS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✗
FC 250	QR & BS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR BS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
EPR 80	QR & BS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR BS	✓	✗	✓	✓	✗	✓	✓	✗	✓	✓	✗
PRW 70	QR & BS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	QR BS	✓	✓	✓	✓	✓	✓	✗	✓	✗	✓	✗

Table 5: Readability of 2D codes printed with TC 47 ink on different paper printing substrates

		T(°C)										
N 160	QR code scanner	42	43	44	45	46	47 (T _A)	48	49	50	51	52
	QR & BS	✓	✗	✗	✗	✗	✓	✗	✗	✗	✗	✗
	QR	✓	✓	✓	✓	✓	✓	✗	✗	✗	✗	✗
	QR BS	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
FC 250	QR & BS	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
	QR	✓	✗	✗	✗	✗	✓	✗	✗	✗	✗	✗
	QR BS	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
EPR 80	QR & BS	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
	QR	✓	✓	✓	✓	✗	✓	✗	✗	✗	✗	✗
	QR BS	✓	✗	✗	✗	✗	✓	✗	✗	✗	✗	✗
PRW 70	QR & BS	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
	QR	✗	✓	✓	✓	✗	✗	✗	✗	✗	✗	✗
	QR BS	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗

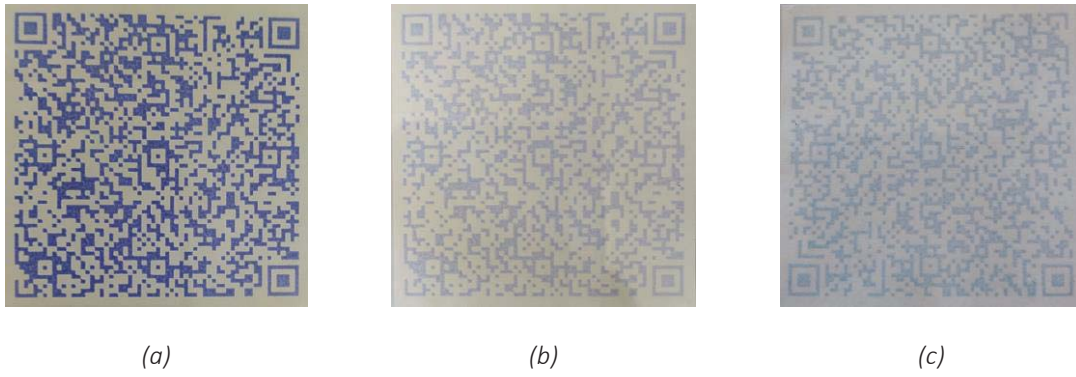


Figure 6: 2D code printed with TC 15 ink on EPR 80 substrate, photographed at 10 °C (a), 15 °C (b) and 20 °C (c)

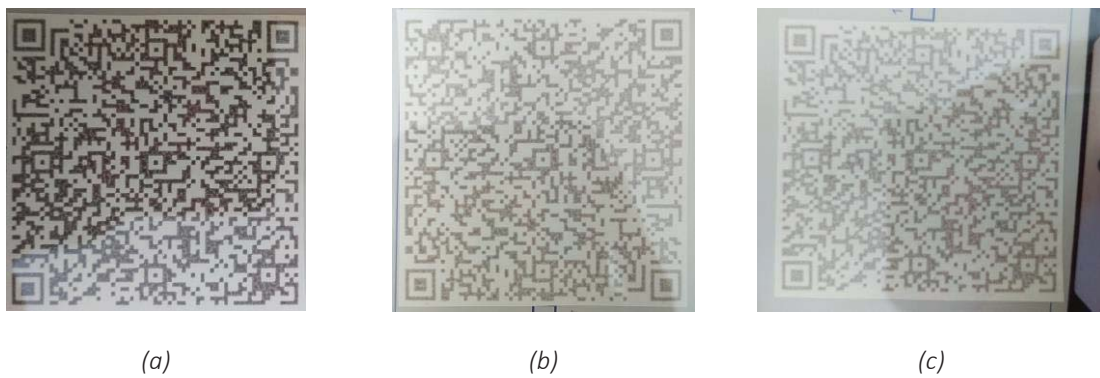


Figure 7: 2D code printed with TC 31 ink on EPR 80 substrate, photographed at 26 °C (a), 31 °C (b) and 36 °C (c)

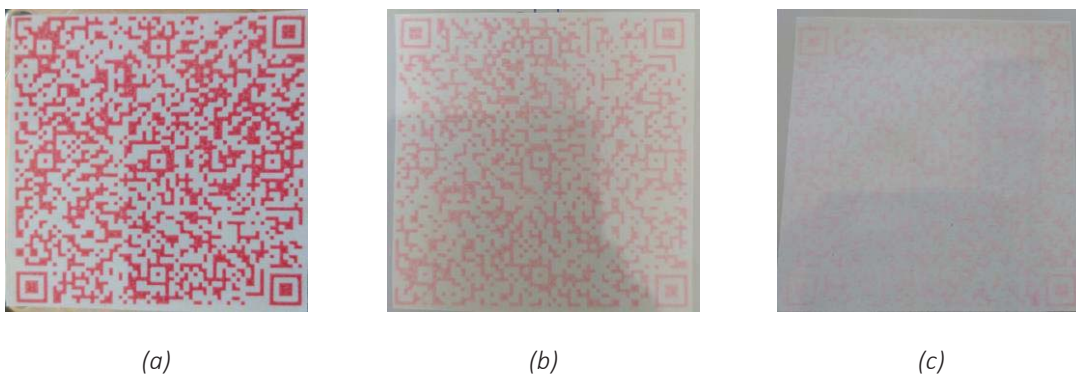


Figure 8: 2D code printed with TC 47 ink on EPR 80 substrate, photographed at 42 °C (a), 47 °C (b) and 52 °C (c)

4. CONCLUSIONS

The aim of this research was to determine which temperature range of a particular TC ink provides readability of 2D codes in proposed Smart Tags. The results show dysfunctionality of the application for QR codes printed with TC 15 and TC 31 printing inks. The component of the Smart Tag system through TC inks did not satisfy the criterium of the change in coloration inside the defined temperature range, which affected the readability of the QR codes. TC 47 partially met the criteria of functional printing ink, in the case of N 160 and EPR 80 substrates and QR skener. Further research should be based on TC inks with functional properties investigated and adjusted in detail and aim to examine all printing parameters. All the elements that affect functional properties of Smart Tag system must be known, predictable and repeatable, so they can fulfil its purpose. In addition, the influence of the room temperature on the functional application must also be considered, along with the temperature of the packed product. The thickness of the printing substrate and eventual barrier properties of the packaging with this kind of Smart Tags should also be considered. Detail adjustment and investigation of all elements creating Smart

Tags are necessary for their complete function. Such knowledge and understanding of functional properties could put Smart Tags into more frequent commercial use. The quality of the mobile's camera and the application for scanning the code also had an influence on the readability of the information provided by the Smart Tag, and also should be considered in future research.

7. REFERENCES

- Hakola, L. & Linna, H. (2005) Detection of printed codes with a camera phone. *Proceedings of 32nd International Research Conference, Iarigai, 4-7 September 2005, Porvoo, Finland*. pp. 355-362.
- Hakola, L., Vehmas, K. & Smolander, M. (2021) *Functional inks and indicators for Smart Tag based intelligent packaging applications*. *Journal of Applied Packaging Research*. 13 (2) Available from: <https://scholarworks.rit.edu/japr/vol13/iss2/3> [Accessed 10th september 2022]
- Jakovljević, M., Kulčar, R., Tomašegović, D., Friškovec, M. & Klanjšek Gunde, M. (2017) Colorimetric description of thermochromic printing inks. *Acta graphica*. 28, 7-14.
- Jakovljević, M., Lozo, B., Klanjšek Gunde, M. Spectroscopic evaluation of the colour play effect of thermochromic liquid crystal printing inks. *Coloration Technology 2017*, 133, 81–87, doi:10.1111/cote.12257
- Kulčar, R., Friškovec, M., Hauptman, N., Vesel, A. & Gunde, M.K. (2010) Colorimetric properties of reversible thermochromic printing inks. *Dyes and Pigments*. 86, 271-277. Available from: doi: 10.1016/j.dyepig.2010.01.014
- Mahović Poljaček, S., Tomašegović, T., Leskovšek, M. & Stanković Elesini, U. (2021) Effect of SiO₂ and TiO₂ Nanoparticles on the Performance of UV Visible Fluorescent Coatings. *Coatings*. 11 (8), 928. Available from: doi: 10.3390/coatings11080928
- Rizwan, Z. (2016) *QR Code History: Evolution of the popular 2D Barcode*. Available from: <https://scanova.io/blog/blog/2016/07/26/qr-code-history/>, updated 2021 [Accessed 10th september 2022]



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