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Development of an irreversible hydrochromic ink for smart packaging

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Abstract

Smart materials are based on chemical-physical processes that react to environmental factors or a specific stimulus. These factors or a predefined stimulus lead to structural changes. In this way, several smart materials can react to various influences such as temperature, UV light, or other. Smart materials of the type of hydrochromic inks change their colour under the influence of water or humidity. This stimulus-induced colour change process can occur in either reversible or irreversible form. Irreversible hydrochromic inks are preferable for a significant indication of the influence of water or moisture. Therefore, this research project focuses on the development and investigation of an irreversible hydrochromic ink for piezoelectric inkjet printing. For this purpose, the theoretical aspects of the chemical compound are discussed and the concept behind an irreversible hydrochromic ink is introduced. Several concentrations are evaluated and characteristic properties like viscosity, surface tension, particle size, and characteristic remission are analysed.

Keywords: smart materials, colour irreversibility, piezoelectric inkjet, spectrophotometry

1. Introduction and background

This research work is part of an overall concept of inkjet-printed multi-functional sensors and their use via smart devices. Smart materials of the type of hydrochromic inks change their structure under the influence of water or moisture in a way that they also change their colour. This stimulus-induced colour change process can occur in either reversible or irreversible form. This colour changing behaviour can be used to develop printable sensors (Bilgin and Backhaus, 2017). Therefore, the focus of this research is on irreversible hydrochromic inks, which change their colour under the influence of water and remain in their condition (Figure 1). The following irreversible hydrochromic ink was developed for piezoelectric inkjet printing based on a solvent-based matrix in which a hydrochromic dye is embedded. In the following, different experimental concentrations of a hydrochromic ink will be investigated. The viscosity, surface tension and particle size distribution of the concentrations and their suitability for inkjet printing will be analysed. Additionally, the colour change behaviour before and after contamination will be described. Various types of hydrochromic materials can be found in different ranges. Hydrochromic dyes or indicators can be combined with a desiccant such as silica gel to detect the moisture content of the desiccant (e.g. super absorber in nappies). Natural hydrochromic phenomena are also found in the environment, such as the skeleton flower (*Diphylleia grayi*). The flower has white petals but becomes translucent when it is in contact with water. After a drying period, the petals turn white again (Yong, et al., 2015). Some materials have hydrochromic properties, for example, the reversible copper(II) sulfate, which shows a white colour in a dry state and a blue colour in a humid state. Another example is the reversible cobalt(II) chloride, which shows blue colour in the dehydrated state and a red colour after hydration as hexahydrate.

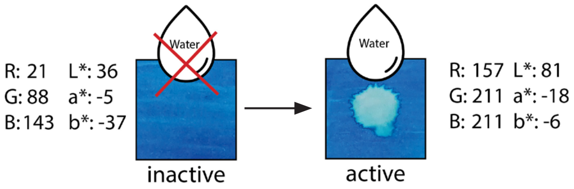
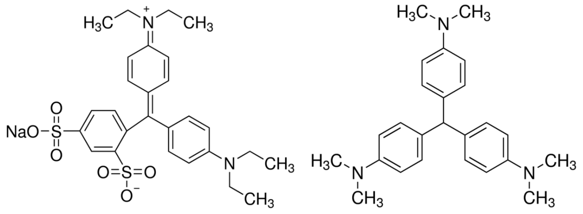


Figure 1: Hydrochromic ink (irreversible): left inactive (blue) and right active (transparent)

An alternative way of developing hydrochromic materials is microencapsulation. Microcapsule has an inner core, which often contains a dye or active ingredient, and a shell, which has functionality such as elasticity, a predefined breaking strength, or permeability (Ghosh, 2006). In this way, the permeability can release an active ingredient due to water or moisture (e.g. medication, coatings, etc.).



a) *b)*

Figure 2: Structural formula of (a) Patent blue V (2020), and (b) Crystal violet (2020) dyes

This research is based on a triphenylmethane dye, a leuco dye that is colourless in its triphenylmethane partial structure. Due to electron-supplying substituents (auxochromes), at least two aromatic rings in the ortho-position that are attached to a central unsaturated carbon atom can form a chromophore that can shift the absorption further into the long-wave range (invisible colour). Through adding a second auxochrome (CH3)2N group to the structure, the conjugative interaction, and delocalization of the π-electrons of the structure increases and forms, as a result, the dye malachite green. When a third auxochrome group is added, a hypsochromic shift occurs in the opposite direction and the dye crystal violet is formed (Figure 2). The application area of triphenylmethane dyes is in the production of printing inks, indicators, copy papers, smart coatings, etc. (Klöckl, 2015). Patent blue V (Figure 2) is also a triphenylmethane dye and is used in inks, food colouring (E 131) and colouring of papers. According to the regulation EU no. 231/2012 of the European commission, Patent blue V (E 131) consists essentially of calcium, sodium or potassium compounds. The structural formula of the compound is composed as follows (EFSA Panel on Food Additives and Nutrient Sources added to Food, 2013):

> N-(4-((4-(diethylamino)phenyl)(2,4-disulfophenyl)
> methylene)-2,5-cyclohexadien-1-ylidene)
> -N-ethylethanaminium, hydroxide, inner salt,
> sodium salt.

Patent blue V is manufactured through the “condensation and sulphonation of N,N-diethylaniline, and 3-hydroxybenzaldehyde in acidic conditions (sulphuric acid) to produce the substance under leuco form” (ibid.).

The ink eraser contains on one side a colourless felt impregnated with an oxidising agent for erasing, and on the other side a pen with an ink eraser resistant ink for correcting the previously erased area. Sodium hydrogen carbonate ($NaHCO_3$) is used as an oxidising agent to erase the triphenylmethane dye. Because of the sp^2-hybridisation of the central carbon atom, the triphenylmethane dye is coloured. This is attributable to the reason that the molecules are completely planar. The π-electrons of the double bonds and the non-binding electrons of the substituents are delocalized over the entire molecule. Consequently, the electrons are more easily excited and low-energy radiation from the visible spectrum can be absorbed more easily. The non-absorbed but reflected spectral component causes the perceptible colour impression. The invisible mechanism: anions negatively charged with water such as the hydroxide ion (OH^-) or the hydrogen sulphite ion (HSO_3^-) attack the central carbon atom and are added together. As a result, the geometry of the dye molecule is changed and the central carbon atom is sp^3-hybridised. Thus, the delocalising (resonance) of the electrons is consequently restricted, whereby visible light can no longer interact with the electrons. (Blume, 2003)

The Patent blue V now absorbs only UV radiation instead of visible light and is no longer in the visible wavelength range and therefore it appears colourless. When developing a hydrochromic inkjet ink, the chemical process of an ink eraser was used. Through the addition of the hydrogen sulphite ion ($HSO3^-$) from

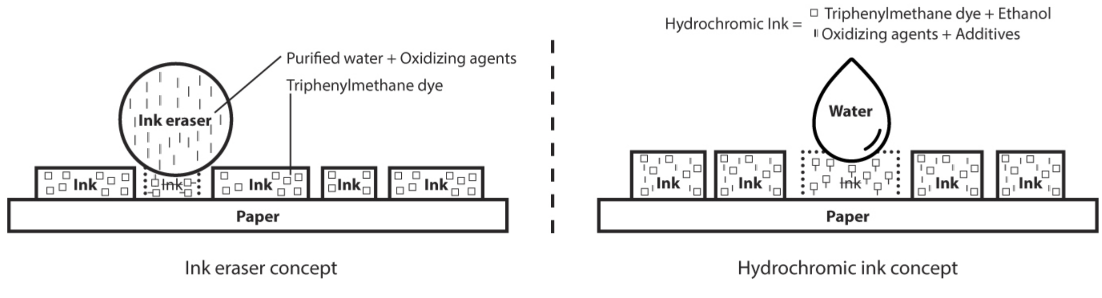


Figure 3: Concepts of (a) ink eraser and (b) hydrochromic ink

the hydrogen carbonate to the central carbon atom, the geometry of the triphenylmethane dye Patent blue V is modified. The result is that it loses its hybridised sp^2 planarity that is necessary for the colouration, changes its structure, and takes the tetrahedral arranged sp^3 form and becomes invisible. Figure 3 shows the concept behind the hydrochromic ink. The ink eraser concept (Figure 3a) is based on the principle that the ink has firstly to be applied to the paper. The ink eraser, which consists of purified water, oxidising agents, and other additives, changes the geometry of the ink and becomes invisible. The principle of the irreversible hydrochromic ink (Figure 3b) is based on a formulated ink that consists of a triphenylmethane dye Patent blue V, ethanol, oxidising agent (sodium hydrogen carbonate) and other additives that are necessary for the printability. After printing the hydrochromic ink, the ink is ready to react with water. On contact with water, the reaction of the oxidising agents with the triphenylmethane dye is stimulated and the colour becomes invisible. (Blume, 2003)

The irreversible hydrochromic ink is a part of the development of a smart code that can be applied with other smart materials in an inkjet process as printable sensors. For example, an irreversible photochromic ink was already presented in a previous publication (Bilgin and Backhaus, 2018). Possible technical solutions to read and analyse the smart code were also presented in a previous publication (Bilgin and Backhaus, 2019).

2. Materials and methods

The hydrochromic ink was developed for piezoelectric inkjet printing and is based on the solvent ethanol, to which the dye Patent blue V, a defined amount of sodium hydrogen carbonate, and additives were added. For the printing process of the hydrochromic ink, a piezo inkjet printer, commonly used in the non-professional printer segment, was used (Epson Stylus Photo 1500W / 1430W / Artisan 1430 / EP-4004). The printer showed the following technical parameters: print head IH710-9 (Part Code: F173090), MicroPiezo TFP® print head technology; thin film piezo element 1/1000 mm (PZT piezo crystal element based on lead zirconium titanate); droplet size 1.5 picolitres at 8 kHz up to 32.5 picolitres, the print head is adjustable to 5 ink droplet sizes per nozzle; nozzle configuration: 90 nozzles for black (K), 90 nozzles per colour (CMY and light variants of C and M); max. printing resolution 5760 dpi × 1440 dpi (horizontal × vertical).

The colour change process (decolourising process) of the hydrochromic ink was measured with a spectral densitometer (TECHKON SpektroDens). It is used to examine the colour values (RGB and CIE $L^*a^*b^*$) of the different colour change states (a process of decolourisation). Technical parameters: polarising filter off; type of light D50; 2° standard observer; diameter of measuring orifice 3 mm.

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

The particle filtration process was performed through filtration equipment listed in Table 1 where also the materials used for the experiment are presented.

Table 1: Experimental materials and filtration equipment

Substrate	**Inapa tecno**, oxygen pure high-white recycled paper; format: 210 mm × 297 mm (A4), grammage: 80 g/m²
Dye	**Hydrochromic blue** (Patent blue V), N-(4-((4-(diethylamino)phenyl)(5-hydroxy-2,4-disulfophenyl)methylene)-2,5-cyclohexadiene-1-ylidene)-N-ethylethanaminium, hydroxide, inner salt, sodium salt; CAS Number: 129-17-9; Chemical formula: $C_{27}H_{33}N_2O_7S_2\,Na$; Molar mass: 566.66 g·mol^{-1}
Oxidising agent	**Sodium hydrogen carbonate**; CAS Number: 497-19-8; Chemical formula: Na_2CO_3; Molar mass: 105.99 g·mol^{-1}
Ink base	**Ethanol**; CAS Number: 64-17-5; Chemical formula: C_2H_6O; Molar mass: 46.069 g·mol^{-1} **E24**, Octopus Fluids GmbH & Co KG; colourless, pH 7.86; Conductivity: <5 mS/cm; Viscosity: 3.00 mPa·s
Ink additive	**Urea** (humectant); Chemical formula: CH_4N_2O
Filtration equipment	**Millex-SV** (SLSV025LS); Pore size: 5.0 µm **Millex-HPF HV filter** (SLHVM25NS); Pore size: 0.45 µm **Membrane filter Express®** (PLUS PES); Pore size: 0.22 µm Filtration area: 3.9 cm²; Material: hydrophilic polyvinylidene fluoride (PVDF)

Rheological properties (viscous flow behaviour) were analysed with the help of a rotational rheometer (Physica MCR 101) through a corresponding cone and plate measurement system (CP50-1); diameter 49.966 mm; cone angle 1°. Surface tension was controlled by using of SITA pro line bubble pressure tensiometer. This measuring method was used for the dynamic qualification of the wetting properties and to determine the optimum bubble lifetime. A standardised paper Inapa tecno was used in experiment to ensure the comparability of the samples. A solvent ink based on ethanol was used for the inkjet process, as logically water-based ink cannot be used.

All investigations were performed under controlled laboratory conditions. An air-conditioning system was used to ensure the reproducibility of the experiments. All deviations were continuously observed and recorded in protocols. The temperature during the experiments was 20 °C (±1 °C) and the relative humidity was 55 % (±1 %).

3. Results and discussion

3.1 Experimental concentration of hydrochromic ink

Various experimental concentrations of a hydrochromic ink are described in detail below. In previous test series, suitable oxidising agents and solvents were identified for suitability to form a hydrochromic ink (Bilgin and Backhaus, 2020). Furthermore, the most suitable concentration of oxidising agents and dyestuff (Patent blue V) was identified. Therefore, the developed hydrochromic ink prototype version four was used, which is described as 4.1.1 to 4.5.1 (Table 2). With the different concentrations of the hydrochromic ink, the solvent quantities remain constant at 10 ml and only the concentration of the dye Patent blue V and the oxidising agent sodium bicarbonate differ. These concentrations are used in the following examinations.

Table 2: Different concentrations of the hydrochromic ink

Ink	Patent blue V [g]	Sodium bicarbonate [g]	Ethanol [ml]
4.1.1	0.10	0.10	10
4.2.1	0.08	0.08	10
4.3.1	0.06	0.06	10
4.4.1	0.04	0.04	10
4.5.1	0.02	0.02	10

3.2 Evaluation of an inkjet-compatible viscosity

In the following, the rheological properties, especially the viscous flow behaviour of the water-reactive hydrochromic ink, were analysed. Each of the five concentrations in Table 2 was examined to determine its viscous flow behaviour (Figure 4). All inks show pure Newtonian flow behaviour with a low viscosity that is suitable for inkjet printing. The viscosity of the base ink E24 is about 4.24 mPa·s, which also serves as a reference for an inkjet ink to which the viscosity should be adjusted (the function of E24 is described below). Ethanol, which serves as a base and solvent for the hydrochromic ink, has a viscosity of about 1.32 mPa·s. The solvent shows the lowest viscosity value of all materials. The various concentrations of the hydrochromic inks have the viscosity around 1.89 mPa·s, above that of ethanol. The viscosity increase is caused by an increase in the amount of sodium bicarbonate and Patent blue V that is dissolved in ethanol. When these components are dissolved, their molecular structure is destroyed and the molecules are dispersed in the solvent separately from each other.

Figure 5 summarizes the results of the rheological investigation. The aim was to examine the rheological properties of current hydrochromic inks and to adjust their properties for inkjet printing. Therefore,

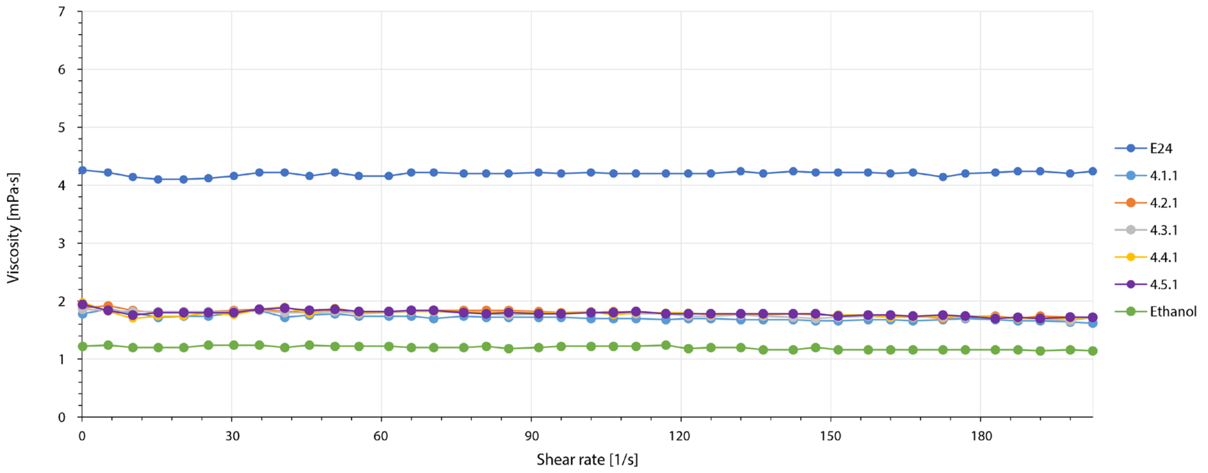


Figure 4: Viscosity analysis of all concentrations in comparison

a target process window with a minimum of 1 mPa·s (marked yellow) and a maximum of 25 mPa·s (marked grey) was defined that is in the recommended range from the literature (Magdassi, 2010). Furthermore, a water-based inkjet base ink called E24 (marked blue) specially developed for the Epson printer was used as a reference. As a result, the hydrochromic ink (actual state, marked orange) is below the range of E24 and above the minimum recommended range in the literature. Thus, the hydrochromic ink is located in the printable area. Besides, the viscosity is in the printable range also recommended by Zapka (2018) from 1 mPa·s to 50 mPa·s.

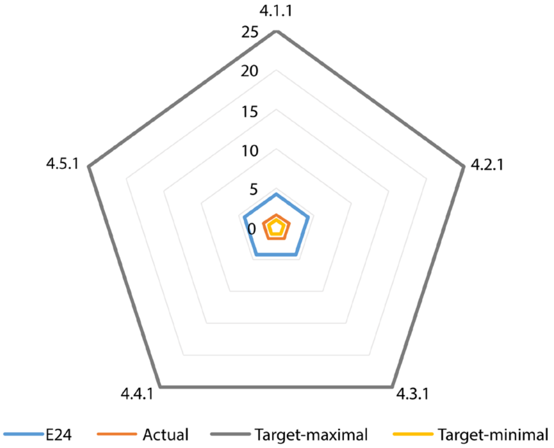


Figure 5: Viscosity analysis of the reference and prototype inks in the range up to 25 mPa·s

3.3 Evaluation of an inkjet-compatible surface tension

Subsequently, the surface tension was examined. Figure 6 describes the reference and prototype inks with different concentrations and their surface tension. The aim was to examine the surface tension of hydrochromic inks and to verify their properties and their suitability for inkjet printing. The mean temperature during the measurement of the surface tension was at around 21.6 °C. As shown in Figure 6, the surface tension of all concentrations is quite close to each other and therefore this concentration range has no significant influence on the change in surface tension. Figure 7 summarizes the results of the examination of the surface tension. As in rheology, a target process window was defined with a minimum of 20 mN/m (marked yellow) and a maximum of 50 mN/m (marked grey), which is within the recommended range from the literature (Hutchings and Martin, 2012). The Epson base ink E24 (marked blue) was also used as a reference. As a result, the hydrochromic ink (actual; marked orange) is below the range of the base ink E24 and above the minimum range recommended in the literature. Consequently, the surface tension of all hydrochromic inks is in the printable process area, above the recommended minimum requirements.

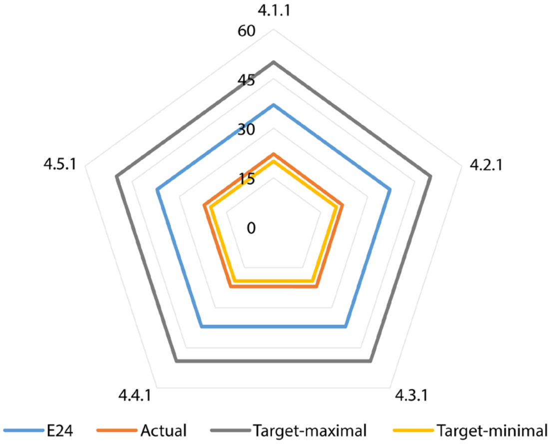


Figure 7: Surface tension analysis of the reference and prototype inks in the range up to 50 mN/m

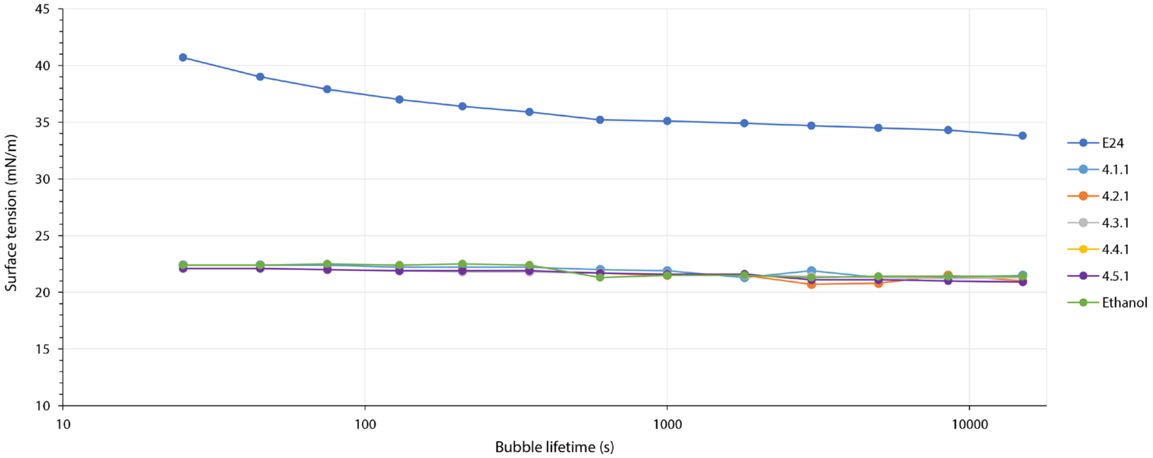


Figure 6: Surface tension of the reference and prototype inks with different concentrations

3.4 Evaluation of an inkjet-compatible particle size

Patent blue V has a solubility of 20 g/l at 20 °C and 100 g/l at 90 °C. According to Otterstätter (1999), it is recommended to work in a concentration range without the potential for crystallisation. Furthermore, the entire solution must be filtered to retain undissolved particles (Figure 8). For this purpose, a test has already been carried out to determine the undissolved particle components in the hydrochromic ink. In this context, the distribution of the undissolved particles in the solution was examined in detail (Bilgin and Backhaus, 2020).

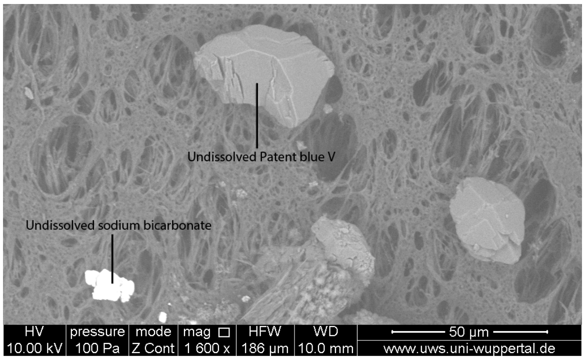


Figure 8: Microscopic examination of particles on a 220 nm filter

Before the inks were used for the printing process, the inks were filtered in three phases and then filled into an inkjet cartridge. Firstly, the particles were filtered with a Millex SV (SLSV025LS) filter membrane with a pore size of 5.0 µm, so that all particles larger than 5.0 µm were filtered out. Afterward, the remaining particles were filtered with a Millex HPF HV (SLHVM25NS) filter membrane with a pore size of 0.45 µm so that only particles smaller than 0.45 µm were present in the ink. Finally, the third filtration process using the Express® membrane filter was applied, in which all particle sizes above 0.22 µm were filtered out. Through the filtration process, the developed irreversible hydrochromic ink shows the recommended particle size range of less than 200–300 nm (Magdassi, 2010). This ensures that harmful residual particles that would otherwise lead to clogging of the inkjet pipes and the nozzles have been eliminated.

3.5 Spectrophotometric analysis

Figure 9 shows the remission curves in a reacted (transparent, marked turquoise) and unreacted state (blue, marked blue). The characteristic of the unreacted hydrochromic ink is visible in the wavelength range from 425 nm to approx. 560 nm, with a peak of the hydrochromic ink in the range of 470 nm. In the reacted state (after the influence of water), the peak extends into the region of 400 nm to 640 nm. This colour change process can also be seen in the CIE $L^*a^*b^*$ values, where a difference in lightness from $L^* = 52$ to $L^* = 87$ can be observed. Thus, statements about the influence of contamination with water/moisture can be determined by colorimetric detection (Bilgin and Backhaus, 2019).

4. Conclusions

This research was demonstrating a hydrochromic ink that changes its colour irreversibly under the influence of water and remains in that state. The theoretical background, colour-change functionality, and the concept of a hydrochromic ink was discussed. Furthermore, this work aimed to investigate the characteristic proper-

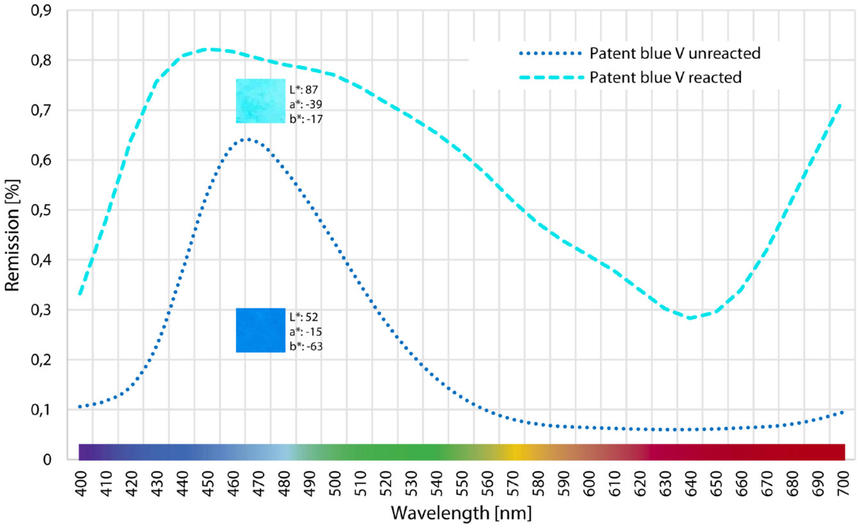


Figure 9: Spectrophotometric analysis of the hydrochromic ink

ties such as viscosity behaviour, surface tension and describe the filtration process to prevent harmful particles to adapt the hydrochromic ink for the piezoelectric inkjet printing. For this purpose, five different concentrations were selected to investigate the characteristic properties of the ink with reference to its suitability as an inkjet ink. Recommended limit values from the literature were used, which served as a guideline for the development of a hydrochromic ink. Besides, a base ink was used as a reference, which was already designed for piezoelectric inkjet printing. The next step in the development of a smart code, which can be applied with other smart materials in an inkjet process as printable sensors was taken.

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