

HYDROCHROMIC INK AS A SECURITY FEATURE FOR PIEZOELECTRIC INKJET PRINTING

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Abstract

Hydrochromic inks change their colour under the influence of water or moisture. This colour change process can become reversible or irreversible. Thus, the focus of this work is on the irreversible colour change, which remains in the state after a shift. Moisture was monitored in several technical processes, in the paper or plastics industry and in printing companies. Humidity that deviates from the norm can cause problems in technical processes and even lead to production breakdowns. Particularly in the case of electronic components, the humidity of the surrounding air should not be too humid (oxidation) or too dry (diffusion). This research project aimed to develop a hydrochromic ink for piezoelectric inkjet printing that would serve as a security feature. The functionality of the developed hydrochromic ink and the theoretical background was discussed as well as the identification of a suitable solvent and criteria for the identification will be shown. Furthermore, suitable oxidizing agents were identified. The resulting ink was printed and tested regarding its lightfastness. Furthermore, the characteristic properties such as the colour change behavior were analyzed.

Introduction

This research work is part of an overall concept of inkjet-printed multifunctional sensors and their decoding through smart devices (e.g. smartphones, tablets, etc.). Hydrochromic inks change their colour under the influence of water or moisture. The colour change process can occur reversibly or irreversibly. This research work is part of an overall concept (Bilgin and Backhaus, 2017) and focuses on the development of an irreversible hydrochromic ink that remains in its condition after a shift (Figure 1). Before this investigation, an irreversible photochromic ink was also developed (Bilgin and Backhaus, 2018). The hydrochromic dye was embedded in a solvent-based inkjet matrix, which has been developed for piezoelectric inkjet printing. Hydrochromic dyes are used for

example in smartphone hardware to document the penetration of water or extreme humidity. Non-standard moisture conditions can cause problems in technical processes and, in the worst case, even lead to production interruptions. Particularly in the case of electronic components, the humidity of the surrounding atmosphere has to be controlled without being too moist (oxidation) or too dry (diffusion). Many materials have hydrochromic properties. Nevertheless, a large number of these materials are reversible, they return to their original state after a defined influence. Furthermore, many hydrochromic dyes are not environmentally friendly and therefore they cannot be used in the food or health sector. For example, copper (II) sulphate, which shows a white color in the

dry state and a blue color in a humid state. Another example is cobalt (II) chloride, which shows a blue colour in the dehydrated state and a red colour after hydration as hexahydrate.



Figure 1: Hydrochromic ink (irreversible) changes its color from blue to transparent

This research work focuses on patent blue V, a triphenylmethane dye. Triphenylmethane dyes are used in different segments. For example, triphenylmethane dyes can be found in the field of food dyes (E 131), the production of printing inks, indicators and other areas. Patent blue V (EU, 2013) consists primarily of calcium, sodium or potassium compounds consisting of [4-(α -(4-diethylaminophenyl)-5-hydroxy-2,4-disulphophenyl-methylidene)-2,5-cyclohexadien-1-ylidene] diethyl-ammonium hydroxide inner salt (ibid.). To produce a leuco-form compound, patent blue V (Figure 2) is prepared by "condensation and sulphonation of N,N-diethyl-aniline and 3-hydroxybenzaldehyde in acidic conditions (sulphuric acid)" (ibid.).

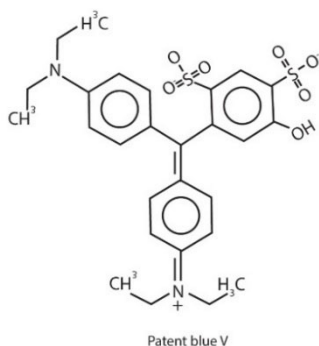


Figure 2: Structural formula of patent blue V

A hydrochromic ink was developed based on the chemical principle of an ink eraser. The ink eraser itself is based on a colorless felt impregnated with an oxidizing agent and on the other hand, an ink-erase resistant ink for correction. Sodium sulphite (Na_2SO_3), sodium hydrogen carbonate (NaHCO_3) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_5$) were used as oxidizing agents to obtain the best erasing effect. Because of the sp^2 -hybridization of the central carbon atom, the coloring of triphenylmethane dyes can be attributed to the fact that the molecules are completely planar. In this case, the π -electrons of the double bonds and the non-bonding electrons of the substituents are delocalized over the whole molecule. As a result, the electrons can be excited easier and low-energy radiation from the visible spectrum can be absorbed more efficiently. Unabsorbed but reflected spectral components cause the perceivable color impression. The mechanism of the ink eraser is as follows: Anions negatively charged with water such as the hydroxide ion (OH^-) or the hydrogen sulphite ions (HSO_3^-) attack the central carbon atom and are added together. The geometry of the triphenylmethane dye molecule is changed and the central carbon atom is sp^3 -hybridized. Thus, the delocalization (resonance) of the electrons is consequently restricted, whereby visible light can no longer interact with the electrons (cf. Blume, 2003). The patent blue V absorbs now only UV radiation instead of visible light and is no longer in the visible wavelength range and therefore it appears colorless. For the development of a hydrochromic inkjet ink, this chemical process was constructed in a reverse order, which was the aim of this can be found further down in the results of this research.

Methods

In the following, the equipment (Table 1) and materials (Table 2) of this work are introduced. The hydrochromic ink (described in results) was printed with a piezoelectric inkjet printer that is commonly used in the non-professional printer segment. The decolonization process (color change of the contaminated ink) was measured by a spectral densitometer. The UV light source for the lightfastness test was measured through a spectroradiometer. The analyzing process of the solubility test was performed by using a laser scanning confocal microscope.

Table 1: Technical parameters of equipment used

Piezoelectric inkjet printer	Epson Stylus Photo 1500W / 1430W / Artisan 1430 / EP-4004 Technical parameters: Print head: IH710-9 (Part Code: F173090) MicroPiezo TFP® print head technology based on silicon wafer-based MEMS Thin-film piezo element: 1/1000mm Droplet size: 1.5 picoliters at 8 kHz) 5 droplet sizes per nozzle Nozzle Configuration: 90 Nozzles Black (K) 90 Nozzles per Colour (CMY+Lc, Lm) Max. Printing resolution: 5760dpi x 1440dpi (H x V)
Spectral densitometer	TECHKON SpectroDens Technical parameters: Polarizing filter: off Type of light: D50, 2° normal observer Diameter of measuring aperture: 3 mm
Spectroradiometer	UVpad E (Opsytec Dr. Gröbel GmbH) Photodiodes: 512 Spectral area: 240 - 480 nm \pm 5 nm Irradiance: 0 - 5000 mW/cm ² Irradiation dose: 1 mJ/cm ² - 600 J/cm ² Spectral ranges: UVA, UVB, UVC, VIS
Laser scanning confocal microscope	Keyence 3D laser scanning confocal microscope Measurement equipment: VK-X Series Magnification: 50x (used)

Table 2 shows the materials used for the experiment. A standardized paper was used to carry out the experiment to ensure the comparability of the samples. A solvent-based ink based on ethanol was used for the inkjet process, as logically no water-based ink can be used due to its functionality.

Table 2: Experimental materials

Substrates	Inapa Tecno, oxygen pure high-white recycled paper, Format: 210 x 297 mm (A4), Grammage: 80 g/m ²
Dye	Hydrochromic blue (Patent blue V) N-(4-((4-(diethylamino)phenyl)(5-hydroxy-2,4-disulfophenyl)methyl-ene)-2,5-cyclohexadien-1-ylidene)-N-ethylethanaminium, hydroxide, inner salt, sodium salt CAS Number: 129-17-9 Chemical formula: C ₂₇ H ₃₃ N ₂ O ₇ S ₂ Na Molar mass: 566.66 g·mol ⁻¹
Oxidizing agents	Sodium hydrogen carbonate CAS Number: 497-19-8 Chemical formula: Na ₂ CO ₃ Molar mass: 105,99 g·mol ⁻¹ Sodium sulphite CAS Number: 7757-83-7 Chemical formula: Na ₂ SO ₃ Molar mass: 126.043 g·mol ⁻¹ Sodium thiosulfate CAS Number: 7772-98-7 Chemical formula: Na ₂ S ₂ O ₃ Molar mass: 158.11 g·mol ⁻¹ Sodium bicarbonate CAS Number: 144-55-8 Chemical formula: NaHCO ₃ Molar mass: 84.01 g·mol ⁻¹

Base (Ink)	Ethanol CAS Number: 64-17-5 Chemical formula: C_2H_6O Molar mass: $46.069 \text{ g}\cdot\text{mol}^{-1}$
Additives of the ink	Humectants: Urea (CH_4N_2O)
Equipment (Filtration)	Millex-SV (SLSV025LS) • Pore Size: $5.0 \mu\text{m}$ (5000 nm) Millex-HPF HV Filter (SLHVM25NS) • Pore Size: $0.45 \mu\text{m}$ (450 nm) Filtration Area: 3.9 cm^2 Material: Hydrophilic Polyvinylidene Fluoride (PVDF)

Standardization

All experiments were carried out under controlled laboratory conditions, with reproducibility being ensured by an air-conditioning system. Any deviations were recorded in protocols. The temperature: $20 \text{ }^\circ\text{C}$ ($\pm 1 \text{ }^\circ\text{C}$) and the relative humidity: 55% ($\pm 1\%$) were continuously observed and recorded.

Results

A hydrochromic ink was developed, which was based on the reverse chemical process of an ink eraser. The ink was adapted for piezoelectric inkjet printing in a later publication. To ensure that the hydrochromic ink will not react with water, a water-based base ink was logically avoided and an ethanol solvent was used instead, to which a defined amount of sodium hydrogen carbonate and additives were added. When reacting with water, the addition of the hydrogen sulphite ion (HSO_3^-) from the hydrogen carbonate to the central carbon atom changes the geometry of the triphenylmethane dye patent blue V so that the dye becomes colorless. The geometrical change is due to the result that the blue V patent loses its hybrid-

ized sp^2 planarity, which is necessary for the coloration and changes its structure to become the tetrahedral arranged sp^3 shape. The hydrochromic ink has been developed according to the concept of an ink eraser (Figure 3, Left). For example, after writing with a triphenylmethane dye (patent blue V) in a fountain pen, the writing is transferred to the paper. To correct, the chemical components of an ink eraser are required. The chemical compounds of an ink eraser consist of purified water, oxidants and other additives to remove the ink colour. For this purpose, the formulated hydrochromic ink (Figure 3, Right) is based on a triphenylmethane dye (patent blue V), an ethanol-based solvent, an oxidizing agent (sodium hydrogen carbonate) and other additives that are necessary for the printability of the ink.

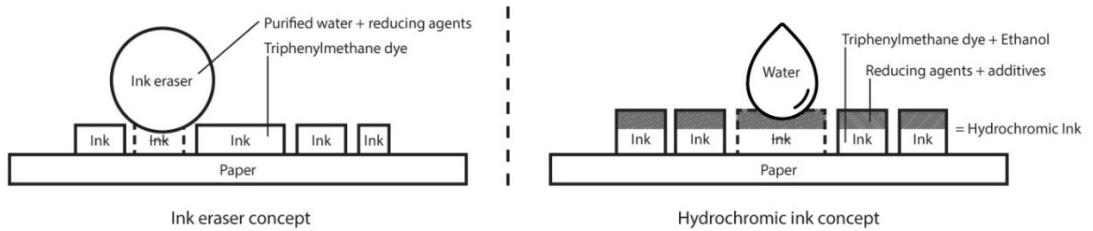


Figure 3: Ink eraser and hydrochromic ink concepts

Developing a hydrochromic ink based on triphenylmethane dyes requires the use of a solvent-based ink, because of the disadvantage that a water-based ink cannot be used due to the reactivity of the hydrochromic dye with water. The dye patent blue V and the solvent should form a homogeneous phase in a homogeneous solution. The agglomeration and sedimentation of particles must be considered, as these can lead to clogging of the inkjet nozzle and impair the printing process (Magdassi, 2010).

Table 3 provides the criteria for the identification of a solvent-based ink. These are solubility, homogeneity (the application of the hydrochromic solution on a substrate), agglomeration and sedimentation. As expected, the dye patent blue V has dissolved in all solutions. The solutions purified water and E24 (a water-based basic inkjet ink specially developed for the Epson

printer) were unsuitable due to their water base for this experimental series. An important criterion was the homogeneity of the liquid when applying the samples. The combination of the dye patent blue V and the solvent isopropyl alcohol could not be applied homogeneously since it led to crystallization on the substrate. Another criterion was the agglomeration and sedimentation of the dye solvent complex. After 24 hours, particles were agglomerated and sedimented in all three solutions. Ethanol and methanol demonstrated the most robust solvents in combination with the dye patent blue (grey marked).

Table 3: Criteria for identifying a suitable solvent-based ink

	Solubility	Homogeneity	No agglomeration	No sedimentation
Purified water	✓	✗	✗	✗
E24	✓	✗	✗	✗
Isopropyl alcohol	✓	✗	✗	✗
Ethanol	✓	✓	✓	✓
Methanol	✓	✓	✓	✓

Identification of a suitable oxidizing agent

Table 4: Identification of a suitable oxidizing agent

	Sodium hydrogen carbonate	Sodium sulphite	Sodium thiosulfate	Sodium bicarbonate
Ethanol	++	-	+	+++
Methanol	-	+	-	+

Ethanol and methanol were the most suitable for printing the hydrochromic ink (Table 3). In the following, a suitable oxidizing agent is to be determined (Table 4). Sodium hydrogen carbonate, sodium sulphite, sodium thiosulfate and sodium bicarbonate were included in the closer selection. The best results were observed with sodium hydrogen carbonate or sodium bicarbonate in ethanol. In this process, an instantaneous extinguishing process occurred. Sodium thiosulfate has shown a weak reaction and sodium sulphite none. Sodium sulphite or sodium bicarbonate in methanol were slightly soluble, whereas the other two oxidizing agents showed no significant reaction. Finally, a preliminary test showed that sodium bicarbonate in combination with the dye patent blue V and ethanol provided the clearest and most significant results.

Different concentrations of a hydrochromic ink

Various experimental concentrations of hydrochromic ink are described in detail below. The developed prototype version four was used, which is described as 4.1.1 to 4.4.1 (Table 5). With the different concentrations of the hydrochromic ink, the solvent quantities remained constant at 10 ml and only the concentration of the dye and the oxidizing agent differed.

Table 5: Different concentrations of hydrochromic ink

	Dye	Oxidizing agent	Solvent
4.1.1	0.10 g Patent blue V	0.10 g Sodium bicarbonate	10 ml Ethanol
4.2.1	0.08 g Patent blue V	0.08 g Sodium bicarbonate	10 ml Ethanol
4.3.1	0.06 g Patent blue V	0.06 g Sodium bicarbonate	10 ml Ethanol
4.4.1	0.04 g Patent blue V	0.04 g Sodium bicarbonate	10 ml Ethanol

Patent blue V has a solubility of 20 g/l at 20 °C and 100 g/l at 90 °C in water. According to Otterstätter (1999), it is recommended to work in a concentration range without the potential for crystallization. Furthermore, it is important that the entire colorant solution must be filtered to avoid undissolved particles. This procedure enables the complete solubility of the dye patent blue V at a dye concentration of < 0.2 g in 10 ml ethanol. Sample preparation for microscopic particle size analysis: In the following, a particle size analysis was carried out to examine the distribution of the particles and their size from various samples to determine the suitability for an inkjet-compatible ink. Therefore, it is determined how the particle size is distributed on a glass substrate after oxidative drying. –Note that this investigation does not determine the particle distribution in the inkjet ink itself. – A sample of 0.1 ml was diluted in 2 ml ethanol (1:20) from the inkjet-capable samples (Table 4). The diluted samples were positioned under a laser scanning confocal microscope, placed under a 50-fold magnification and marked with a reference scale of 10 µm. The method of microscopic particle counting was used, whereby a sample of 100 particles was also randomly selected. Figure 4 shows the particle distribution of the hydrochromic dye in different concentrations. The particle distribution illustrates the

partial solubility of the patent blue V dye in the solvent.

Although the hydrochromic dye is partially soluble in the solvent and there are rest solid particles suspended in the liquid. In all graphs, a left-sided distribution can be seen, which already indicates an increased particle frequency of 1 μm to approx. 11 μm . Particle frequencies of more than 11 μm occur in reduced quantities. The particles found indicate that the crystals have not dissolved. Probably the dye has to be dissolved in further work at an increased temperature. In this case, the hydrochromic inks have been filtered in two steps before being

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 , to remove all particles larger than 5.0 μm . Finally, 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 (450 nm) remain in the ink. This means that the hydrochromic ink is nearly the recommended particle size range of less than 200 – 300 nm (Magdassi, 2010). Consequently, it was ensured that harmful residual particles do not lead to clogging of the inkjet pipes and the nozzle.

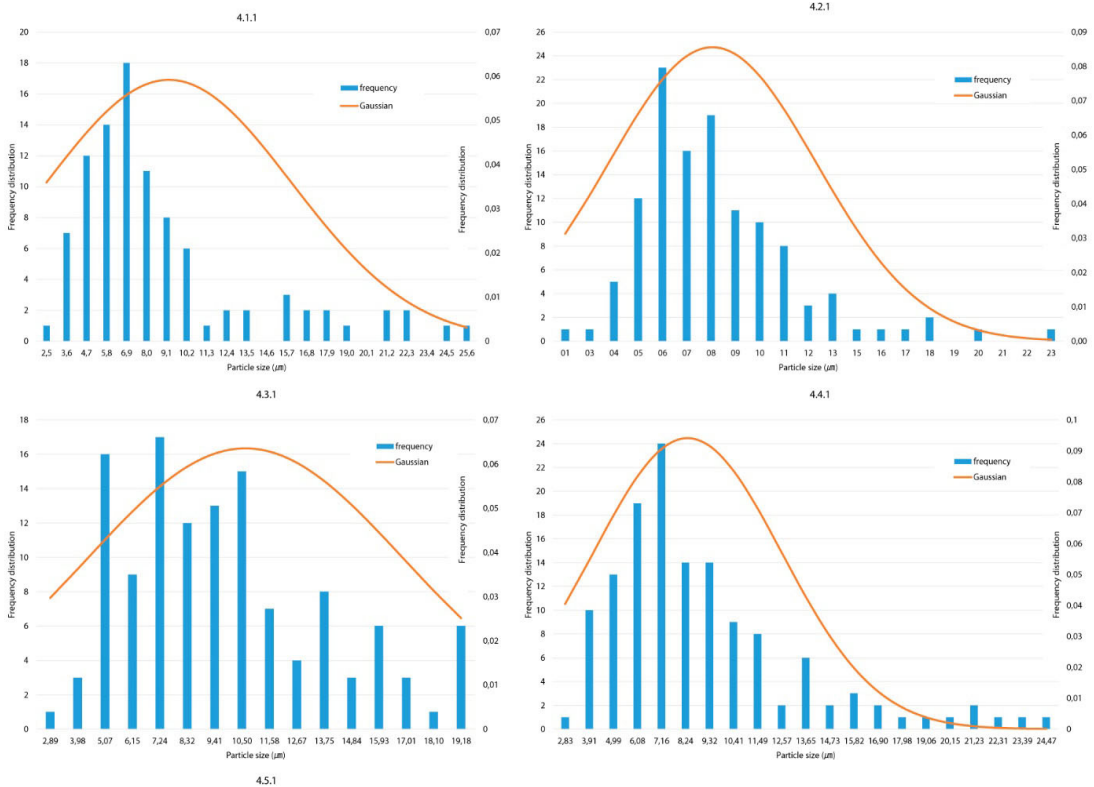


Figure 4: Particle size analysis

Lightfastness test

The dye patent blue V was examined with regard to its lightfastness since the literature mentions that the dye should have no constant lightfastness and it fades quickly under the influence of light. Scotter (2015) describes patent blue V as moderately light stable. He also describes Patent Blue V as fading in the presence of sulphur dioxide, ascorbic acid, fruit acids and alkaline media. Experiment: Strips were printed with hydrochromic ink and were partially covered with an opaque layer (cardboard stencil) and exposed to direct UV-A light for a distinct duration. Examination recipe of the hydrochromic ink: 0.04g patent blue V with 0.1g sodium hydroxide solution in 5ml ethanol and additives (Table 1). For the exposure of the samples, the selected UV light source (Figure 5) shows a high peak at a wavelength of about 370 nm, where the wavelength range of UVA (315-400nm) is located. Therefore, the light

source was measured at different heights. For the lightfastness analysis, the position 18 cm: 0.3 mW/cm² of nearly direct contact to the light source was chosen. The position 0 cm: 0.06 mW/cm² describes the farthest distance from the measuring sensor to the light source. Half of the distance from the sample to the light source is 9 cm: 0.19 mW/cm².

Figure 6 shows the time dependence curve of light exposure to the hydrochromic surface from several hours to a maximum of 9 days. CIE L* a* b* is a colour space defined in 1976 by the International Commission on Illumination (CIE). L* (lightness) represents the range from 0 (white) to 100 (black). The samples show gradually decreasing color coordinates at a different duration of exposure. Below, two different compositions of the ink are examined with regard to their lightfastness. For the experimental setting two different formulations of patent blue V were used: Va (patent blue V + ethanol) and Vb (patent blue V + ethanol + sodium bicarbon-

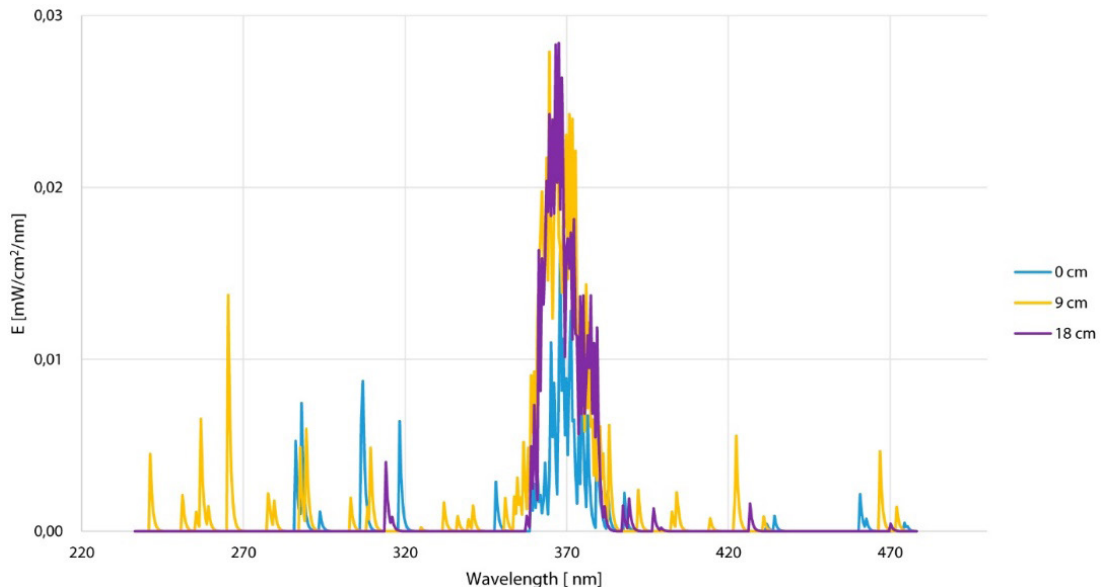


Figure 4: Wavelength of an ultraviolet light source

ate). The diagram shows that the formulation Va without an oxidizing agent (sodium bicarbonate) was already slightly brighter at the beginning (L^* : 54.53) than Vb with an oxidizing agent (L^* : 51.09).

by a color difference Va of ΔE 18.79 and Vb of ΔE 18.00 after a continuous exposure period of UVA (Figure 7). In a follow-up examination, it should be determined whether it might be more effective to examine the hydrochromic colour in the blue (b^*) coordinate in addition to the L^* coordinate since larger changes are visible here.

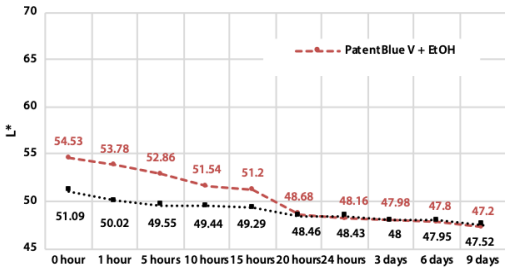


Figure 6: Lightfastness test under the observation of the L^* -value

Both compositions become progressively darker in colour more precisely in their lightness L^* coordinate. After 20 hours, the two curves approximate. Thus, during the unexposed state, Va exhibited an L^* value of 54.53 and decreased its value to 48.16 after 24 hours. Whereas Vb exhibited at the beginning an L^* value of 51.09 and reached after 24 hours an L^* value of 48.43. After more than one week (9 days) of continuous exposure, Va reached an L^* value of 47.2 and Vb an L^* value of 47.52. Consequently, the hydrochrome dye darkened significantly

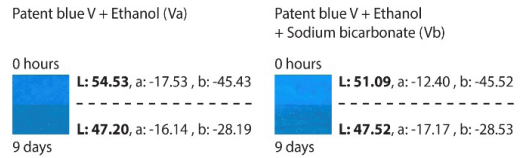


Figure 7: Va and Vb before and after exposure

Figure 8 shows the reflection spectrum, which represents the overlap of the two curves. Here the concentrations patent blue V in ethanol and patent blue V in ethanol + sodium bicarbonate are very similar in their spectral properties. The characteristic of the hydrochromic ink can be recognized in the range wavelengths from 425 nm to approx. 560 nm, where its peak of the hydrochromic ink was located in the range of 465 nm. The recognition process of the color of the hydrochromic ink can be performed by computer vision and the evaluation of RGB or CIE $L^*a^*b^*$ values (Bilgin and Backhaus, 2019).

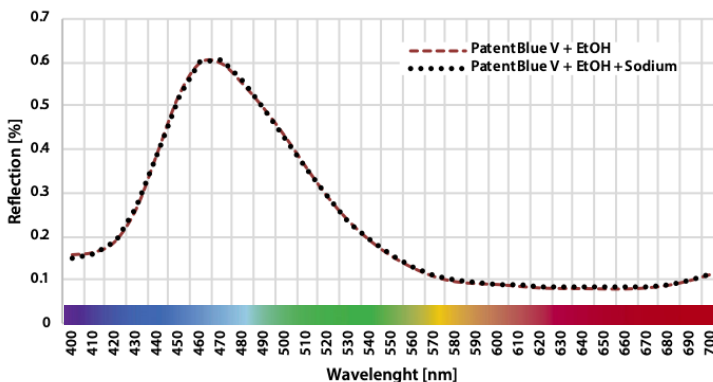


Figure 8: Lightfastness test | reflection spectrum of patent blue V in ethanol with and without sodium bicarbonate

Conclusions

Hydrochromic inks change their colour under the influence of water or moisture. This research work focuses on the development of an irreversible hydrochromic ink based on a triphenylmethane dye, which is named patent blue V. When contaminated with water, the ink switches from one colour to another and remains irreversibly in its new state. In this way, the hydrochromic dye was embedded in a solvent-based inkjet matrix developed for piezoelectric inkjet printing and based on the chemical principle of an ink eraser. The development of a hydrochromic ink based on triphenylmethane dyes requires the use of a suitable solvent. Therefore a set of criteria was defined which helps to identify a suitable solvent. Another criterion was the identification of a suitable oxidizing agent. Sodium sulphite, sodium hydrogen carbonate and sodium thiosulphate and others were used as oxidants to achieve the best erasing effect. Additionally, the solubility of the compounds was evaluated. In this case, the hydrochromic samples were filtered in two phases before being filled into an inkjet cartridge. Finally, the lightfastness of the hydrochromic ink was analyzed. In the next step of the study, different concentrations of the hydrochromic ink will be investigated. Physical properties such as viscosity, surface tension and particle size distribution will be investigated to develop a suitable hydrochromic ink for piezoelectric inkjet printing. Furthermore, the reaction behavior of the hydrochromic ink will be examined.

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