

# Investigation of a Hydrochromic Ink Used As a Safety Feature

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## Abstract

Hydrochromic inks change their colour by impact of water or moisture. Depending on the ink's components, this colour change process can be reversible or irreversible. Here, focus is on irreversible colour changes, without any re-change of the ink's color. Moisture is 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). The aim of this research project is to develop a hydrochromic ink for piezoelectric inkjet printing that serves as a security feature. The functionality of the developed hydrochromic ink and the theoretical background will be discussed. Furthermore, the identification of a suitable solvent will be discussed and criteria for the identification will be shown. Furthermore, suitable oxidizing agents will be identified. The resulting ink will be printed and tested regarding to its light fastness. Furthermore, the characteristic properties such as the colour change behavior will be analyzed.

## 1. Introduction

This research work is part of an overall concept of inkjet printed multi-functional sensors and their decoding via smart devices. One of the sensors' function is detection of water. For this, inks are required which contain dyes that change their color irreversibly by impact of water and do not re-change when water is reduced or removed (Fig. 1). There, are such inks can be got for some printing technologies but unfortunately there are no inks available that fulfill the high requirements for inkjet printing.

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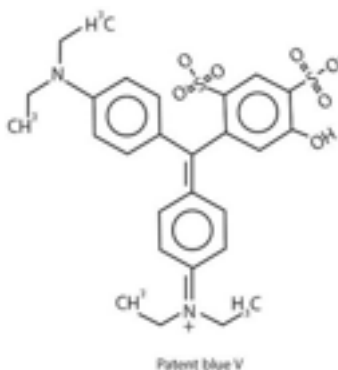
Electronic devices e.g. smartphones are marked with irreversible hydrochromic ink in order to document the influence of moisture and water in case of functional failure. Furthermore, there are various hydrochromic dyes that are harmful. Therefore, they cannot be used in the food or health sector. For example, copper (II) sulfate, which shows a white color in dry state and a blue color in humid state. As well cobalt (II) chloride, which shows a blue colour in the dehydrated state and a red colour after a hydration as hexahydrate.



**Fig 1.** Hydrochromic ink (irreversible) changes its color from blue to transparent

During prior investigations, because of the same reasons an irreversible photochromic ink was already developed (Bilgin and Backhaus, 2018). For the current investigations, the hydrochromic dye is embedded in a solvent-based fluid matrix, which has been developed for piezoelectric inkjet printing.

This research work focuses on patent blue V a triphenylmethane dye. Triphenylmethane dyes are used in different segments e.g. as food colorants (EU food additive number: E 131), printing inks, indicators.. Patent blue V (EU, 2013) consists primarily of calcium, sodium or potassium compounds consisting of [4-( $\alpha$ -(4-diethylaminophenyl)-5-hydroxy-2,4-disulphophenyl-methylidene)-2,5-cyclohexadien-1-ylidene] diethyl-ammonium hydroxide inner salt (ibid.). In order to produce a leuco-form compound, patent blue V (Fig. 2) is prepared by “condensation and sulphonation of N, N-diethylaniline and 3-hydroxybenzaldehyde in acidic conditions (sulphuric acid)” (ibid.).



**Fig 2.** Structural formula of patent blue V

A hydrochrome ink was developed based on the same chemical principle like an ink eraser. The function of an ink eraser bases on two components: a colorless felt impregnated with an oxidizing agent and an ink-erase resistant ink for correction. Sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) and sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}$ ) were used as oxidizing agents to obtain the best erasing effect. Because of the  $\text{sp}^2$ -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  $\pi$ -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 ink eraser takes place as follows: Anions negatively charged with water such as the hydroxide ion ( $\text{OH}^-$ ) or the hydrogen sulphite ion ( $\text{HSO}_3^-$ ) attack the central carbon atom and are added together. The geometry of the triphenylmethane dye molecule is changed and the central carbon atom is  $\text{sp}^3$ -hybridized. Thus, the delocalizing (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 dye for inkjet inks, this chemical process was constructed in a reverse order. This can be found further down in the results of this research.

## 2. Methods

The hydrochrome ink (described in chapter results) was printed with a piezoelectric inkjet printer (Epson Stylus Photo 1500W / 1430W / Artisan 1430 / EP-4004), commonly used in the non-professional printer segment. 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 ink droplet sizes per nozzle; Nozzle Configuration: 90 Nozzles Black (K), 90 Nozzles per Colour (CMY+Lc,Lm); Max. Printing resolution: 5760dpi x 1440dpi (Horizontal x Vertical). The decolonization process (color change of the contaminated dye) was measured by a spectral densitometer (TECHKON SpectroDens). In this way the RGB and CIEL\*a\*b values were used to determine indirectly the decolonization process (via change of the dye's colour). Technical parameters: Polarizing filter: off; type of light: D50, 2° normal observer; diameter of measuring aperture: 3 mm. For the lightfastness test, the UV light source was measured with a spectroradiometer UVpad E (Opsytec Dr. Gröbel GmbH). There, 512 photodiodes measure the spectrum in the spectral area of 240 - 480 nm  $\pm 5$  nm, irradiance, 0 - 5000 mW/cm<sup>2</sup>, irradiation dose: 1 mJ/cm<sup>2</sup> - 600 J/cm<sup>2</sup>, spectral ranges (UVA, UVB, UVC, VIS). The analyzing process of the solubility test was performed by using a Keyence 3D laser scanning confocal microscope. Table 1 shows the materials used for the experiment. A Standardized paper

(Table 1) was used to carry out the experiment in order to ensure the comparability of the samples. A solvent-based ink based on ethanol is used for the inkjet process, as logically no water-based ink can be used due to its functionality.

### 2.1. Materials

Substrates	Inapa tecno, oxygen pure high-white recycled paper, Format: 210 x 297 mm (A4), Grammage: 80 g/m <sup>2</sup>
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 <sub>27</sub> H <sub>33</sub> N <sub>2</sub> O <sub>7</sub> S <sub>2</sub> Na Molar mass: 566.66 g·mol <sup>-1</sup>
Oxidizing agents	Sodium hydrogen carbonate CAS Number: 497-19-8 Chemical formula: Na <sub>2</sub> CO <sub>3</sub> Molar mass: 105,99 g·mol <sup>-1</sup>  Sodium sulfite CAS Number: 7757-83-7 Chemical formula: Na <sub>2</sub> SO <sub>3</sub> Molar mass: 126.043 g·mol <sup>-1</sup>  Sodium thiosulfate CAS Number: 7772-98-7 Chemical formula: Na <sub>2</sub> S <sub>2</sub> O Molar mass: 158.11 g·mol <sup>-1</sup>  Sodium bicarbonate CAS Number: 144-55-8 Chemical formula: NaHCO <sub>3</sub> Molar mass: 84.01 g·mol <sup>-1</sup>
Base (Ink)	Ethanol CAS Number: 64-17-5 Chemical formula: C <sub>2</sub> H <sub>6</sub> O Molar mass: 46.069 g·mol <sup>-1</sup>
Additives of the ink	Humectants: Urea (CH <sub>4</sub> N <sub>2</sub> O)
Equipment (Filtration)	Millex-SV (SLSV025LS) <ul style="list-style-type: none"> <li>● Pore Size: 5.0 μm (5000 nm)</li> </ul> Millex-HPF HV Filter (SLHVM25NS) <ul style="list-style-type: none"> <li>● Pore Size: 0.45 μm (450 nm)</li> </ul> Filtration Area: 3.9 cm <sup>2</sup> Material: Hydrophilic Polyvinylidene Fluoride (PVDF)

*Table 1. Experimental materials*

## 2.2. 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 °C (+/- 1 °C) and the relative humidity: 55% (+/- 1%) was continuously observed and recorded.

## 3. Results

In the following a hydrochromic ink was developed, which is based on the reverse chemical process of an ink eraser. The ink will be adapted for piezoelectric inkjet printing in a later publication. In order to ensure that the hydrochromic ink can react with water, a water-based base ink was logically avoided and a solvent as an ink matrix was used based on ethanol, to which a defined amount of sodium hydrogen carbonate and additives (Table 1) were added. When reacting with water, the addition of the hydrogen sulphite ion ( $\text{HSO}^-$ ) 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 hybridized  $\text{sp}^2$  planarity, which is necessary for the coloration and changes its structure to become the tetrahedral arranged  $\text{sp}^3$  shape. The hydrochromic ink has been developed according to the concept of an ink eraser (Fig. 3, left). For example, after writing with a triphenylmethane dye (patent blue V) in a fountain pen, the writing is transferred to the paper. In order to make a correction, 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. For this purpose, the formulated hydrochromic ink (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.

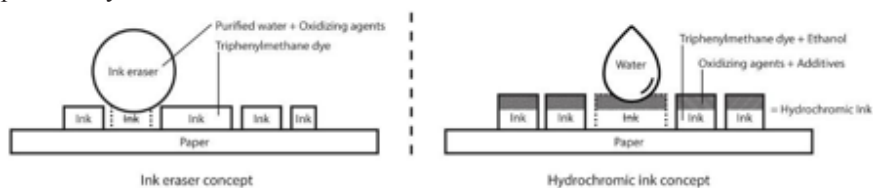


Fig 3. Ink eraser and hydrochromic ink concepts

### 3.1. Identification of an appropriate base ink

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 to 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).

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

*Table 2. Criteria for identifying a suitable solvent-based ink*

Table 2, provides the criteria for the identification of a solvent-based ink. These criteria were 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 experiment series. An important criterion was the homogeneity of the liquid when applying the samples. The solvent isopropyl alcohol could not be applied homogeneously, since it led to crystallization on the applied surface. 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 demonstrating the most robust solvents in combination with the dye patent blue (grey marked).

### **3.2. Identification of a suitable oxidizing agent**

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

*Table 3. Criteria for identifying of a suitable oxidizing agent*

In Table 2, ethanol and methanol were identified as suitable for printing. In the following a suitable oxidizing agent is to be determined (Table 3). Sodium hydrogen carbonate, sodium sulfite, 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 sulfite none. Sodium sulfite 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.

### 3.3. Different concentrations of a hydrochromic ink

Various experimental concentrations of a hydrochromic ink are described in detail below. The developed prototype version four was used, which is described as 4.1.1 to 4.5.1 (Table 4). With the different concentrations of the hydrochromic ink, the solvent quantities remain constant at 10 ml and only the concentration of the dye and the oxidizing agent differ.

	Dye	Oxidizing agents	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

Table 4. Different concentrations of the hydrochromic Ink

### 3.4. Evaluation of the solubility

In the following, a particle analysis was carried out to examine the distribution of the particles and their size from various samples in order 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  $\mu\text{m}$ . The method of microscopic particle counting was used, whereby a sample of 100 particles was also randomly selected.

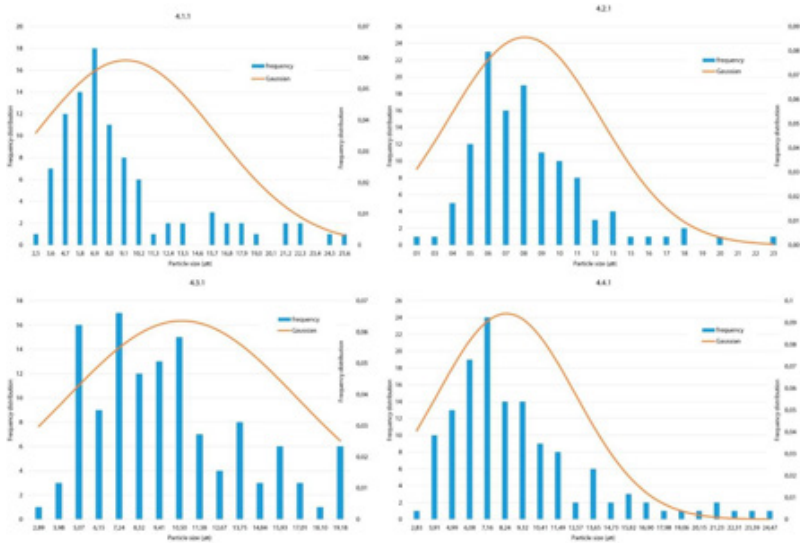


Fig 4. Particle size analysis

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 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 corridor of < 0.2 g in 10 ml ethanol.

Fig. 4 shows the particle distribution of the hydrochromic dye in different concentrations (Table 4). The particle distribution illustrates the partial solubility of the patent blue V dye in the solvent. The distribution already shows that the hydrochrome dye was not completely dissolved in the solvent and that there are still solid particles in the liquid. In all diagrams, a particle distribution between 1 µm and approx. 25 µm can be recognized. From the left - sided distribution in the diagrams (4.1.1, 4.2.1 and 4.4.1) it can be seen that the frequency of the particles is more in the range of approx. 3 µm to approx. 11 µm. Particle frequencies of more than 11 µm occur in reduced quantities. For this reason, 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, so that 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 is ensured that harmful residual particles do not lead to clogging of the inkjet pipes and the nozzle.

### 3.5. *Light fastness test*

The dye Patent Blue V has been investigated with regard to its light fastness, as it is mentioned in the literature that the dye has no constant light fastness and 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. In the following the experimental setup of a lightfastness test will be introduced: Strips printed with hydrochromic ink 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: 0.05g patent blue V with 0.1 g sodium hydroxide solution in 5ml ethanol and additives. For the exposure of the samples the selected UV light source (Fig. 5) shows a high peak at a wavelength of about 370 nm, where the wavelength range of UVA (315-400nm) is located. For the lightfastness analysis, the position 18 cm: 0.3 mW/cm<sup>2</sup> of nearly direct contact to the light source was chosen. The position 0 cm: 0.06 mW/cm<sup>2</sup> 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/cm<sup>2</sup>.



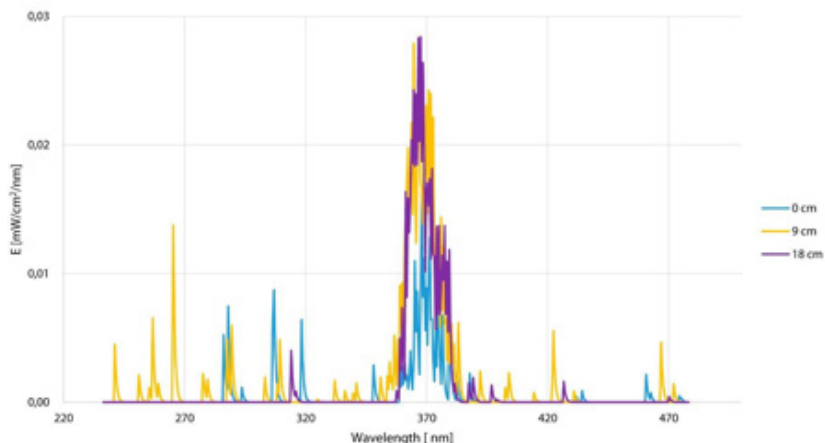


Fig 5. wavelength of an ultraviolet light source

Fig. 6 shows the time curve of light exposure to the hydrochromic surface after several hours and maximum 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 properties at different duration of exposure. Below, two different compositions of the ink are examined with regard to their light fastness. 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 bicarbonate). The diagram shows that the formulation Va without oxidizing agent (sodium bicarbonate) is already slightly brighter at the beginning ( $L^*$ : 54.53) than Vb with oxidizing agent ( $L^*$ : 51.09).

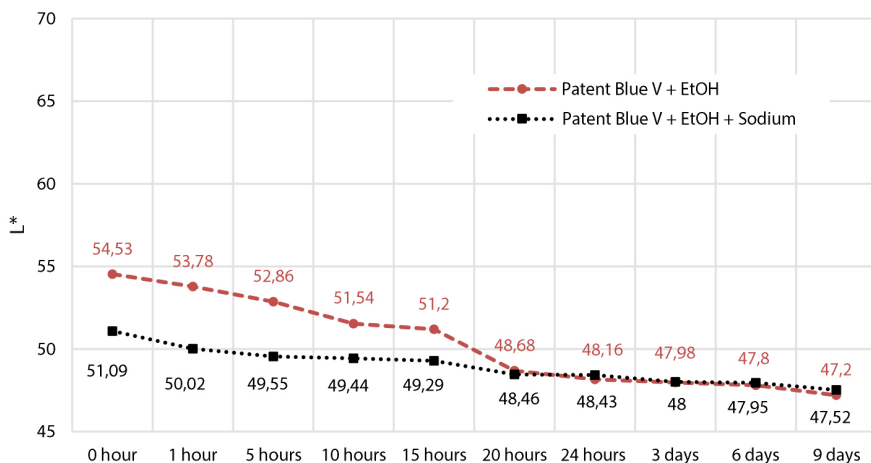


Fig 6. Lightfastness test under observation of the  $L^*$ -value

Both compositions become progressively darker in colour more precisely in their brightness. 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 a L\* value of 47.52. Consequently, the hydrochrome ink darkened significantly by a color difference Va of  $\Delta E$  18.79 and Vb of  $\Delta E$  18.00 after a continuous exposure period of UVA (Fig. 7).



Fig 7. Va and Vb before and after exposure

Figure Fig. 8 shows the remission curves, which show 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. This proximity indicates that the patent blue V has an almost identical spectral distribution, independent of the embedding of sodium bicarbonate. 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 is 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).

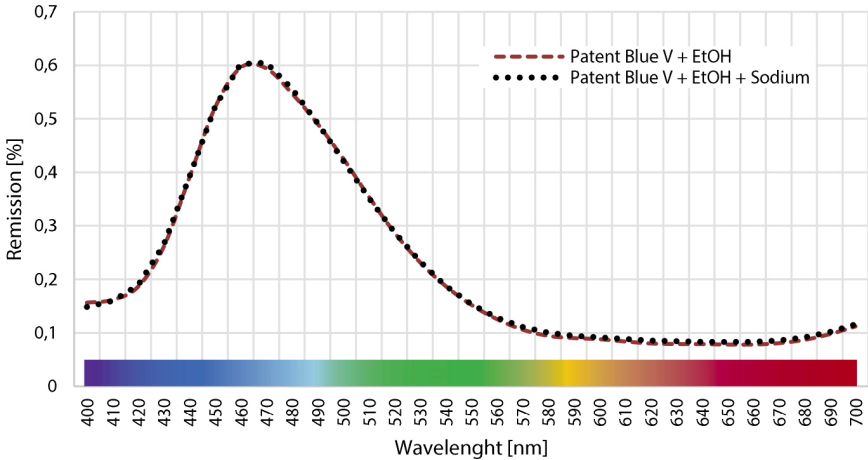


Fig 8. light fastness test: Remission curve of patent blue V in ethanol with and without sodium bicarbonate

#### 4. Conclusions

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 changes its colour and remains irreversibly in its new transparent state. The development of a hydrochromic ink based on triphenylmethane dyes uses a compatible ethanol-based solvent. Sodium sulphite, sodium hydrogen carbonate and sodium thiosulphate and others were examined as oxidants to achieve the best erasing effect. The best result was achieved with sodium bicarbonate. It was demonstrated that dye components in the hydrochromic ink based on patent blue v do not dissolve completely. This problem could be compensated with a double filtration process. It is recommended to use an additional finer filtration degree than in the experiment. During the lightfastness test, the sample was exposed with UV-A light of an intensity of 0.3 mW/cm<sup>2</sup> for a duration of 9 days (216 hours). In this case, the patent blue dye was darkened in the opposite way to the information in the literature. 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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