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Cyanotype – from hand craft to industrial print

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Short abstract

In this extended abstract, first, a history of cyanotype is presented. The aim of this research is to change the process of cyanotype from hand craft to industrial application. A test form is developed which serves as a photo mask for the cyanotype process. Printing experiments on an industrial, modular, label printing press Gallus RCS 330-HD are conducted at 5 m/min on foil and paper. The flexographic unit is used to apply the main components necessary for the cyanotype process, a UV curer is utilized for exposure and the gravure unit for washing out the remains with distilled water. This is a novel technique and application for the cyanotype process. Quality of the printed Prussian blue layers is evaluated using a spectrophotometer, measuring the CIE $L^*a^*b^*$ values of solid and halftone patches. The results show that the Prussian blue is homogeneously distributed over the printed area. As expected, small details are transferred well, since the cyanotype process has already been established for blueprints in the past. Future applications for cyanotype are discussed, as the presented industrial process gives the opportunity to fabricate, e.g., electrochromic (EC) devices, which can contain a Prussian blue layer within their layer stack. Thus, our process could serve as an alternative to coating processes for EC devices.

Keywords: flexography, rotogravure, gravure printing, blue print, Prussian blue

1. Introduction and background

The technique of cyanotype is a photographic process, which is known for at least 150 years. It can be traced back to its inventor, the English astronomer Sir John Herschel (Herschel, 1842). Cyanotype became first widely known trough Anna Atkins, who utilized the process to document plants in 1843 (Atkins, 1843, Figure 1a). Under the name of blueprint, the cyanotype was also used by Herreshoff Manufacturing Company for the first copies of technical drawings using the light tracing process (MIT Museum, 1919, Figure 1b).

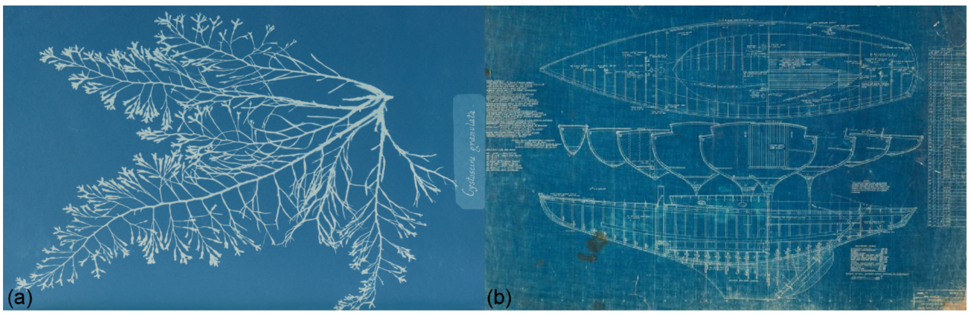

Figure 1: Examples for cyanotype: (a) artwork created by A. Atkins (1843) using cyanotype which shows plants like "Cystoseira granulata" from 1843 and (b) Historical blueprint of a "828 Class Knockabout" yacht (MIT Museum, 1919)

In this process a light blocking object is used or an original is first drawn onto a translucent substrate (Mrhar, 2013) which is then placed on a sheet of paper which was prepared with a layer of liquid containing light-sensitive iron(III) complexes. The arrangement is then exposed to light, so that the object or original serves as a photomask. Where exposed to the light the liquid is photodecomposed and reacts to form an insoluble, blue pigment, also known as *Prussian blue.* The remaining unexposed areas do not undergo this reaction and can therefore be washed out afterwards. On a white substrate, these areas then appear pale. Cyanotype can therefore be used to create multiple copies of an original. Today, cyanotype is still enjoying worldwide attention for artwork and illustrations and was added to the list of intangible cultural heritage by UNESCO in 2018 (Unesco, 2018).

Prussian blue is considered one of the earliest synthetic color pigments. It owes its deep blue color to an absorption of light in the yellow, reddish range and reflection of blue light as the complementary color. The principle of cyanotype is based on the photodecomposition of iron(III) complexes, which are e.g. contained in ammonium ferric citrate or ferric ammonium oxalate. In these, the light-sensitive iron(III) carboxylate is chemically reduced induced by UV-light to give iron(II). The iron(II) complexes can further react with also added potassium ferricyanide to give $Fe_4[F(CN)_6]_3$ or *Prussian blue*. While Prussian blue is not solvable in water the iron(III) containing chemicals (ammonium ferric citrate or ferric ammonium oxalate) are and can be washed out with water, so that only the distinctive blue colored Prussian blue remains. (Ware, 2003)

In printing or artwork application cyanotype can be considered as a mainly manual task. Firstly, potassium hexacyanidoferrate(III) is mixed with green ammonium iron(III) citrate or iron ammonium oxalate in the ratio 2:1 or 1:1 and dissolved in distilled water. The solution is applied to a watercolor paper e.g. using a brush. This paper appears now in a colored *Prussian green*. After the applied solution has dried, a photomask is placed on the coated watercolor paper and exposed to a source of UV radiation (e.g. direct sunlight or a UV lamp). When the photomask is removed, the unexposed areas are still Prussian green, the exposed areas contain reacted and unreacted parts and it appears in a *Prussian brown* tone. The coated watercolor paper must then be washed, using water to remove the unexposed components and fix the exposed areas. The fixed areas take on the Prussian blue hue, which becomes slightly darker when later on exposed to oxygen. This blue pigment is stable to light and insoluble in water. (Maehrle, 2020)

Although Prussian blue is also used in modern applications, such as automatic darkening of window panes by electrochromic (EC) devices, a modern printing process has not yet been established. The aim of this work is therefore to close this gap and find a suitable process for an automated printing of cyanotype with a modern printing setup. For this purpose, two proven conventional printing processes, flexography and gravure printing, are used. In this work, the transition from mainly manual tasks of the historical cyanotype printing to modern, industrial machines is developed and printing parameters are discussed. Furthermore, experiments are carried out to influence the saturation of the blue hue in the cyanotype in order to obtain further variation possibilities.

2. Materials and methods

2.1 Preliminary test

A test form was designed (see Figure 2) and printed on an overhead transparency foil (3561 overhead projector transparencies, thickness 0.13 mm, *Avery Denison*, Ohio, USA) using a laser printer (Bizhub C258, 1 800 × 600 dpi, *Konica Minolta Holdings K.K.*, Marunouchi, Japan) as a photomask for the manual task of cyanotype.

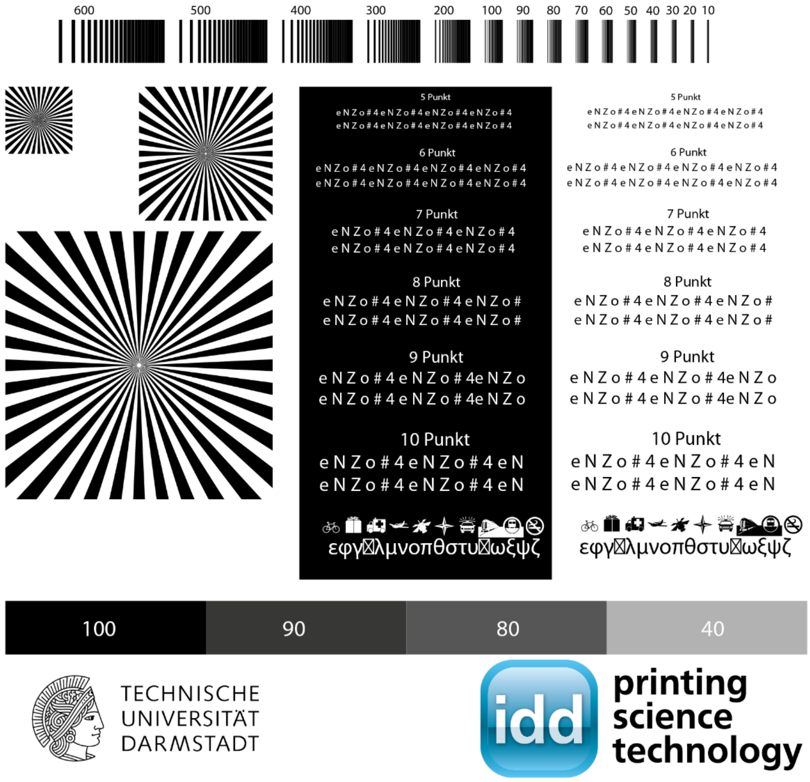

Figure 2: Layout of the test form with line spacing bars, siemens stars, negative and positive font field with fonts in 5 to 10 points size, a solid field (100 %) and halftone fields of 90, 80 and 40 %

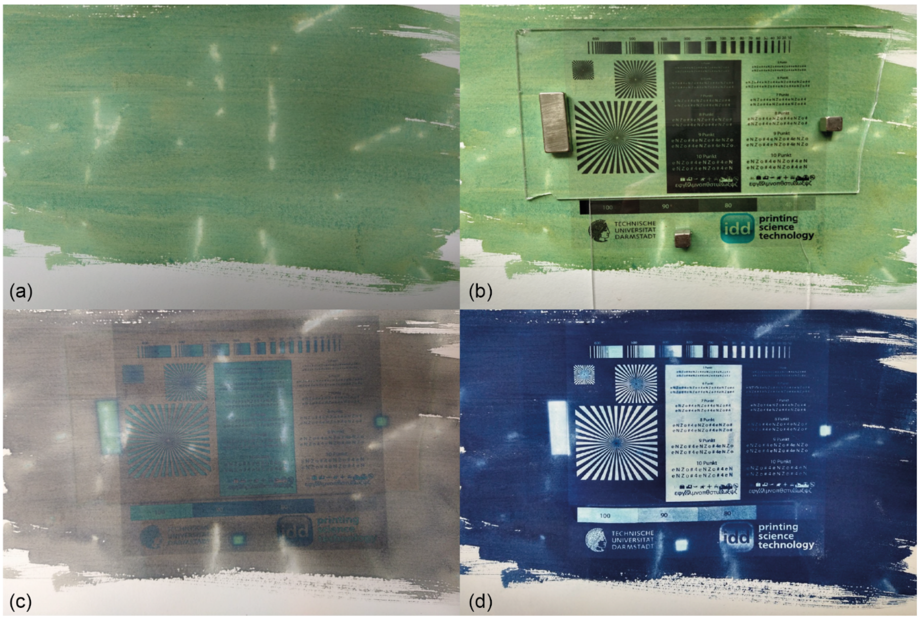

Figure 3: Preliminary test of the cyanotype workflow: (a) Prussian green after applying and drying of solution (A) onto paper, (b) overhead test form foil with quartz glass placed on (a), (c) Prussian brown after UV lightning and removing of the test form, (d) after washing Prussian blue developed

A solution (A) of 20 g potassium hexacyanidoferrate(III) red (*Kremer Pigmente*, Aichstetten, Germany) and 10 g green ammonium iron(III)citrate green (*Kremer Pigmente*, Aichstetten, Germany) with 200 ml distilled water was prepared. The aquarelle paper used was Mixed Media Universalblock (*Hahnemühle*, Dassel, Germany) in the size 30 cm × 40 cm in 310 g/m^2. Solution (A) was applied to the watercolor paper with a brush and appears in Prussian green (Figure 3a). The test form printed on the overhead transparency foil was placed on the substrate coated with the dried solution (A), i.e. the iron (III) complex, (Figure 3b) and weighted down with a quartz glass. Afterwards, this setup was exposed with a UV dryer (*IST Metz GmbH*, Nürtingen, Germany) with a lamp power of 200 W/cm at a transport belt speed of 5 m/min. After exposure, solution (A) appears in a Prussian brown (Figure 3c). The watercolor paper was then washed out under running water and solution (A) now appears in Prussian blue (Figure 3, d).

It was noticed that the aquarelle paper curls after the application of solution (A) and the overhead transparency warps after UV exposure, which shows that the UV curing unit was set to strong. To prevent the paper from warping, it is recommended to mount the aquarelle paper on a frame before applying solution (A). Nevertheless, a result can be examined (Figure 4a). Characters are displayed well in the positive field (Figure 4b) up to a font size of 5 points. A very good resolution up to seven points can be seen in the font negative field (Figure 4c). The Siemens stars shows a very good line resolution down to the smallest resolutions. The line spacing bars (Figure 4d) also show a clean spacing, up to a spacing of 0.5 mm with a line width of 0.4 mm. Unfortunately, not all line distances can be evaluated because, as described above, the paper has warped in some areas. The solid field and the halftone fields (Figure 4e) still shows a good resolution in the 90 % and 80 % fields, but the 40 % field is completely closed and shows no halftone. So the tonal value curves show a convergence of the halftone dots towards a solid field, especially of the 40 % halftone field. But even in this field, an exact evaluation is not possible due to the warpage of the paper. However, this preliminary test shows that a Prussian blue is quite easy to produce and halftones can be achieved.

Figure 4: (a) Sample of the cyanotyped test form on aquarelle paper, (b) positive font field, (c) negative font field, (d) line spacing bars, (e) solid and halftone fields

After the success of this preliminary test, it was considered how the solution could be processed via an inline printing press.

2.1.1 Printing setup

A label printing press, Gallus RCS 330-HD (*Heidelberg Group Company*, Wiesloch, Germany), was selected for the inline process (Figure 5a) that has the following features: A large variety of printing methods (flexographic, gravure, rotary screen, offset and inkjet printing) can be used simultaneously and their sequence can be easily changed. Another degree of freedom is provided by the possibility of printing different colors or materials. The label printing press offers the possibility of UV, hot air or IR curing after each printing unit without changing the web guide of the substrate.

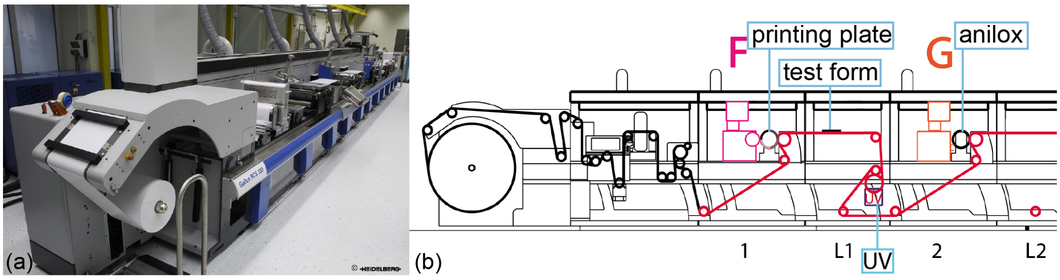

Figure 5: (a) Label printing press, (b) technical draw of the printing units Flexography (F) and Gravure (G) with web guide of the substrate in red and UV exposure

A corona treatment unit for conditioning the film web is also included. In our case, we decided to use the flexography and the gravure printing unit (Figure 5b). Flexography printing is a proven conventional printing process which plays an important role in the packaging industry (cardboard, foils, etc.) and is based on the letterpress technology (Nisato, Lupo and Ganz, 2016). We use this printing unit to apply the solution (A) with a solid and halftone flexographic printing plate which has 90 %, 80 % and 40 % patches (Figure 6). Gravure printing is a high volume mass production for catalogues, cardboards, etc. which provides high resolution and best edge definition in its printing form (Nisato, Lupo and Ganz, 2016). But these possibilities are not of interest in our case. We change the function of the Gravure unit and use it as a washing unit, to develop the Prussian blue.

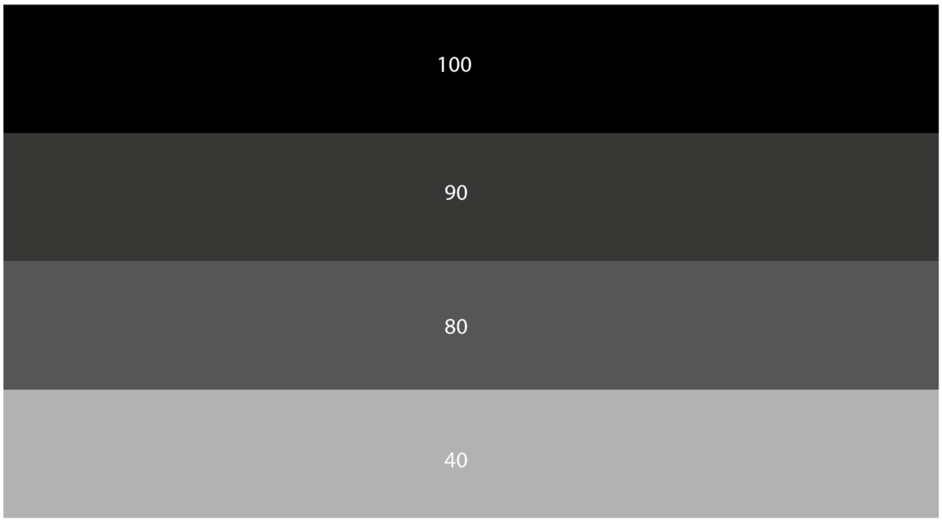

Figure 6: Layout of the flexographic printing plate used, showing the patches of solid (100 %) and halftones (90 % to 40 %)

2.1.2 Experimental setup

In the flexographic printing unit, an anilox roller (*Zecher GmbH*, Paderborn, Germany) with specifications of 7.9 cm^3/m^2, Haschur engraving, 160 l/cm and a Nyloflex ACE (Flint Group, Luxembourg) printing plate with the layout as shown in (Figure 6) were always used. The printing speed of 5 m/min was limited due to low viscosity (1 mPa·s) of the used solution (A) and was always used, for the printing tests. All other variated parameters are listed in (Table 1).

Table 1: Parameters used (marked with an "x") in the printing trials of this work for the different printing trials indicated by the trial number; the columns are marked in the Prussian green, Prussian brown and Prussian blue color results

Trial number	Substrate	Corona treatment	Test form printed on overhead foil	UV exposer	Gravure washing unit	Running water
Prussian green						
x2	natural coated offset paper 80 g/m²					
x5	natural coated offset paper 80 g/m²				x	
Prussian brown						
x1	natural coated offset paper 80 g/m²			x		
Prussian blue						
x4	natural coated offset paper 80 g/m²			x	x	
x3	natural coated offset paper 80 g/m²		x	x	x	
x6	natural coated offset paper 80 g/m²		x	x		x
x7	HOSTAPHAN PET film 125 µm	x		x	x	

Two substrates were used for the printing tests. A natural coated offset paper (*Igepa, Maxi Offset - FSC®*, 80 g/m², 0.1 mm thickness, Hamburg, Germany) and a PET film (*HOSTAPHAN®* GN 4600A PET film, *Mitsubishi Chemical Group Corporation*, 96 µm thickness, chemically treated on one side, Tokyo, Japan) which was treated with a corona pretreatment (*Arcotec GmbH*, Mönsheim, Germany) with a performance to a maximum of 3000 W with a performance of 40 % at 5 m/min. After applying solution (A) with the flexographic printing unit, the already known test form (Figure 2) printed on the overhead transparency foil, was fixed with tape onto the paper, as a photomask. This test form printed on the overhead transparency foil was removed after development by a UV Hg lamp, 120 W/cm (*Uviterno*, Berneck, Switzerland) at a power of 60 % at 5 m/min. For the gravure unit, another anilox roller (*Zecher GmbH*, Paderborn, Germany) with specifications 13.0 cm³/m², HIT engraving, 100 l/cm was used. The ink chamber of the gravure unit was filled with distilled water instead of a graphical ink to make it usable for a washout.

2.1.3 Measurement setup

The spectral densitometer *Spectrodens* (*Techkon*, Königstein, Germany) was used to determine the CIE $L^*a^*b^*$ values. The spectral densitometer was used with the following measurement geometries: Illuminant D50, viewing angle 2°, no polarizing filter and white reference absolute. The printed solid and halftone patches were measured, each at five different points in one sample, to get a mean value difference (Δ) of the $L^*a^*b^*$ values.

3. Results and discussion

Flexographic printing produced a uniform Prussian green (Figure 7a). After UV expose, the patches reached the Prussian brown (Figure 7b) state. Washing out the patterns with water, by the gravure printing unit or by rinsing under running water, resulted in the classic Prussian blue (Figure 7c) effect.

It was optically recognized, in the used natural coated offset paper, that the halftone patches achieved a more uniform printout compared to the solid area. This is due to the low viscosity and the slow printing speed. It was also recognized that the classic brush application achieved a richer color impression for the Prussian green, brown and blue, which was clearly due to the applied film thickness.

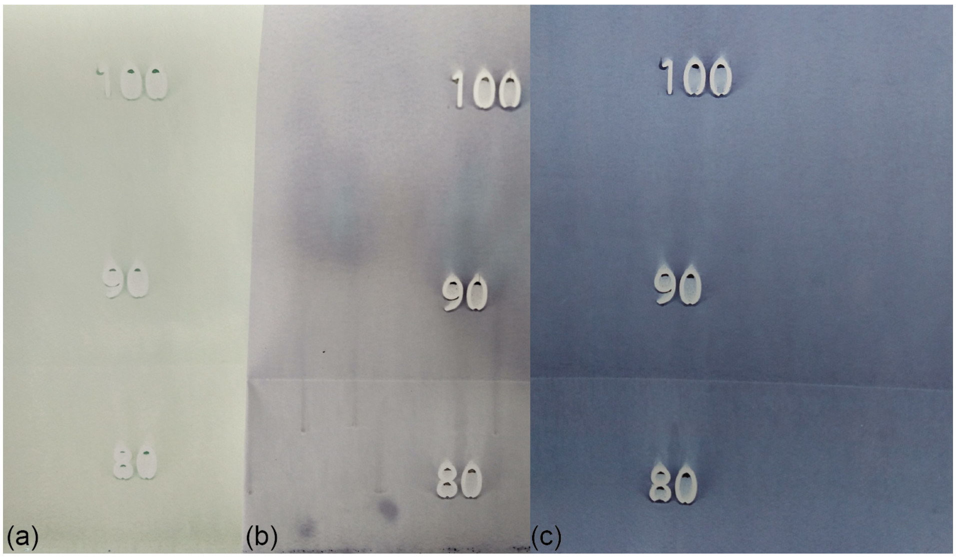

Figure 7: Printed results: (a) Prussian green, (b) Prussian brown and (c) Prussian blue

The Prussian green could be reproduced well on the offset paper and anchored well in the paper, with a mean value of about ±1 Δ in the $L^*a^*b^*$ measurement. Also washing out the substrates with water by using the gravure printing unit had no significant effect, only around one point in the Δ in brightness (L^*) and the color axes (a^*, b^*) (Table 2). Washing out by rinsing under running water removed the Prussian green layer.

Table 2: Prussian green in L, a* and b* values without (x2) and with washing (x5) of solid and halftone patches*

Trial number	**x2**	**x5**	**x2**	**x5**	**x2**	**x5**	**x2**	**x5**
Patches	100 %	100 %	90 %	90 %	80 %	80 %	40 %	40 %
L^*	92.51	91.22	91.83	90.02	90.76	88.95	92.78	92.19
a^*	−0.42	−0.71	−2.49	−3.37	−4.20	−5.05	0.82	0.26
b^*	−1.10	−1.45	3.51	4.02	7.46	7.17	−4.02	−3.27

However, a clear tendency was observed between the Prussian brown and the Prussian blue. In the mean value are only ±2 Δ in the $L^*a^*b^*$ measurement for the trial number x1 and x4. The Δ in brightness (L^*) decreased slightly after washing and generation of the Prussian blue. On the color axes (a^*, b^*) the Δ of the hue shifted to an obvious blue tone (Table 3). A color example for better visualization of trial number x1 and x4 (Figure 8) shows the Δ in $L^*a^*b^*$ between the shades of Prussian brown and Prussian blue in the 90 % patch.

Table 3: Prussian brown to Prussian blue L, a* and b* values of samples exposed to UV light without (x1) and with washing (x4) of solid and halftone patches*

Trial number	**x1**	**x4**	**x1**	**x4**	**x1**	**x4**	**x1**	**x4**
Patches	100 %	100 %	90 %	90 %	80 %	80 %	40 %	40 %
L^*	83.24	79.8	75.22	71.4	77.5	70.36	84.75	82.38
a^*	2.33	1.54	1.98	0.90	2.04	−0.31	2.53	1.26
b^*	−9.87	−13.16	−10.34	−15.4	−9.82	−16.56	−9.39	−11,50

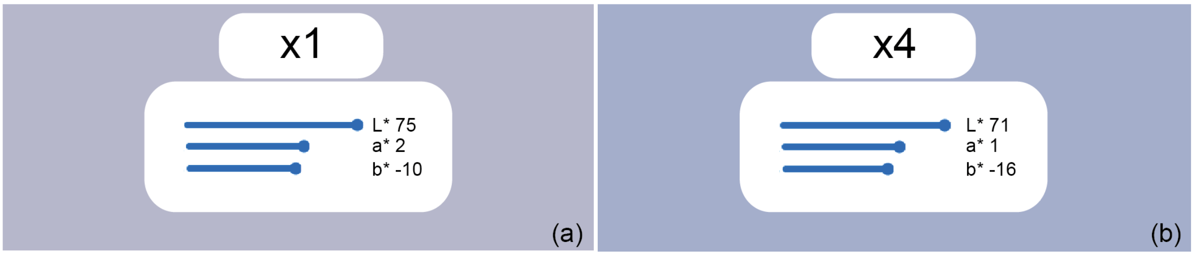

Figure 8: Color example between Prussian brown (a) and Prussian blue (b) in the 90 % patch

The Δ in the patches of the $L^*a^*b^*$ values between washing out the samples by the gravure printing unit or by rinsing under running water are very small (Table 4). In the perceptual lightness (L^*) the Δ of L^* is only around 2–5 points of the solid and halftone patches. These appear slightly darker after washing out with the gravure unit. The Δ of green-magenta (a^*) axis (0.3–2.5 points in the (a^*) and the Δ of the blue-yellow axis (b^*) (0.4–3 points in the (b^*) are negligible. This is a good result, which shows that the gravure printing unit could be used instead of rinsing under running water. Also it shows that the mean value in the trials x3 and x6 is under ±2 Δ in the CIE $L^*a^*b^*$ measurement. When using the test form printed on the overhead transparency foil, a residue of Prussian green (Sample x6, Figure 9a) was visually perceived in the gravure printed sample. The sample rinsed under running water shows no residue of Prussian green (Sample x6, Figure 9b). Since Prussian blue is even used as a drug to bind poisons (radioactive cesium and thallium), this should not cause a health problem.

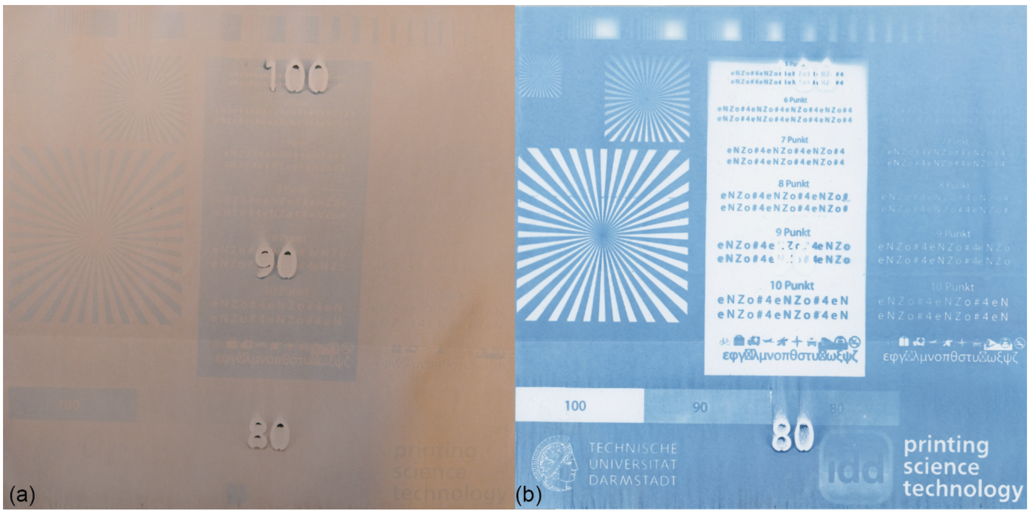

Figure 9: (a) Sample x6 of the test form exposed in Prussian brown with a residue of Prussian green, (b) Sample x6 of the test form by rinsing under running water with no residue of Prussian green

Table 4: The L, a* and b* values of samples washed using the gravure printing unit (x3) or rinsed under running water (x6) of solid and halftone patches*

Trial number	**x3**	**x6**	**x3**	**x6**	**x3**	**x6**	**x3**	**x6**
Patches	100 %	100 %	90 %	90 %	80 %	80 %	40 %	40 %
*L**	78.57	82.67	69.37	71.31	65.44	71.42	83.04	88.24
*a**	1.2	0.70	0.1	−1.58	−0.71	−3.18	1.77	1.41
*b**	−13.1	−13.53	−14.64	−18	−14.35	−17.65	−11.08	−9.12

When printing on HOSTAPHAN® PET film, only a slight Δ in the patches of the brightness (*L**) of the color tone, compared to printing on the natural coated offset paper, was observed (Table 5). The mean value in the trial number x7 was also under ±2 Δ in the CIE *L*a*b** measurement.

Table 5: Comparison of PET and offset paper; L, a* and b* values between solid and halftone patches*

Trial Number	**x3**	**x7**	**x3**	**x7**	**x3**	**x7**	**x3**	**x7**
Patches	100 %	100 %	90 %	90 %	80 %	80 %	40 %	40 %
*L**	78.57	85.22	69.33	80.93	65.44	82.54	83.04	82.298
*a**	1.12	−0.07	0.1	−2.19	−0.71	−3.05	1.77	0.61
*b**	−13.1	−10.78	−14.64	−14.54	−14.35	−14.66	−11.08	−11,37

4. Conclusions and outlook

Even in the preliminary tests, it was seen that lines, small fonts and other details could be reproduced very well. This is not surprising, since the blueprinting technique was used exactly for this purpose. But for the first time, a cyanotype process could be reproduced on an inline press. One can discuss whether the use of flexographic printing is suitable for printing the solution (A), or whether another printing process (gravure printing for a better edge definition, screen printing to generate a stronger Prussian blue) should be used for this purpose. Another option can be to make the solution (A) more viscous for flexographic printing with a thickener to achieve better printing results. This could allow to an application for screen printing. Also, parameters would need to be adjusted (e.g. optimal UV exposure, print speed) to refine the printing process. Converting the gravure unit to a washing out unit, however, was successful and showed that an inline printing process is possible. The spectralphotometric measurments in the mean value showed only small deviations in the trials of a maximum of ±2 Δ in the CIE *L*a*b** measurement. The Prussian blue of the offset paper and the PET foil shows only small differences, which brings us to the conclusion, that we can compare the gravure washing unit with a rinsing under running water. The Prussian blue can be used for two applications. Firstly, for battery systems as a cathode material and secondly, for electrochromic windows to achieve an efficient energy management of buildings, by allowing for a switchable window darkening. It should also be possible to print further stacked layers in order to be able to produce an electrochromic function exclusively with printing techniques. Conjugated electrochromic polymers for flexible EC devices generally lack a fully colorless bleached state (Macher, et al., 2019). Printing, so far, is only possible using screen printing while this gives a strong bleached state (Rueff, 2007). These are unsatisfactory results for EC devices.

Further work is pending to use additional printing technologies, speeds, optimal exposure and design elements for pattern generation for the cyanotype and electrochromic functions. Layer thickness of the Prussian blue layers shall be measured in future research.

Acknowledgements

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