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STABILITY OF UV CURABLE INKS APPLIED IN THREE LAYERS ON PAPERS CONTAINING STRAW PULP AFTER ARTIFICIAL AGEING

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Abstract: *In order for prints to be considered high quality, regardless of the type of printing substrate, they must retain the initial optical quality achieved during printing and years after the printed product has been used or stored. The rate at which print quality deteriorates over time depends on several factors. The composition of the printing substrate, the composition of the printing ink, the technique of applying the ink to the substrate, and the interaction between the ink and the substrate have the greatest influence on the initial quality. In addition to the listed influences on the durability of the print quality, the conditions under which the print was used or stored, such as humidity, temperature, microorganisms, and air quality, also have an effect. Paper is the most commonly used printing substrate, and considering the favourable ecological components of this material, it will be used more and more in the future. The need for alternative raw materials to wood in its production will also become more pronounced. Precisely because of the cellulose fibres that make up its basis, paper is subject to many degradation changes. In this research, the optical and colorimetric stability of prints on paper with straw pulp from different cereals were monitored after two cycles of accelerated ageing of 48 hours, performed according to the ASTM D 6789-02 standard. As the stability of prints in which UV curable inks were applied in three layers on laboratory paper by screen and gravure printing techniques was monitored in parallel, it was determined that screen prints have better colorimetric stability compared to gravure prints. It was also observed that for both types of inks, the most significant degradation occurs in the first 48 hours of accelerated ageing, while further prolonging the exposure time of the prints irradiance through the daylight filter does not show any significant continuation of the degradation.*

Key words: Artificial ageing, gravure printing, paper, straw pulp, screen printing, UV curable inks

1. INTRODUCTION

Paper is one of the most traditional and commonly used printing substrates (Schmidt, Martorana & Jocher, 2022). On the market today we find papers in a variety of compositions, weights, finishes and textures, meeting a wide range of printing needs. Therefore, the choice of paper can affect the absorption of the ink and the clarity of the printed text and image (Dong et al., 2020), and it is crucial to match the type of paper with the intended use. Printing techniques are the methods by which ink is transferred to paper, and the type of technique selected depends on the required quantity, the desired quality, and the intended use of the final product. Printing techniques differ in their cost, complexity, and print quality. The use of UV curable ink, compared to more traditional alternatives, is becoming an increasingly popular option due to the simplicity of the printing technology and the more environmentally friendly composition (Robert, 2015). The advantage of these specially formulated inks is that, after being printed on the substrate, they dry onto the surface under intense UV light. The print drying mechanism takes place in seconds because, as soon as the print head applies the ink to the substrate, the UV light that is built into the printing mechanism meets the printed design to instantly cure it. In this way, high resolution prints are obtained. The curing process itself affects the properties of the print, making it less susceptible to fading or damage over time. Due to the drying process, there is no risk of smearing or smudging. The composition of the UV curable inks does not contain any a solvent that evaporates, so the print is the result of 100% ink deposition on the surface of the substrate. There is no absorption of the ink into the substrate, resulting in a more intense colour. According to the composition UV curable inks are a mixture of monomers, oligomers, colorants, photo initiators and other additives that are activated by ultraviolet (UV) light. Namely, when exposed to UV light, the monomers and oligomers in the ink will polymerize and, by forming strong bonds between the ink particles (Hakeim et al., 2018), they will form a strong coloured layer on the surface, which results in printing with a long service life (Havlínová et al., 2002). In general, printing with

UV curing inks has a significantly longer lifespan compared to traditional inks, as they are not prone to fading or other damage over time (Karlovits & Gregor-Svetec, 2011).
In this paper, the optical stability of UV prints obtained by two printing techniques where UV curable inks were applied in three layers was studied. Accelerated ageing was performed as a simulation of natural ageing to determine the multicolour print quality deteriorates over time to evaluate the long-term behaviour of prints on papers with cereal pulp under the expected conditions of use. It is known that the conditions under which the prints were used or stored, such as humidity, temperature, microorganisms, pollutants and air quality, have a significant effect on the surface of printed products as well as a paper as a cellulose based porous printing substrate.

2. METHODS

This research is divided into the following steps: laboratory production of straw pulp containing papers; gravure and screen printing with UV curing inks; accelerated ageing of multicolour prints (C+Y+M) and evaluation of the stability of prints upon ageing.
First step for producing laboratory papers with straw pulp was collecting the straw after harvesting field crops of wheat, barley, and triticale. The collected straw was prepared for processing into semichemical pulp by purification and cutting into pieces ranging from 1 to 3 cm. This unbleached straw pulp obtained by the soda method (Plazonic, Bates & Barbaric-Mikocevic, 2016) was added into the pulp of recycled wood fibres in a proportion of 30% during laboratory production of paper at the Rapid Köthen sheet former (FRANK-PTI GmbH, Birkenau, Germany) according to EN ISO 526 9-2:2004 standard (Table 1).

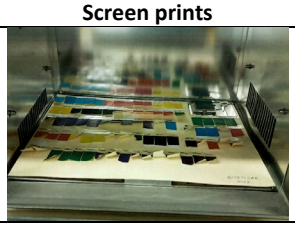
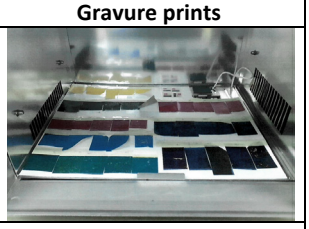
Table 1: Abbreviations used for marking laboratory-made papers

Abbreviation	Pulp composition	Paper production	Paper grammage, g/m²
K	100% recycled wood pulp	commercial	42.5
100N	100% recycled wood pulp	laboratory	42.5 ± 2.6
70N30W, 70N30B, 70N30TR	70% recycled wood pulp + 30% straw pulp	laboratory	
* W = wheat pulp; B = barley pulp; TR = triticale pulp			

To achieve multicolour prints on produced laboratory paper substrates, printing was performed with yellow, cyan and magenta inks applied in layers in specific order regarding the printing technique used. For gravure printing, the UV Solarflex curing inks (Sun Chemical) were applied to laboratory papers using the laboratory equipment KPP Gravure System with an impression cylinder of mechanical hardness (HS) 65 Shore and an engraved printing plate at an angle of 37° with a diamond needle at an angle of 130°, with a screen of 40 lines/cm. First applied ink was yellow and after its curing, with a Technigraf Aktiprint L 10-1 dryer containing a UV-C tube with ultraviolet light from 100 nm to 380 nm with a source power of 120 W/cm and an intensity of 60%, the magenta ink was applied and cured at same conditions and the cyan ink was last applied and cured at the same conditions.
Screen printing of the samples was performed using Ultragraph UVAR UV inks from Maragraph GR on a Shenzhen Juisun semi-automatic machine using squeegee with a mechanical hardness of 75 Shore and a mesh size of 120 lines/cm. The desired multicolour print was obtained by multiple application of three colours (Y+C+M). The prints were dried in a TM -UV750L (380V/12.5 kW) produced by Tamprinter with two 5.6kW UV lamps.
Artificial ageing was performed in a Suntest XLS+ test chamber which emits diffused light and near-ultraviolet electromagnetic radiation in the wavelength range from 290 nm to 800 nm through a daylight filter where the prints previously cut in strips (20 mm × 50 mm) were placed. According to ASTM D 6789-02 standard, the artificial ageing procedure in two cycles of 48 hours was carried out (Table 2). In accelerated ageing device, most often controlled parameters are light, heat and humidity. Xenon arc spectrum modified with specific filters used in this test chamber gives a good simulation of sunlight. The ultraviolet part of the solar spectrum is very often responsible for the initiation of weathering degradation of material. A material must absorb light in order to affect that material. Fading of an ink is caused by the light, i.e. by the motion of the energy it carries. The energy is inversely proportional to the wavelength (Aydemir & Yenidoğan, 2018). The shorter wavelengths possessing higher photon energies are more

strongly absorbed in most polymeric materials and have a greater potential to break chemical bonds in that material (Jacques, 2000).

Table 2: Accelerated ageing procedure

Accelerated ageing procedure	Screen prints	Gravure prints
Samples in test chamber		
Equipment	Suntest XLS+ test chamber	
Standard	ASTM D 6789-02	
Wavelength (nm)	300 - 800	
Irradiance (W/m^2)	765 ± 50	
Filter	daylight	
Relative humidity (%)	47	48
Temperature of ambient (°C)	21.2	21.5
Total duration of process (h)	96 (2 cycles of 48 h)	

The stability of UV curable inks applied in three layers on papers containing straw pulp after artificial ageing was evaluated based on optical stability by measuring spectrophotometric values of each print and by the colour difference (ΔE^*_{00}) calculation. The colorimetric values of prints were determined using an X-Rite SpectroEye spectrophotometer. Colour data were measured under illuminant D50, 2° standard observer. The colour difference between the colorimetric values of the prints before and after artificial ageing was calculated according to Equation 1 (Luo, Ciu & Rigg, 2001):

$$\Delta E^*_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right)} \quad (1)$$

Where: ΔE_{00}^* – total colour difference, the Euclidean colour difference; $\Delta L'$ – the transformed lightness difference between prints before and after accelerated ageing; $\Delta C'$ – the transformed chroma difference between prints before and after accelerated ageing; $\Delta H'$ – the transformed hue difference between prints before and after accelerated ageing; R_T – the rotation function; k_L, k_C, k_H – the parametric factors for variation in the experimental conditions; S_L, S_C, S_H – the weighting functions.
The colour difference threshold differs in ΔE value depending on the area of application and formula used for calculation of colour difference. In graphic arts and printing industry, for most demanding products, the maximum acceptable ΔE colour difference is 1.5 (Dedijer et al., 2018).

3. RESULTS AND DISCUSSION

From the results of the Euclidean colour difference (Figures 1 and 2), it is visible that the multicolour brown prints show different optical stability regarding the used paper substrate and technique of applying UV curable inks. If we look at the composition of the paper as a printing substrate, the greater stability of the prints was noticed in paper without the addition of cereal straw pulp. With the addition of cereal straw to paper pulp, the colorimetric stability of the multicolour prints on such printing substrates after exposing to conditions of accelerated ageing decreases. It has been noticed that the prints obtained by the screen printing technique (Figure 1) show far greater optical stability of multicolour brown prints compared to prints obtained by gravure printing (Figure 2). After artificial ageing the observed change in colour, ΔE^*_{00}, of screen prints ranged from 1.16 to 1.96, while the changes for gravure prints were greater (ΔE^*_{00} = 2.34 - 4.19). If the colour difference value is above 5, a standard observer can recognize the print before and after ageing as prints with two different colours indicating that the print has low optical ageing stability (Mokrzycki & Tatol, 2011).

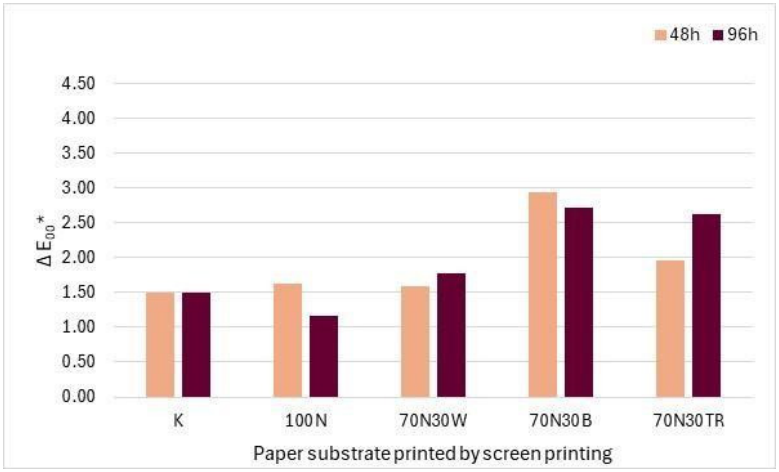


Figure 1: The Euclidean colour difference of UV curable inks applied by screen printing on paper substrates after artificial ageing

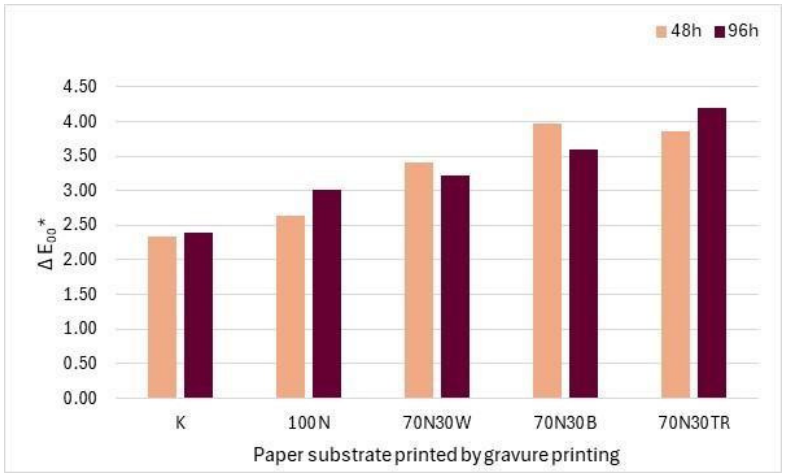


Figure 2: The Euclidean colour difference of UV curable inks applied by gravure printing on paper substrates after artificial ageing

From Figures 1 and 2 it is visible that optically more stable brown prints were achieved by screen printing on papers with the addition of straw pulp up to 30% (70N30W, 70N30B, 70N30TR) than by gravure printing on papers without the addition of straw pulp (N). Regarding the cereal type mixed in the paper pulp, best results are shown in the papers with added wheat pulp (70N30W) for both printing techniques. Papers with added barley pulp (70N30B) show slightly better results for gravure printing than screen printing in comparison with papers with triticale added pulp (70N30TR). This difference in the stability of gravure and screen multicolour prints achieved with three layers of inks applied one over the other is interesting as the results of previous study (Bates et al., 2023) showed that monocolour prints made with the gravure and screen printing processes after accelerated ageing of 48 hours reach a colorimetric difference of up to $\Delta E_{00}^* \leq 2$. In that study it was noticed that from all analysed monocolour prints gained by gravure and screen printing technique, the most colour difference was in cyan prints. As the cyan ink is the last printed ink brown prints printed made by gravure printing and in screen printing the last applied ink was magenta that could be the reason for lower optical stability of gravure print.

It was also observed that for both printing techniques of applying UV curable inks, regardless of the composition of the paper printing substrate, the most significant colour degradation occurs in the first 48 hours of accelerated ageing, while further prolonging the exposure time of the prints irradiance through the daylight filter does not show any significant continuation of the colour degradation. The only different colour change after 96 hours was observed on paper substrates with 30 % triticale pulp (70N30TR) when

printed with both printing techniques. It is therefore very important to know the desired lifetime of the printed graphic product.

4. CONCLUSIONS

The colour changes that occur on printed paper containing straw pulp upon ageing were analysed. As the colour stability of brown prints in which UV curable inks were applied in three layers on laboratory paper substrates by screen and gravure printing techniques was monitored in parallel, it was determined that screen prints have better colorimetric stability compared to gravure prints regardless of the composition of paper substrate. Of all the cereal straw pulps, the addition of wheat pulp to the recycled pulp provides the paper substrates for obtaining the most stable prints after ageing. The conclusion is that when choosing a printing substrate, it is very important to consider the desired lifetime of the graphic product and choose a paper substrate on this basis.

5. ACKNOWLEDGMENTS

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