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OPTICAL STABILITY OF LABORATORY PAPERS WITH WHEAT PULP PRINTED BY DIGITAL TECHNIQUE AFTER ARTIFICIAL AGEING

Valentina RADIĆ SELEŠ[1], Irena BATES[1], Ivana PLAZONIĆ[1], Maja RUDOLF[1], Katja PETRIC MARETIĆ[1], Vesna DŽIMBEG-MALČIĆ[1]

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Abstract

Paper as cellulose based substrate is highly susceptible to photolytic damage caused by excessive exposure to light and temperature. Hence the focus of this research was to assess whether the wheat pulp used as a raw material for laboratory paper production can provide same or even better optical stability than papers from recycled wood pulp. For a better insight into the stability of the paper as printing substrate, study was expanded on prints made by digital technique on papers with different content of wheat pulp. Unprinted and printed papers were artificial aged using a xenon lamp with a daylight filter during 48 and 96 hours. Optical stability degradation of unprinted and printed papers was observed through Reflectance spectra (R) and by Euclidean colour difference (ΔE_{00}).

The results in this study indicated that addition of wheat pulp provide better optical stability of printed and unprinted laboratory papers.

Keywords: optical stability, artificial ageing, UV ink-jet, wheat pulp

1. Introduction

Wheat straw is a fibres material, produced annually in huge quantities worldwide in a much shorter growing cycle than wood. The utilization of non-wood fibrous raw materials for pulping and papermaking industry is the most economically justified solution fitting with the EU's environmental directives, which aim is to reduce the consumption of wood fibres in paper and board products and replace it with other plant biomasses [1]. As the fibres are the key element of each paper composition it is important to estimate which types of fibres can be used for manufacturing paper product grades such as linerboard, corrugated medium, writing and printing papers. Paper structure and its properties will also be dependent upon manufacturing processes [2]. From the moment of its formation, paper is exposed to numerous endogenous and exogenous factors which affecting the deterioration of paper and in fact each component of paper composition affects its appearance and stability.

Natural paper ageing is irreversible change that occurs slowly over time and is the best indicator of the paper optical permanence. Light, heat and moisture are the most important factors that affect the paper stability. Several methods of simulation of the natural aging process are used, since the process of natural ageing is impractical for researches because of the involved parameter of time [3]. The analyses of ageing processes represent a complex issue since chemical and mechanical properties of paper elements and ink components are simultaneously changed during the ageing process [4]. Paper optical stability is extremely important in graphic industry because it contributes mostly to the overall paper appearance and appeal [5].

Digital printing technique is a rapidly developing technology and in some areas nowadays is competing with the offset printing technique. It is predicted that digital printing technique will grow dramatically as presses become cheaper with improvements in print quality. Ink jet printing process as a fast growing digital printing technique is a computer to press process where, inkjet heads deposit droplets of ink on paper in response to instructions from the digital file for the job. The image is produced by means of a dot matrix that creates the letter or graphic image [6]. The aim of this research was to investigate the influence of the wheat pulp in the laboratory made paper substrate printed by ink jet printing technique on optical stability during the artificial ageing period. The optical stability of digital printed laboratory papers was observed through colour degradation. The degradation of the colour was estimated through the reflectance spectra (R) and Euclidean colour difference (ΔE_{00}).

2. Experimental part

2.1. Materials and Methods

2.2 Laboratory papers

Straw as agricultural residue after wheat harvesting was manually cut into 1 to 3 cm long pieces and converted into semi-chemical pulp according soda method [7]. Pulping conditions are presented in Table 1.

Table 1: Pulping conditions

Type of straw	*Pulping method*	*Extraction conditions*
Wheat	*Soda pulping*	*Temperature of 120°C, alkali level of 16% for 60 min, and a 10:1 liquid biomass ratio*

Provided unbleached wheat pulp were mixed with recycled wood pulp in different ratios (10%, 20% and 30%). Laboratory papers of approx. 42.5 g/m^2 were formed by a Rapid-Köthen sheet former (FRANK-PTI) according to standard EN ISO 5269-2:2001. Laboratory papers made only with recycled wood pulp were used as a reference for evaluating the optical stability of papers containing wheat pulp [8]. In total, 4 types of laboratory papers were formed. Workflow of laboratory paper production is presented at Figure 1.

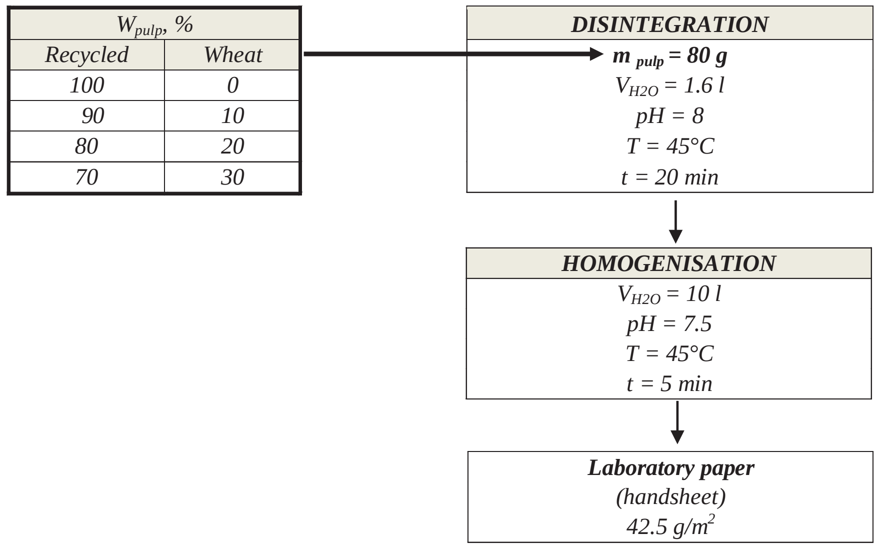

Figure 1: Workflow of laboratory paper production

2.3 Printing of commercial and laboratory produced paper substrates by digital technique

All laboratory made papers and commercial paper consisted of 100% recycled wood pulp were printed by digital EFI Rastek H652 UV curable ink jet printer. Solid areas of cyan and yellow ink with the resolution of 600 x 600 dots per inch (dpi) (respectively with high quality mode 8 pass) and printing speed of 12.10 m^2/ hr were printed on each paper. Unprinted and printed papers were cut in dimensions of 2 x 5 cm and used as test samples for artificial ageing treatment.

2.4 Artificial ageing

Unprinted and printed samples were exposed to accelerated ageing treatment in test equipment SunTEST XSL+ according to standard ASTM D 6789-02 [9] under conditions summarized in Table 2.

Table 2: Conditions used during artificial ageing process

Wavelength (nm)	*290 - 800*	
Irradiance (Wm^{-2})	*765 ± 50*	
Test equipment	*SunTEST XSL+, Id.No. 196 Rotronic Hygrolog, Id.No. 180/2*	
Duration process (h)	*48*	*96*
Ambient condition	*24.8°C 54.7 % RH*	*23.5°C 47.4 % RH*
Filter	*daylight*	

2.5 Optical properties

To determine the influence of wheat pulp on the optical stability of the unprinted and printed laboratory papers colour degradation were analysed on 39 different samples. Abbreviations used in marking all samples are listed in Table 3.

Table 3: Abbreviations used in marking samples subjected to optical analysis

C	commercial 100 % recycled paper
N	laboratory paper with 100 % recycled pulp
1NW	laboratory paper with 10% wheat pulp
2NW	laboratory paper with 20% wheat pulp
3NW	laboratory paper with 30% wheat pulp
p.	printed paper
unp.	unprinted paper
c.	cyan
y.	yellow
unag.	unaged paper
ag.	artificially aged paper

2.5.1 Reflectance values

Papers reflectance spectra measurements were processed using X-rite spectrophotometer with standard illuminate D50 and 2° observer, in the interval of the wavelengths from 400 nm to 700 nm for every 10 nm. Reflectance values (R) were measured for all paper samples before and after ageing. Optical measurements were repeated 10 times on each paper.

2.5.2 The colour differences or Euclidean difference (ΔE_{00})*

Euclidean difference (ΔE_{00}*) off all paper substrates printed with cyan and yellow ink after artificial ageing was calculated based on measured colorimetric CIE L*a*b* values which were carried out by X-rite spectrophotometer. In the CIE L*a*b* colour space the value L* represents the lightness of the colour, value +a* represents redness or the value –a* represents greenness and the value +b* represents yellowness or the value –b* represents blueness [10]. The colour differences of all printed papers were calculated with the following equation [11] using unaged paper as reference:

$$\Delta E_{00}^{*} = \left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_c S_c}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C} \frac{\Delta H'}{k_C S_H} \quad [1]$$

where: ΔL’ is the transformed lightness difference between print before and after artificial ageing, ΔC’ is the transformed chroma difference between print before and after artificial ageing, ΔH’ is the transformed hue difference between print before and after artificial ageing, *RT* is the rotation function,

KL, KC, KH are the parametric factors for variation in the experimental conditions and *SL*, *SC*, *SH* are the weighting functions.

Tolerances [12] of colorimetric differences (ΔE_{00}) are presented in Table 4.

Table 4: Tolerances of Euclidean differences

Euclidean difference value	Euclidean difference tolerance
< 1	Average human eye does not see the difference
1 - 2	Very small difference - optimal
2 - 3	Moderate difference
3.5 - 5	Difference
> 5	Great difference

3. Conclusion

3.1 Reflectance values

Figures 3-6 present the experimental results of reflectance measurements before and after artificial ageing in the visible part of the electromagnetic spectrum for all analysed paper and print samples.

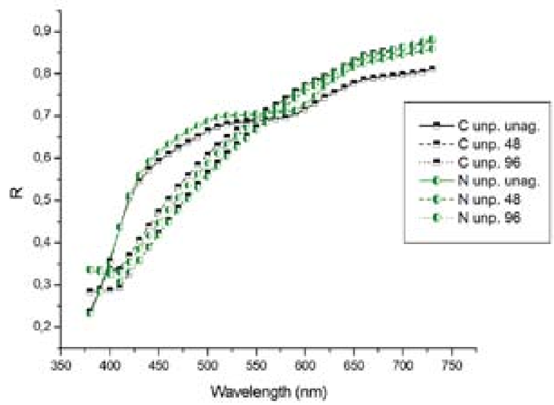

Figure 3: The influence of ageing time on reflectance spectra of unprinted recycled papers –commercial (C) and laboratory (N)

From reflectance spectra presented in Figure 3 it is evident that the highest deterioration for both unprinted recycled papers (commercial (C) and laboratory (N)) occurs in the first 48 hours of artificial ageing ($\Delta Rmax_{(Cunp.unag. – Cunp.ag.48)}$ =13.9%; $\Delta Rmax_{(Nunp.unag. – Nunp.ag.48)}$ = 17.5%). After both periods of artificial ageing treatment it is noticed that reflectance values drop significantly in the blue part of spectrum while in the red part reflectance values slightly increase.

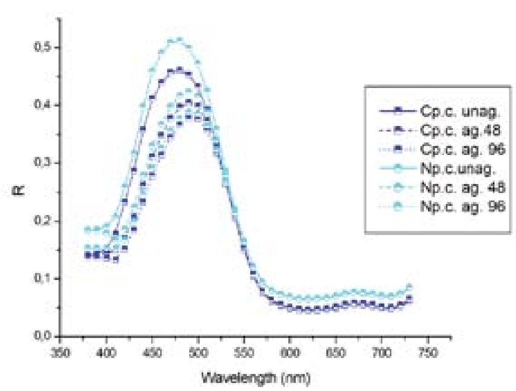

Figure 4: The influence of ageing time on reflectance spectra of recycled papers – commercial (C) and laboratory (N) printed with cyan ink

Cyan prints on both type of recycled papers present expected reflectance curves (Figure 4). The highest reflectance values were obtained on laboratory paper (N). The influence of artificial ageing on cyan prints is visible as reflectance decreasing in blue part of spectrum. Namely, first 48 hours of artificial ageing have the highest impact on reflectance values of prints ($\Delta Rmax_{(Cp.c.unag. – Cp.c.ag.48)}$ = 10%; $\Delta Rmax_{(Np.c.unag. – Np.c.ag.48)}$ = 12.9%) what was also noticed for unprinted papers, while further ageing had negligible impact ($\Delta Rmax_{(Cp.c.ag.48 – Cp.c.ag.96)}$ = 3.3%; $\Delta Rmax_{(Np.c.ag.48. – Np.c.ag.96)}$ = 3.9%).

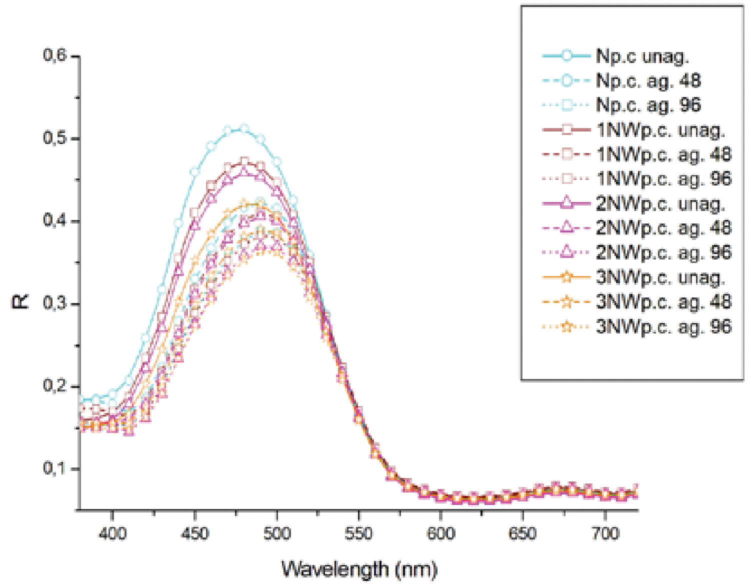

Figure 5: The influence of ageing time on reflectance spectra of cyan prints made on laboratory papers without (N) and with wheat pulp (1NW, 2NW, 3NW)

Figure 5 shows that unaged printed paper without wheat pulp (N) exhibit the highest reflectance value of all prints and reaches its maximum value at aprox. 480 nm (R_N = 51.2%), while values in the red part of the spectrum are low and stable. The highest degradation of all cyan prints occurs after first 48 hours of artificial ageing on printed laboratory paper N ($\Delta Rmax_{(Np.c.unag.–Np.c.ag.48)}$ = 12.9%). After additional 48 hours of artificial ageing, degradation is still visible but significantly lower ($\Delta Rmax_{(Np.c.ag.48. – Np.c.ag.96)}$ = 3.9%). Others prints show very similar behaviour. It is clearly visible that reflectance values of all prints drop with addition of wheat pulp into papers. Namely, prints made on papers with 30% of wheat pulp (3NW) exhibit the lowest reflectance values before and after artificial ageing ($\Delta Rmax_{(3NWp.c.unag.–3NWp.c.ag.48)}$ = 5.3%; $\Delta Rmax_{(3NWp.c.unag.–3NWp.c.ag.96)}$ = 7.8%,).

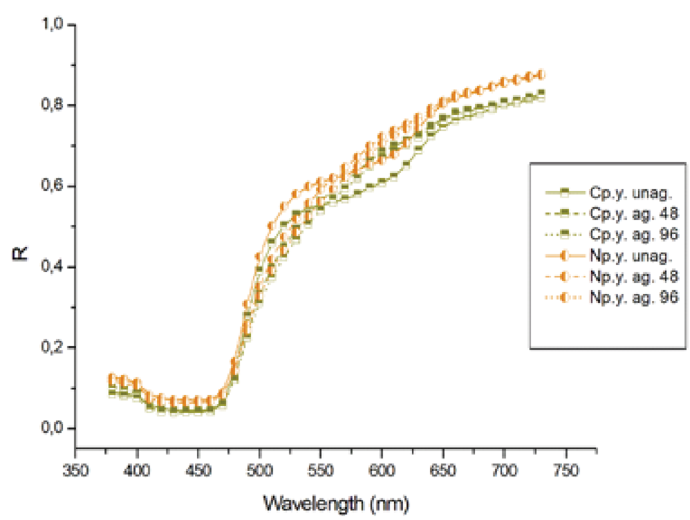

Figure 6: The influence of ageing time on reflectance spectra of recycled papers – commercial (C) and laboratory (N) printed with yellow ink

Yellow prints on both types of recycled papers present expected reflectance curves where the papermaking process have not shown significant influence on reflectance values (Figure 6). The influence of artificial ageing on yellow prints is visible as a slight increase in reflectance values in red part of spectrum ($\Delta Rmax_{(Cp.y.unag.. – Cp.y.ag.96)}$ = -6.5%; $\Delta Rmax_{(Np.y.unag.. – Np.y.ag.96)}$ = -4.6%).

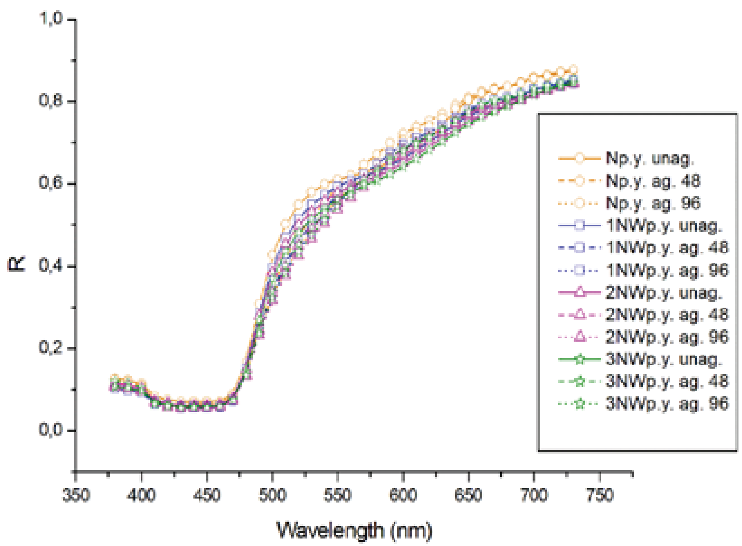

Figure 7: The influence of ageing time on reflectance spectra of yellow prints made on laboratory papers without (N) and with wheat pulp (1NW, 2NW, 3NW)

From Figure 7 it is visible that addition of wheat pulp in laboratory papers (1NW, 2NW, 3NW) decreases the reflectance values of yellow prints. However a slight increase of reflectance values in green and red part of the spectrum after all periods of artificial ageing is noticed ($\Delta Rmax_{(Np.y.unag.. – Np.y.ag.96)}$ = 11%; $\Delta Rmax_{(1NWp.y.unag.. – 1NWp.y.ag.96)}$ = 7.8%; $\Delta Rmax_{(2NWp.y.unag.. – 2NWp.y.ag.96)}$ = 7.5%; $\Delta Rmax_{(3NWp.y.unag.. – 3NWp.y.ag.96)}$ = 5.1% at 510 nm).

3.2 Euclidean difference

Table 5: Euclidean colour difference (ΔE_{00}) between unprinted and with cyan or yellow ink printed papers after artificial ageing

Euclidean colour difference values (ΔE_{00})						
	48 hours			**96 hours**		
	Unprinted	**Cyan**	**Yellow**	**Unprinted**	**Cyan**	**Yellow**
C	6.96	6.22	3.95	8.66	8.24	4.70
N	8.13	7.00	4.30	9.04	8.72	5.56
1NW	6.56	5.33	3.19	7.23	6.92	4.18
2NW	3.70	4.91	3.06	5.18	6.69	4.11
3NW	4.39	3.57	2.62	4.84	4.82	3.33

The highest value of colour difference is perceived on the unprinted laboratory paper without wheat pulp (N) after 96 hours of artificial ageing, while laboratory papers with 20% and 30% of wheat pulp (2NW, 3NW) show the lowest values in colour differences (Table 5). The first ageing period (48 hours) has the highest impact on colorimetric values (L*a*b*) of unprinted papers.

It is also visible that cyan prints made on laboratory paper without wheat pulp (N) have shown the highest value of colour difference after 48 and 96 hours of artificial ageing. The slightest changes are noticeable on cyan prints made on laboratory papers with 30% wheat pulp (3NW) after both periods of artificial ageing.

Yellow prints follow the same trend as cyan prints but have significantly lower ΔE_{00} values.

The aim of this research was to point out the influence of the wheat pulp addition into paper on optical stability of prints. Taking into account all obtained results, the following could be concluded:

- It is proven how commercial paper achieves higher optical stability than laboratory paper,
- The highest colour degradation of cyan and yellow prints occurs in first 48 hours of artificial ageing,
- Yellow ink provides prints with higher optical stability than cyan ink,
- Addition of wheat pulp positively influences on optical stability of all analysed samples (unprinted and printed laboratory papers),

The results in this research suggest that the optical stability of printing substrates formed with wheat pulp could be additionally improved if papers would be formed in industrial production.

4. Acknowledgements

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MEASUREMENT OF THE INK PENETRATION INTO LABORATORY PAPERS WITH WHEAT PULP AND ITS INFLUENCE ON PRINT QUALITY

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Abstract

Awareness of environmental issues has led to the increase in use of recycled printing papers or to the introduction of new alternative sources of cellulose fibres instead of virgin wood fibres. As recovered wood fibres cannot provide the same quality level of paper products as virgin ones, alternative sources of virgin cellulose fibres need to be identified. Therefore, the laboratory printing papers were produced using a wheat pulp in varying weight proportions and mixing with pulp from recycled paper. The print quality depends on the characteristics of the printing substrate, wherein the ink penetration is one of the important parameter. This study investigated ink penetration into laboratory papers made of different contents of pulp and their correlation with prints quality. The solid areas were printed on laboratory printing papers with cyan, yellow and magenta UV ink jet inks under standardized printing conditions.

At last, the ink penetration inside laboratory papers were analyzed based on two methods (microscopic and spectroscopic) and their effect on rub resistance and print quality was also observed. Analyzed print quality parameters (ink optical density, mottling, colorimetric values) indicated that wheat pulp in the laboratory papers provides equal print quality compared to laboratory papers made from recycled pulp. The highest degradation of print quality was observed on laboratory papers with 30% of wheat pulp printed with cyan ink, as a result of the greatest measured average ink penetration depth.

Keywords: ink penetration, wheat pulp, laboratory paper, print quality, UV ink jet

Introduction

Ink absorption by printing substrate depends on physical and chemical properties of printing substrate and inks and substrate-ink interaction. Laboratory made printing substrate has very open surface which leads to deep ink penetration into paper structure [1]. Penetration of the ink can be occurred as surface dispersion on the cellulose fibres or diffusion through the cellulose fibres in paper composition. Papers which consist of a cellulosic fibres network with several additives are heterogeneous printing substrates and laboratory formed ones have even more inhomogeneous structure. Uncontrolled ink movement inside the porous structure of the printing substrate can affect print quality issues, such as optical ink density, colorimetric values, mottling, print gloss, print rub-off and print through [2].

The research presented in this paper focuses on the impact of the ink penetration in laboratory papers with wheat pulp on the overall print quality. In pulp and paper industry wood is still the most common used raw material, but the utilization of non-wood fibres is increasing trend in the last few years. Wheat straw is chosen as agricultural residue and renewable, economical and natural resource of virgin cellulose fibres. In European countries like Germany, Italy, Netherlands, France, Spain, Greece, Hungary and Croatia agricultural production is relatively high because of adequate climate [3]. Adding wheat fibres to pulp of wood fibres to create a paper is of great importance considering that they are currently burned or plugged back into the ground [4].

To achieve the high quality of print it is necessary to be aware of the substrate characteristics and possibilities of each printing techniques.

Traditional technologies are still main printing techniques for printing books, magazines, newspapers and packaging, while digital printing process is getting more and more popular.

Due to its ability to provide the required quality of the prints on a wide variety of substrates, digital printing process is complementary technology to traditional technologies for short runs. Ink jet printing, together with laser printing, is the fastest growing area of the printing industry. Ink jet is one of the most common non-impact printing technologies, where the ink is ejected directly onto a substrate from a jet device driven by an electronic signal and printing is performed without printing plates [5,6]. In this technology, a finite amount of liquid (ink or dye) is transferred directly onto a printing substrate [7].

Experimental Part

<u>Laboratory papers</u>

The straw of the most common crop species in Croatia, wheat (Triticum spp.), collected after the harvest was manually cut using scissors into 3 cm long pieces and conducted into semichemical pulp according soda pulping method [8]. Obtained wheat pulp was added in proportions of 10%, 20% and 30% to reference pulp of recycled paper.

Laboratory papers of approx. 42.5 g/m^2 were formed in a Rapid-Köthen sheet former (FRANK-PTI) according to standard EN ISO 5269-2:2004 [9]. In total, according to their composition 4 different laboratory papers were formed and their roughness of the felt side was determined by Surface roughness tester TR200 (Innovatest Europe BV, Maastricht, The Netherlands [8]) (Table 1).

Table 1: Laboratory papers composition and their roughness

Laboratory papers			
Mark	**Composition**		**Roughness**
	Wheat pulp (W), %	**Recycled pulp (N), %**	**R_a (µm)**
N	*0*	*100*	*4.15 ± 0.34*
1NW	*10*	*90*	*4.13 ± 0.43*
2NW	*20*	*80*	*4.24 ± 0.34*
3NW	*30*	*70*	*4.59 ± 0.51*

Printing of laboratory papers

In order to examine print quality of laboratory papers containing wheat pulp, samples were printed by digital EFI Rastek H652 UV curable ink jet printer. Solid areas of cyan, magenta and yellow inks with the resolution of 600 × 600 dots per inch (dpi) (respectively with high quality mode 8 pass) and printing speed of 12.10 m^2/hr were printed on each laboratory papers.

Sample preparation for cross section

The cross sections samples, for the microscopic method of ink penetration depth analysis, were prepared from strips, 10 mm × 30 mm cut prints, and then embedded in epoxy resin. Epoxy resin is a mixture of Epofix resin (contains bisphenol-a-diglycidylether) and Epofix hardener (contains triethylenetetramine) which must be prepared in vol. ratio 15 : 2 just before its usage. The embeddings were dried at room temperature for 12 hours prior to grinding and polishing which were performed using a Buehler Grinder Machine and Struers DAP-V Polishing Machine.

Analysis

The analysis of laboratory papers printed with yellow, cyan and magenta inks was divided in two parts.
The first part, *analysis of ink penetration depth*, was made by microscopic method (processing the microscopic image taken on prepared cross section samples of each print) which was compared to spectroscopic method (calculated ink penetration depth according to Kubelka-Munk theory from reflectance measurements (R_{∞}, R_0, R_p, R_q)) [10,11].

Microscopic method

The cross section of samples was observed at 200× magnification using an Olympus GX 51 light microscope with Analysis software and the captured images were further analyzed with Image J software. Image J was used to determine the maximum ink penetration value within the printing substrate. The ink penetration depth (Hp_m) was calculated from the 50 sections obtained from the microscopic images (equation 1).

[1]

where *l* is maximum ink penetration value and *d* is a local thickness of the paper in measuring section.

Spectroscopic method

Using non-destructive method an ink penetration depth (Hp_s) was determined through surface analysis by using reflectance values based of the Kubelka-Munk theory (equation 2) [12-14]. The ink penetration depth was determined from average reflectance value of 50 spectrophotometric measurements.

$$Hp_s = \frac{ln\frac{(1-R_0 \times R\infty)(1-R_p \times R\infty)(1-R_q /R\infty)}{(1-R_0 /R\infty)(1-R_p /R\infty)(1-R_q \times R\infty)}}{ln\frac{1-R_0 \times R\infty}{1-R_0 /R\infty}} \times D \qquad [2]$$

where R_∞ is the reflectance value of unprinted laboratory paper over opaque pad of unprinted laboratory papers, R_o is the reflectance value of unprinted laboratory paper over a standard black background, R_p is the reflectance value of printed laboratory paper over opaque pad of unprinted laboratory papers, R_q is the reflectance value of the reverse side of printed laboratory paper placed over opaque pad of unprinted laboratory papers and *D* is an average value of unprinted laboratory paper thickness.

Required reflectance values (*R*) were measured by spectrophotometer eXact, X-Rite (D65/10º) at 452 nm (brightness).

The second part, *analysis of print quality*, is focused on rub resistance, mottling (print unevenness), optical ink density and colorimetric values of prints made on laboratory papers with and without wheat pulp.

Mottling

The evaluation of mottling was performed by digital microscope PIAS-II using software which is built on international print quality standards ISO-13660. Mottling parameter is defined in large-scale (>1270 µm) where the observed area was divided into 100 uniform tiles (1.27 mm × 1.27 mm). In each tile, 900 measurements of reflectance are made in small non-overlapping square areas (42.3 µm × 42.3 µm) and the mean (m_i) of those reflectance measurements was calculated. Mottling is defined as the standard deviation of the mean reflectance values of the tiles according to equation 3.

$$Mottle = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(m_i - \left(\frac{1}{n}\sum_{i=1}^{n} m_i\right)\right)^2} \qquad [3]$$

where m_i is the mean value of the reflection coefficient and *n* is the total number of tiles [15].

Optical ink density

The optical ink density (D_i) was determined by densitometer SpectroEye, X-Rite (D50/2º) to perceive the ink film thickness on laboratory papers according to equation 4.

$$D_i = \log\frac{I_0}{I} \qquad [4]$$

where *I* is the light intensity of the light remitted by the ink film in relation to the intensity of light I_0 remitted by unprinted laboratory paper.

Colorimetric values

The optical properties of the printed laboratory papers were monitored with spectrophotometer SpectroEye, X-Rite at D50/2º, which are observed through colorimetric values: *L** (lightness), *a** (coordinate of green/red colour), *b** (coordinate of blue/yellow colour).

The Euclidean colour difference (ΔE_{00}^*) was used to evaluate the influence of wheat pulp addition in laboratory paper on print quality. ΔE_{00}^* were calculated according to equation 5, using the printed laboratory paper without wheat pulp (N) as reference and printed laboratory papers with wheat pulp (1NW, 2NW, 3NW) [16].

$$\Delta E^*_{00} = \left(\frac{\Delta L'}{K_L S_L}\right)^2 + \left(\frac{\Delta C'}{K_C S_C}\right)^2 + \left(\frac{\Delta H'}{K_H S_H}\right)^2 + R_T \frac{\Delta C'}{K_C S_C}\frac{\Delta H'}{K_H S_H} \quad [5]$$

where **ΔL›** is the lightness difference between prints made on papers without and with wheat pulp, **ΔC›** is the chroma difference between prints made on papers without and with wheat pulp, **ΔH›** is the hue difference between prints made on papers without and with wheat pulp, R_T is the rotation function, K_L, K_C, K_H are the parametric factors for variation in the experimental conditions and S_L, S_C, S_H are the weighting functions.

Rub resistance

Test of rub resistance was performed by test heads with printed surface (against non-printed surface of reference material (face-to-face) in the same plane, under a constant pressure of 3.45 kPa (0.5 p.s.i) and the speed of 60 rpm. In this way it is simulated moving contact on the conveyors, during processing on printing and packaging machines, during distribution and at end use.

The properties of printing substrate and inks and printing process affect significantly rubbing resistance. The properties of printing substrate involved in achieving good rubbing resistance are related to the smoothness, absorption, and drying properties of the paper surface.

The analysis of the rub resistance of the prints was performed in accordance with standard BS 3110:1956 by Rub and Abrasion tester Hanatek [17]. Rub resistance of printed laboratory papers was defined based on Euclidean colour differences (ΔE_{00}) of the prints before and after testing (ΔE_{00}* were calculated according to equation 5) [16]. Optical properties of printed laboratory papers was determinated using a spectrophotometer SpectroEye, X-Rite at D50/2º.

As the ink penetration into the paper substrate is a complex issue, several approaches to determine the ink penetration depth are asked. Microscopic and spectroscopic methods, which are the most common ones, are complementary and their combination can provide the best insight to real ink distribution in substrates and its influence on the print quality [2].

The microscopic images presented at Figure 1 are cross sections of the cyan prints made on laboratory papers without and with wheat pulp. Cyan prints have the highest penetration depth (Hp_s) compared to all printed laboratory papers observed by spectroscopic method (Figure 2).

Microscopic method provides less reliable results due to some factors that affect the accuracy of the results, such as penetration of resin and dimension of observed sample.

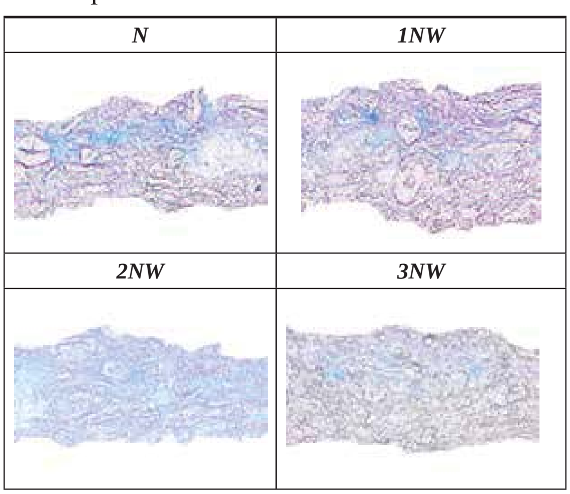

Figure 1: Microscopic images (cross section) of ink penetration of cyan prints on substrate without (N) and with wheat pulp (1NW, 2NW, 3NW)

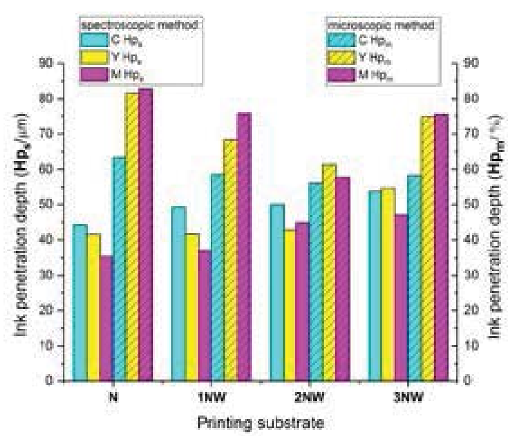

Figure 2: Ink penetration depth determined by spectroscopic and microscopic methods

Observing all laboratory papers printed with cyan, yellow and magenta inks, the highest maximum ink penetration depth values (Hp_m) were observed on magenta prints according to microscopic method, while those prints had the smallest average ink penetration depth values determined by spectroscopic method. These results indicate that cyan, yellow or magenta inks do not have uniform distribution within the same laboratory paper.

According to spectroscopic method the addition of wheat pulp into laboratory papers provide a slight increase of average ink penetration depth values.

Surface analysis results defined by instruments (mottling, optical ink density and average ink penetration depth) are summarized in figure 3.

On all laboratory papers without and with wheat pulp printed with ink jet inks approximately equal optical ink density were achieved. Cyan ink as the most penetrating ink causes the highest mottle of prints. Adding the wheat pulp into laboratory papers increases the mottling values of cyan and magenta prints, while on yellow prints this influence is negligible.

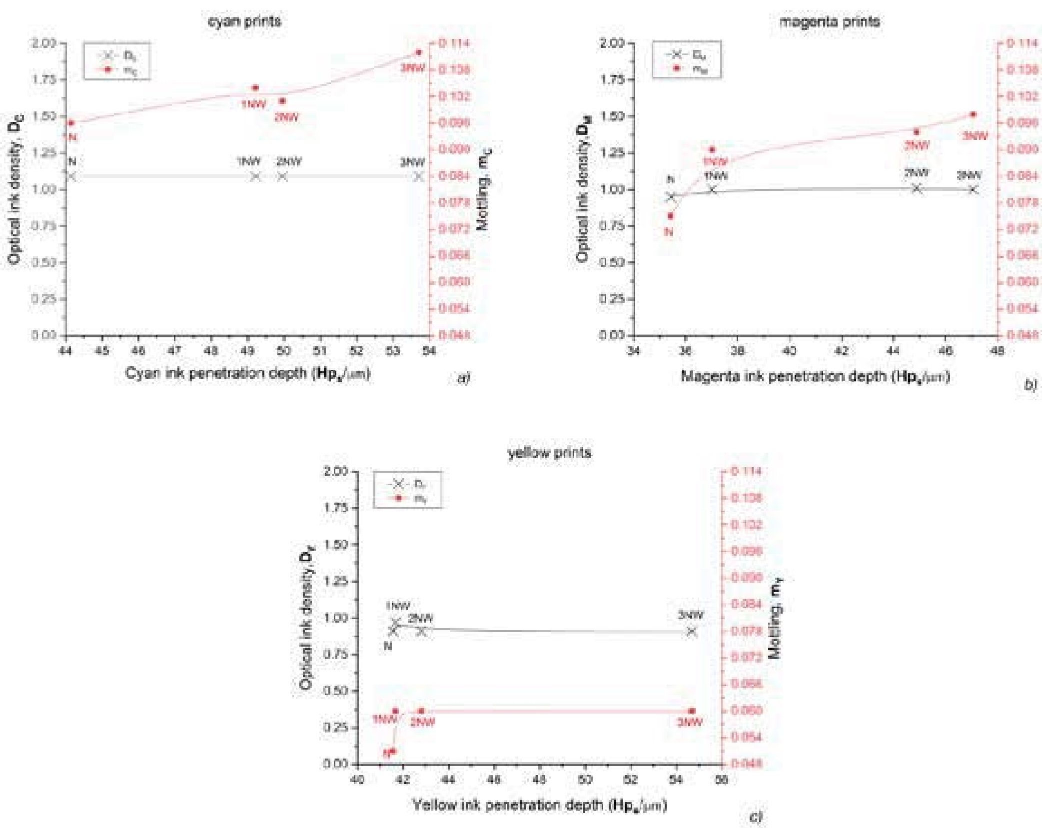

Figure 3: The values of mottling (unevenness of solid areas) and optical ink density respect to depth of ink penetration determined by spectroscopic methods on cyan prints (a), magenta prints (b) and yellow prints (c)

Table 2: Colorimetric difference (ΔE00) between prints made on substrate without (N) and with wheat pulp (1NW, 2NW, 3NW)

	ΔE_{00}		
Prints	*N vs. 1NW*	*N vs. 2NW*	*N vs. 3NW*
Cyan	2.04	2.64	5.01
Magenta	1.32	1.79	2.06
Yellow	1.32	2.13	2.38

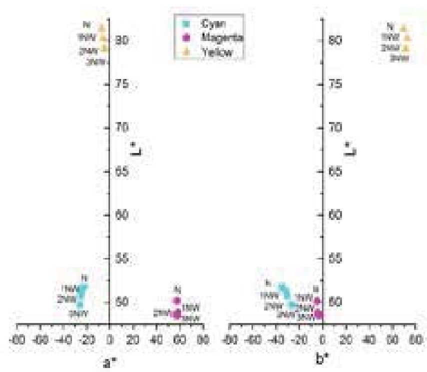

Figure 4: Colorimetric values of prints

From figure 4 it is visible that achieved colorimetric values of prints made on papers without and with wheat pulp (*L*a*b**) are nearly equal.

In order to evaluate the differences in print quality between prints made on papers without (N) and with wheat pulp (1NW, 2NW, 3NW) the colorimetric differences (ΔE_{00}) were calculated (equation 5) and presented in Table 2. Among the colorimetric difference results cyan prints have the highest ΔE_{00} value ($\Delta E_{00} \geq 5$), which is defined as big noticeable difference in the tone that standard observer can recognize [18].

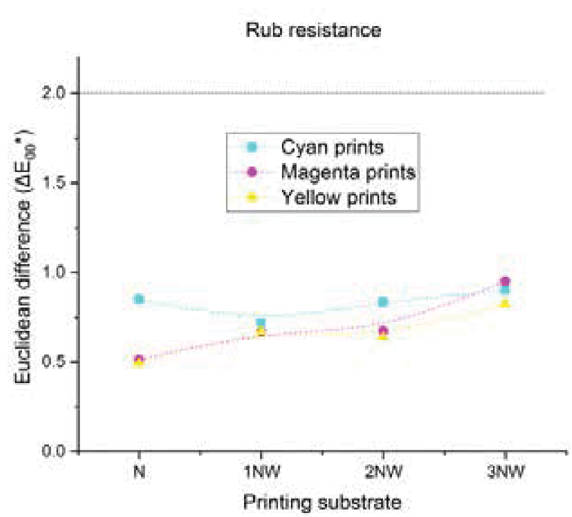

Figure 5: Euclidean difference of prints before and after testing rub stability

From values of Euclidean colour difference presented on figure 5 it is notable that all observed prints are stable to rubbing according to tolerance definition, where $\Delta E_{00}^* \leq 2$ is classified as very small difference [18]. The values are in the range from 0.49 to 0.95, wherein the differences increase with higher proportion of wheat pulp in paper, which is expected due to roughness values of laboratory papers (Table 1.).

Conclusion

On the basis of data obtained from the ink penetration measurements and its influence on print quality, the following conclusions can be drawn:

- microscopic method is important for visual insight into paper-ink interaction, while spectroscopic method provided more objective results of ink penetration depth;
- addition of wheat pulp into laboratory paper reduces differences between maximum and average ink penetration depth which can indicate the uniform distribution of the ink into paper substrates;
- regardless of portion of wheat pulp into laboratory papers, prints made with yellow and magenta inks achieve required print quality, while only noticeable degradation of print quality based on colorimetric values is measured on laboratory papers with 30% of wheat pulp printed with cyan ink;
- based on all observed print quality parameters (ink optical density, mottling, colorimetric values, rub resistance) it is proved that wheat pulp in laboratory papers provides equal print quality compared to laboratory papers made from recycled pulp;
- experimental observation of ink penetration into laboratory papers confirmed that wheat pulp could be used for certain categories of printing papers.

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