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KEYNOTE LECTURES

INVITED PAPERS

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CHEMICAL DEGRADATION OF PRINTS MADE ON PAPERS WITH WHEAT PULP

I. Plazonic[1], I. Bates[1], Z. Barbaric-Mikocevic[1] and B. Lajic[1]

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Keywords: wheat pulp; laboratory paper; digital printing; chemical stability; spectrophotometric values

Abstract: Nowadays, the production of paper and paper products has significantly focused on alternative nonwood raw materials. Croatia, as agricultural country, produces a large quantity of straw as a by-product of the crop farming. Therefore, straw is an interesting alternative raw material for cellulose fibres which could replace wood fibres sources. Today straw is used in animal food industry, biofuel industry, construction industry and as material in artistic expressions because of its numerous advantages. The potential utilization of that kind of crop residues in paper and packaging industry is of great importance considering a global deficiency of wood raw material. In this research, the wheat straw was converted into pulp and mixed with recycled wood fibres in order to produce alternative paper substrates. Laboratory formed papers were printed with black UV ink by digital technique. The quality of these prints was observed through the chemical stability to water, alcohol, acid and alkali. Evaluation of chemical degradation on prints was determined based on the spectrophotometric measurements (L*a*b* values) and Euclidean colour difference (ΔE_{00}). Especially in the packaging industry, it is very important that prints have a good chemical stability to substances which are deposited inside the packaging.

Introduction

The demand for paper products is increasingly growing considering that different types of coniferous and deciduous trees became insufficient raw material for the paper production. Therefore, the alternative sources of virgin cellulose fibres for that industry sector are of great importance especially for further generations. Wood is still the most widely used raw material in the pulp and paper production, but the consumption of non-wood fibres has been showing the increasing trend in the last few years. Many useful fibres could be obtained from various parts of plants including leaves, stems (bast fibres), fruits and seeds. However, the most interesting non-wood fibre raw material is straw which represent annually renewable fibre resource available in abundant quantities in many regions all over the world. Nowadays, a growing awareness of environmental and sustainable issues has led to smart utilization of these agricultural residues. For instance, straw is used as a raw material for biofuel [1]. Paper industry and, as a result of that, graphic industry as well, taking into account a global deficiency of wood raw material, needs to be supplied with alternative cellulose fibres [2], whereby straw could represent an interesting replacement.

Regardless to the fibre origin, wood (hardwood and softwood) or non-wood (agricultural residues, industrial residues and naturally growing plants), it is very important that selected fibres provide good quality of the paper. On the other hand, for achieving the high quality final graphic product, the printability of paper and the stability of those prints are important. The extent to which a dried ink film will resist reacting with different chemicals with which it comes in contact is an important property of printing inks, especially in packaging. Namely the inks that react with liquid agents as alkali, acid, water, alcohol will fade, discolour, bleed, etc., and will produced undesirable effects when are used in the printing of packaging which come in contact with them. Therefore, it is very important that inks and the printing substrates which are used have high chemical stability.

The overall aim of this research was to evaluate the chemical degradation of black UV ink applied by digital technique on laboratory made paper substrates with variable content of wheat pulp. For that purpose, the created prints were tested for chemical stability to four different tests liquid agents: water, alcohol, acid and alkali. Evaluation of chemical degradation on the prints was observed through the Euclidean colour difference based on colorimetric values L*a*b*.

Experimental part

The experimental part of this research was divided into four stages: 1. obtaining of straw pulp by chemical treatment; 2. forming laboratory papers with different share of straw pulp; 3. printing paper sheets by digital technique and 4. analysing chemical degradation of prints.

Obtaining of straw pulp by chemical treatment

To obtain cellulosic pulp the agricultural residue of wheat crop was used. After harvesting crops, the straw was collected from the fields and was cut manually into 1 to 3 cm long pieces. The purified straw fragments were weighed and put into the autoclave with the required amount of chemical solution at liquor to solid ratio of 10:1. The 3-litre autoclave was heated to the operating temperature of 120°C, which was then maintained throughout 60 minutes of pulping process. The pulp slurry was removed from black process liquor by decantation. Thereafter, softened pulp was rinsed in two cycles with water and had been transferred into Valley beater (Techlab Systems (TLS), Spain) where appropriate amount of tap water was added in order to maintain the pulp suspension at 1.5% consistency. The fiberization was occurred at pH 9, 24°C and 500 rpm for 40 minutes. Finally, obtained straw pulp was drained by Manual Sheet Former TAPPI (Techlab Systems (TLS) and allowed to dry to moisture content of approximately 7% at the room temperature.

Forming laboratory papers with different share of wheat pulp

Obtained unbleached wheat pulp was mixed with recycled newsprint pulp in different weight shares for forming laboratory papers using a Rapid Köthen Sheet Machine (Frank–PTI GmbH, Birkenau, Germany) needed for this research (Fig.1).

Altogether, three paper sheets (42.5 g/m^2, 20 cm diameter) with variable content of wheat pulp (w = 10%, 20% and 30%) and a control sheet (w wheat pulp = 0%) were formed.

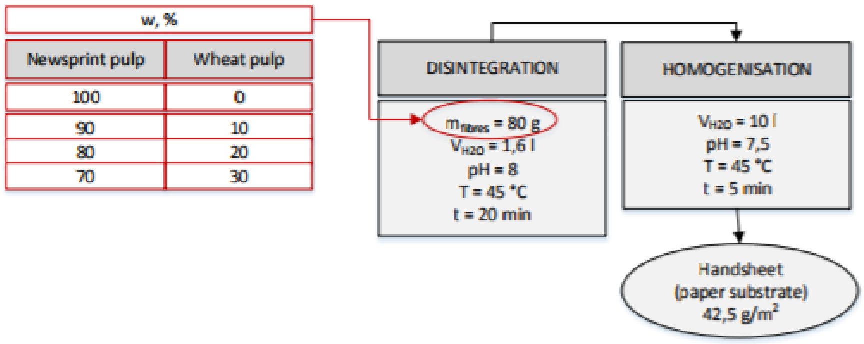

Fig. 1 Workflow of laboratory paper production

Printing paper sheets by digital technique

All paper substrates were printed in full tone black by AGFA, Anapurna M1600, UV curable inkjet printer. The inkjet printings process is a relatively new printing process, which is well suited for a variety of printing applications. The inkjet printing process is characterized by few advantages in comparison with traditionally used printing processes (offset, flexography, etc.). It is a non-contact printing process that requires minimum production space, it can be mounted on the printing production line and used on many different substrates. The inkjet printing process is a computer to print technology, in which a finite amount of liquid (ink) is transferred directly onto a porous media (paper substrate). In other words, no image carrier (printing plate) is needed in the process [3]. Namely, the UV curable inkjet printer has the print-heads of 1024 nozzles with a droplet colour volume of 12 pl, which produce high quality solids and tonal rendering at up to 720 x 1440 dpi. Reproduction is controlled directly by a raster image processor on the basis of the print job described entirely in digital form [4].

Analysing chemical degradation of prints

The prints were tested for resistance to the following agents in accordance with International Standard ISO 2836:2004 [5]. In the field of printing industry, this standard defines methods of assessing the resistance of prints to liquid and solid agents, solvents, varnishes and acids. Test conditions for various liquid test agents used in this research is presented in table 1.

Table 1. Test conditions for various liquid test agents

Test liquid agent	Contact time	Receptor surface	Contact condition
$H_2O_{distilled}$	24 hours	filter paper	1 kg on 54 cm^2
C_2H_5OH (v/v = 96%)	5 minutes	glass tube	-
CH_3COOH (v/v = 1%)	24 hours	filter paper	1 kg on 54 cm^2
NaOH (w/v = 1%)	10 minutes	filter paper	1 kg on 54 cm^2

According to this standard method of assessing the stability of prints is not equal for all used test liquid agents.

- *The method of assessing the stability or resistance of prints to water, acid and alkali*

Print sample was placed on a glass plate and set between four strips (two on each side) of filter paper soaked in the test liquid agent. Another glass plate was placed on top and the sample was put under pressure by applying one kilogram mass on top of the plate. Contact time of prints with water and acid was 24 hours, while with alkali contact time was 10 minutes.

- *The method of assessing the stability or resistance of prints to alcohol*

Print sample was placed in a glass tube containing ethanol and immersed for five minutes.

When the contact time expired, print samples treated with acetic acid and sodium hydroxide were rinse in deionized water until the rinse water has a neutral pH. All prints were dried in an oven prior to assessment (t = 30 minutes, T = 40ºC). Dried chemically treated print samples were compared to untreated print samples and changes in optical properties caused by used test liquid agents were noted and discussed. Chemical stability of prints was monitored through changes in the optical properties of chemically treated samples. The difference between print colour before and after chemical treatment is calculated according to equation 1 [6, 7]:

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

Where:

ΔE_{00}^* – total colour difference, Euclidean colour difference
$\Delta L'$ – the lightness difference between print before and after chemical treatment
$\Delta C'$ – the chroma difference between print before and after chemical treatment
$\Delta H'$ – the hue difference between print before and after chemical treatment
R_T – the rotation function
K_L, K_C, K_H – the parametric factors for variation in the experimental conditions
S_L, S_C, SH – the weighting functions

As all test agents used for evaluation of chemical stability of the prints were liquids, according to the international standard ISO 5637 water absorption tests were carried out as well. All the samples were first dried at 105 ± 2°C during 24 h in an oven. The dried paper samples were weighed (mass m_1) and were immersed in a water bath at 23°C, during a period of 5 minutes. At the end of the immersion period, the paper samples were removed from the distilled water and drained by gravity for 2 minutes before wet weight values had been determined (mass m_2). Water absorption percent was calculated using the equation 2 [8]:

$$M_t(\%) = \frac{m_2 - m_1}{m_1} \times 100 \qquad (2)$$

Where:

Mt	–	the water absorption percent after time t
m1	–	the oven-dry weight of the paper sample
m2	–	the paper sample weight after water immersion

Results and discussion

Optical properties of printed laboratory formed papers with variable content of wheat pulp were evaluated based on spectrophotometric values presented in Table 3.

Table 3. Spectrophotometric L*a*b* values measured on untreated papers printed with black UV ink by digital technique

Untreated black prints	**Share of wheat pulp in laboratory made paper, %**			
	0	**10**	**20**	**30**
L*	27.396	27.214	28.000	28.339
a*	0.102	0.019	0.063	0.103
b*	0.956	1.877	1.402	1.689

All untreated black prints have spectrophotometric L* value expectedly high, concerning that the L* value for ideal dark black is zero. The hue values of a*and b* measured after printing were low and positive.

For analysing the chemical degradation of prints, upper and bottom side of print samples were in contact with different test liquid agents so water absorption of laboratory formed papers used as printing substrate was determinate and results are presented in Fig 2.

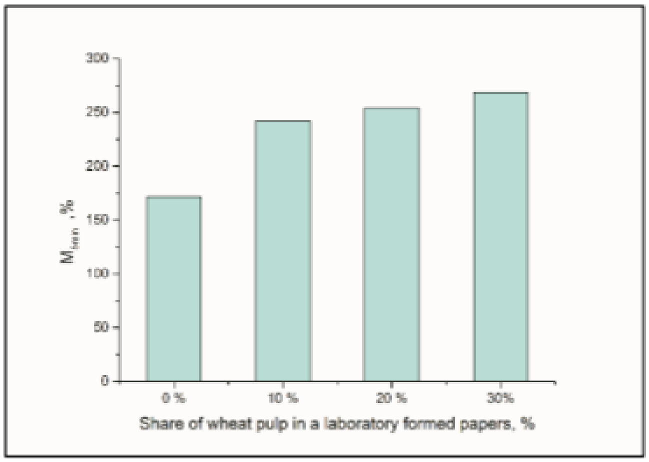

Fig. 2 Water absorption of laboratory formed papers used as printing substrate

Laboratory papers with different contents of wheat pulp showed higher water absorption compared to the control sheet (0% of wheat pulp), which is caused by the chemical constituents of the pulp used in forming laboratory papers. Namely, cellulose and hemicelluloses contain numerous accessible hydroxyl groups so they are greatly responsible for the high water absorption of natural fibres [9]. By adding the straw pulp into the recycled newsprint base, that is by increasing its portion, the content of cellulose and hemicelluloses in laboratory papers is increasing and consequently also the water absorption. A print is considered resistant to a chemical substance when no alteration occurs when it is brought into contact with it, in other words when no change in colour is observed. Evaluation of chemical stability of prints was done based on differences in spectrophotometric L*, a*, b* values (Fig. 3).

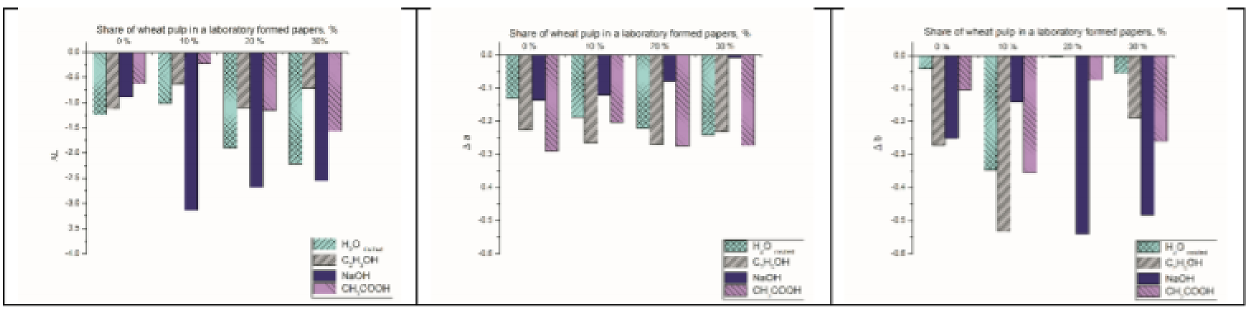

Fig.3 Spectrophotometric differences of prints after chemical treatments

From differences in lightness values it could be notes that lightness of all prints is increased after treatment with all used liquid agents. Prints on paper substrate with variable content of wheat pulp have shown the lowest stability on sodium hydroxide and distilled water. While prints on paper with wheat pulp have same stability on alcohol and acid as control sample (0% of wheat pulp). Differences of a* value of all analysed prints after chemical treatments are negligible. Slightly higher influence of chemicals is observed on b* value, where the sodium hydroxide have shown the highest impact on prints containing 20 and 30% of wheat pulp.

Based on Euclidean colour difference results (Fig. 4), the influence of distilled water, ethanol, sodium hydroxide and acetic acid on the prints was evaluated.

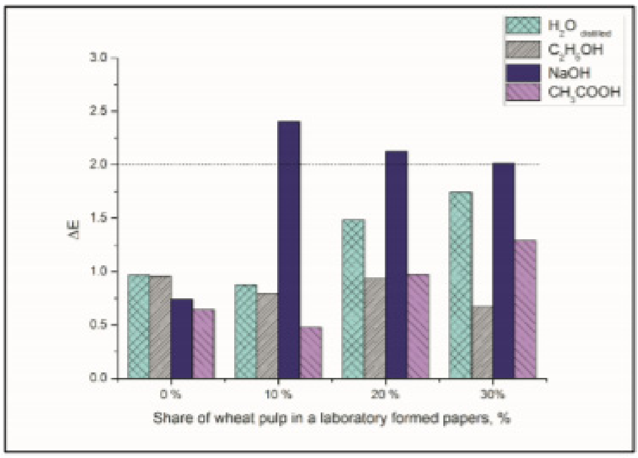

Fig. 4 Euclidean colour difference of prints after chemical treatments

For all prints treated with all test liquid agents ΔE00 is in range from 0.48 to 2.40 which is not visible to an average observer. Comparing the effect of all test liquid agents on prints Euclidean colour difference, the ethanol and acetic acid had the minor influence on prints colour deviation. Water and sodium hydroxide are liquid agents which have shown the highest impact on chemical degradation of prints, especially on prints with wheat pulp. The calculated ΔE00 values are the highest for prints treated with sodium hydroxide what was expected regarding to low alkali resistance of carbon pigment in UV inks [10].

Conclusion

Deviations in colour of prints have shown that highest chemical stability provides prints which not contain wheat pulp that could be explain by high water absorption of virgin fibres. This behaviour of fibres could be reduced by adding sizing agents into the pulp which coating the fibres would control the penetration of liquid into the paper sheet. From the obtained results it could be concluded how paper substrates with variable content of wheat pulp, printed with black UV inkjet technique, have good chemical stability to water, ethanol and acetic acid.

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