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Sadržaj

THE IMPACT OF INORGANIC ACIDS ON COLOUR STABILITY OF DIGITAL PRINTS MADE ON SUBSTRATES WITH WHEAT PULP

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Abstract

Agriculture residues are one of the most abundantly available resources worldwide as millions of tons are produced globally. Wheat is a particularly cultivated species in Croatia, and after each harvest, huge amounts of straw remain in the fields. Efficient utilization of this residue to produce paper as a printing substrate offers advantages as reducing the use of primary wood fibres and thus reducing deforestation. In this research, printing substrates with wheat straw will be evaluated in terms of chemical stability of digital prints influenced by inorganic acids. For that purpose, printing substrates were formed on the Rapid Köthen device from pulp obtained by blending different proportions of wheat pulp and pulp of recycled fibres. Colour prints (C+M, M+Y, C+Y and C+M+Y) were made in full tone by digital printing technique and prints were treated with two inorganic acids under the conditions defined in the international standard ISO 2836:2004. Based on the measured spectrophotometric values of the untreated and acid-treated prints, changes in colorimetric values of L*a*b* and the Euclidean colour difference (ΔE00*) were calculated, and the colour stability of prints was assessed. Based on the obtained results it could be concluded that wheat pulp in printing substrates ensures equal or even better colour stability of prints than pulp from recycled fibres.

Keywords: colour stability, digital prints, inorganic acids, wheat pulp

UTJECAJ ANORGANSKIH KISELINA NA STABILNOST OBOJENJA DIGITALNIH OTISAKA NA PODLOGAMA S PŠENIČNOM PULPOM

Sažetak

Poljoprivredni ostaci jedan su od najrasprostranjenijih svjetskih resursa jer se milijuni tona proizvode globalno. Pšenica je najviše uzgajana vrsta u Hrvatskoj, a nakon svake žetve na poljima ostaje ogromna količina slame. Učinkovita upotreba slame za proizvodnju papira kao tiskovne podloge nudi prednosti poput smanjenja upotrebe primarnih drvenih vlakana i smanjenja krčenja šuma. U ovom će se istraživanju tiskovne podloge s dodatkom pšenične pulpe evaluirati s obzirom na kemijsku stabilnost digitalnih otisaka pod utjecajem anorganskih kiselina. U tu svrhu na uređaju Rapid Köthen načinjene su laboratorijske tiskovne podloge od pulpe dobivene miješanjem različitih udjela pšenične pulpe i pulpe recikliranih vlakana. Otisci s dvije ili tri boje (C+M, M+Y, C+Y i C+M+Y) izrađeni su u punom tonu digitalnom tehnikom tiska te su tretirani s dvije anorganske kiseline pod uvjetima definiranim u međunarodnoj normi ISO 2836: 2004. Na temelju izmjerenih spektrofotometrijskih vrijednosti netretiranih i kiselinom tretiranih otisaka izračunate su promjene kolorimetrijskih vrijednosti L*a*b* te Euklidske razlike u boji (ΔE00*) temeljem kojih je procijenjena stabilnost obojenja otisaka. Na osnovu dobivenih rezultata može se zaključiti da pšenična pulpa u tiskovnim podlogama osigurava jednaku ili čak bolju stabilnost boje otisaka nego pulpa recikliranih drvnih vlakanaca.

Ključne riječi: stabilnost obojenja, digitalni otisci, anorganske kiseline, pšenična pulpa

1. INTRODUCTION

In ancient times, non-wood biomass was the primary raw material for pulp and paper production until the wood raw material had not completely supplanted them. Nowadays, about 90% of fibres used in the paper industry originates from hardwood and softwood, which has contributed to the problem of deforestation causing an imbalance in the ecosystem. All this has led to the growing interest in alternative sources of raw materials for pulping and paper production other than wood [1]. The use of non-wood raw materials accounts for less than 10% of the total pulp and paper production worldwide, of which 44% is straw, 18% bagasse, 14% reeds, 13% bamboo, and 11% others [2]. Annual crops and agricultural residues are mostly used as they are environmentally friendly raw material, cheap and have unlimited availability [3]. Agriculture residues are one of the most abundantly available resources in the world as millions of tons are produced globally which are either burned on the fields or left to rot. Numerous studies were made till today and it was found that fibres obtained from non-wood plants are similar to those of hardwoods, about 1 mm long [4,5,6], and can be used for producing paper of various qualities and strength. All plant fibres are made of cellulose, hemicelluloses, lignin, and pectin, but the proportion of these products varies from one kind of fibre to another. It is important to emphasize that fibres originated from agricultural residues have less lignin and approximately the same share of cellulose as those derived from wood [4,7,8]. These indications imply that this type of raw material should be used more in the paper industry.

However, there is not much research on papers containing the pulp obtained from agricultural residues intended for printing. In this study, the digital printing technique was chosen for the preparation of prints on substrates with wheat pulp because it is a novel technology that is evolving extremely fast and in some areas is competitive with all conventional printing techniques. Because it is economically more cost-effective and creates good print quality, dramatic growth of this printing technique is predicted [9,10]. The focus was on assessing the chemical stability of digital prints made on substrates with wheat pulp, as an alternative to virgin wood pulp, under the impact of strong acids which is extremely important in the labelling and packaging sector of the printing industry.

2. EXPERIMENTAL PART

2.1 Laboratory substrates

Laboratory substrates of approximately 42.5 g/m2, formed by a Rapid-Köthen sheet former (FRANK-PTI) according to standard EN ISO 5269-2:2004 [11], were made entirely from pulp of recycled fibres or from recycled wood pulp with admixture of wheat pulp in three different portions (Table 1.). Semi chemical wheat pulp was obtained from crop residues leftover on Croatian fields after harvesting, which was collected, manually cut, and processed by the soda pulping method [12,13].

Table 1. Mark and composition of substrates

Mark of substrate	Composition		Production type
	Wheat pulp, %	Recycled pulp, %	
K	0	100	commercial
N	0	100	laboratory
1NW	10	90	
2NW	20	80	
3NW	30	70	

2.2 Digital prints

All substrates were printed by a digital EFI Rastek H652 UV curable inkjet printer with a resolution of 600 × 600 dots per inch (dpi) (in high quality mode 8 pass) and a printing speed of 12.10 m2/ h. Each substrate was printed in full tone, where in a certain order one ink was printed on the top of the other, producing four different colours C+M, C+Y, M+Y and C+M+Y, respectively. In total 20 different UV inkjet prints were prepared for chemical stability analysis.

2.3 Inorganic acids treatment

Printed samples were tested for resistance to inorganic acids by the method defined in the international standard ISO 2836:2004 in the field of graphic industry [14]. All prints were cut to dimensions 2 cm x 5 cm before determining chemical stability. The treatment with hydrochloric and sulfuric acid solutions was performed as follows. First, two paper filters were soaked in an acid solution (v/v = 5%). They were then put onto the lower glass plate with a printed sample located in between. Finally, the upper glass plate was placed on top and weighted by a 1kg weight (Figure 1). The printed samples were thus exposed to each acid for 10 minutes, after which each printed sample was washed with distilled water and dried in an oven for 30 minutes at 30°C.

Figure 1. Inorganic acid treatment of prints

For determining the chemical stability of prints on substrates with wheat pulp, strong acids that completely dissociate in an aqueous solution and are used widely in everyday life were selected (Table 2.). Chemical exposure of printed material needs to be considered in every application.

Table 2. Usage of inorganic acids in a broad range of industry and household

Formula	IUPAC name	Uses [15]
HCl	hydrochloric acid	in the manufacture of chemicals, in pulp and paper (although substituted in most enterprises by now), metal products, food products and beverages and in the extraction of crude petroleum and natural gas, in the purification of water and treatment of sewage, and as a general disinfectant and for household cleaning
H_2SO_4	sulfuric acid	in car batteries, in the manufacture of fertilizers, in cleaning products, in the purification of water and treatment of sewage, and in manufacturing of polymers, dyes and paints

2.4 Colour stability assessment

Based on the measured spectrophotometric values of untreated (Table 3) and acid-treated prints, changes in colorimetric values of L*a*b* and the Euclidean colour difference were calculated, and the stability of prints was assessed. Colour data were measured by a spectrophotometer X-Rite SpectroEye under an illuminant D50, 2° standard observers. The following equation (1) was used to calculate the Euclidean colour difference ($\Delta E_{00}{}^*$):

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

Where: ΔE_{00}^* – total colour difference, the Euclidean colour difference
$\Delta L'$ – the transformed lightness difference between print before and after acid treatment
$\Delta C'$ – the transformed chroma difference between print before and after acid treatment
$\Delta H'$ – the transformed hue difference between print before and after acid treatment
RT – 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

3. RESULTS AND DISCUSSION

The colorimetric values, L*a*b*, of each print were measured and the results of the average value and standard deviations are summarized in Table 3. The obtained results of colorimetric values indicate that the paper production method (commercial or laboratory) has a greater impact on the lightness (L*) and the values of a* and b* of prints than the composition of the paper used as a printing substrate. Namely, the colorimetric values of prints made on laboratory substrates (N, 1NW, 2NW and 3NW) are nearly the same, while compared to those measured on prints on the commercial substrate (K) there is a noticeable difference. Due to the different way of paper production (in the case of laboratory papers there is no fibre orientation, as well as no finishing of the paper surface), this was expected because such papers absorb colour differently.

Table 3. Colorimetric values (L*a*b*) with standard deviations of prints before acid treatment

Substrate	Prints											
	C+M			M+Y			C+Y			C+M+Y		
	L*value											
K	23.80	±	1.21	45.14	±	0.74	44.27	±	1.01	20.46	±	1.50
N	27.07	±	1.56	46.49	±	0.95	45.67	±	1.04	23.64	±	1.45
1NW	27.05	±	1.41	46.56	±	0.93	44.62	±	0.90	22.83	±	1.69
2NW	26.46	±	1.43	46.49	±	1.00	44.36	±	1.04	23.84	±	1.74
3NW	26.28	±	1.40	46.16	±	0.99	44.26	±	1.13	23.04	±	2.07
	a* value											
K	17.61	±	2.28	57.58	±	2.61	-57.16	±	1.27	-2.50	±	0.39
N	14.94	±	2.37	56.40	±	2.41	-52.91	±	1.45	-2.56	±	0.41
1NW	13.40	±	2.53	55.36	±	2.34	-52.18	±	2.01	-2.56	±	0.30
2NW	13.31	±	2.30	55.49	±	2.44	-51.40	±	2.17	-2.41	±	0.40
3NW	12.95	±	2.64	55.56	±	2.32	-51.23	±	2.54	-2.66	±	0.43
	b* value											
K	-38.95	±	1.05	38.62	±	2.76	15.67	±	1.26	-2.87	±	0.30
N	-34.18	±	1.50	34.93	±	2.29	16.31	±	1.15	-1.88	±	0.21
1NW	-31.73	±	1.75	34.30	±	2.12	16.29	±	1.33	-1.73	±	0.23
2NW	-31.50	±	1.49	34.51	±	2.16	16.43	±	1.25	-1.57	±	0.24
3NW	-30.71	±	2.03	34.82	±	2.11	16.36	±	1.25	-1.59	±	0.24

Different chemicals can react very aggressively with printed graphic product because they can be absorbed by or attack the material, causing a change in material properties. The impact of strong inorganic hydrochloric (HCl) and sulfuric (H2SO4) acids on the colour stability of the prints on substrates are shown in Figure 2a-c.

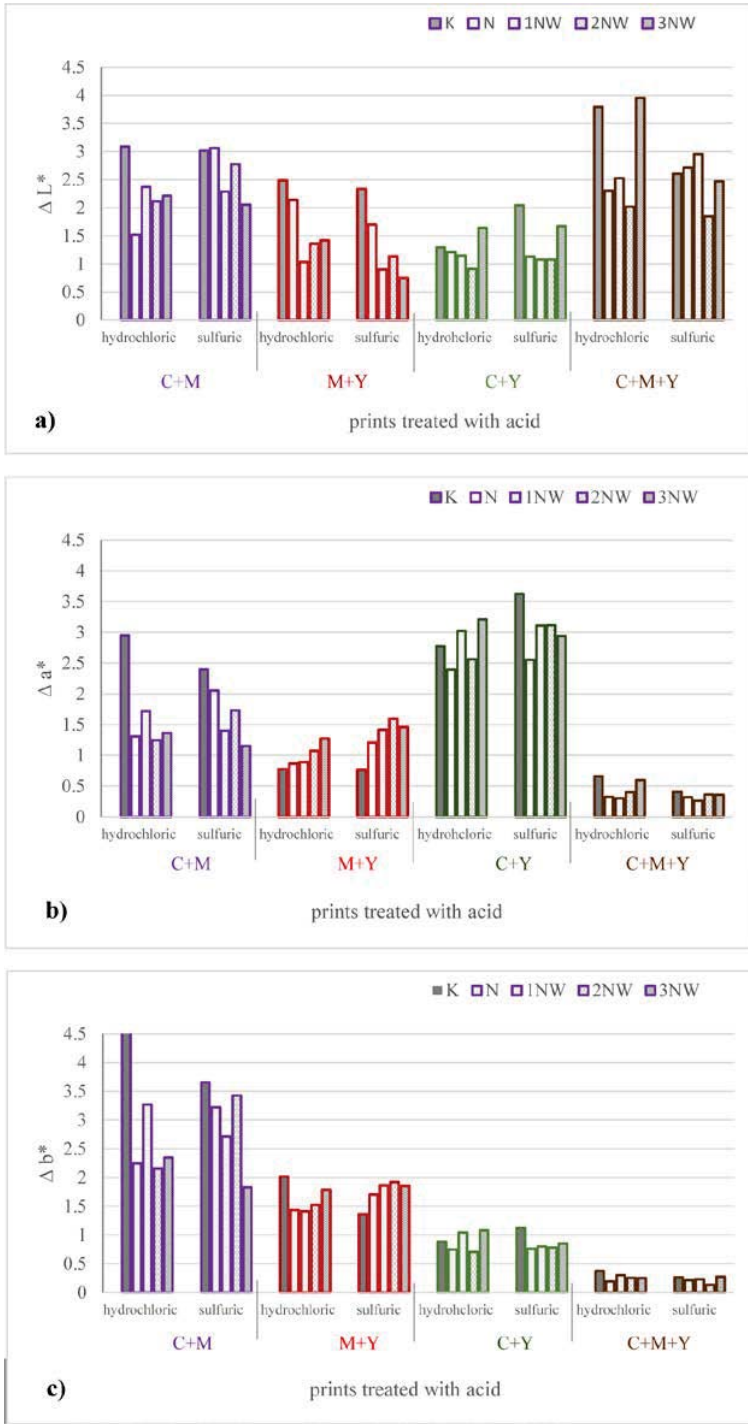

Figure 2. Changes in colorimetric values (ΔL*, Δa* and Δb*) of prints made on substrates with wheat pulp (1NW, 2NW and 3NW) and both control substrates (K and N) after acid treatment

The highest changes in lightness values were observed for C+M+Y prints (ΔL*max. 3.9), while the impact of strong inorganic acids on the lightness of C+Y prints was the smallest (ΔL*max. 2) regardless of the substrate composition. In general, the impact of hydrochloric and sulfuric acids was slightly stronger on all prints on the commercial paper substrate (K) than on any laboratory substrate. Moreover, the addition of wheat pulp to laboratory substrates had a positive effect on the stability of the lightness parameter of the colour, especially on the M+Y print (Figure 2a). The highest changes in Δa* values were observed for C+Y print, while the highest changes in Δb* values were observed for C+M prints regardless of the printing substrate composition. The smallest changes in both colour coordinates were observed for C+M+Y prints (Figure 2b-c).

From the results summarized in Table 4, it can be clearly seen that the impact of strong hydrochloric and sulfuric acids on the colour stability of all prints is relatively small. However, it is interesting that the commercial paper substrate (K) provides prints of lower stability compared to paper substrates produced on a laboratory scale with or without added wheat pulp. This trend was also noticed in a previous study on digital prints in cyan, magenta, yellow, and black after treatment with inorganic acids [16]. The highest colour difference was noticed for the C+M+Y print on a 3NW substrate treated with hydrochloric acid (ΔE_{00}* = 3.08), while the smallest difference in colour was measured on the M+Y print on a 3NW substrate (ΔE_{00}* = 1.08).

Table 4. Colour difference, Δ E00*, of the prints before and after acid treatment

acid / substrate	ΔE_{00}* of prints							
	C+M		**M+Y**		**C+Y**		**C+M+Y**	
	hydrochloric	sulfuric	hydrochloric	sulfuric	hydrochloric	sulfuric	hydrochloric	sulfuric
K	2.72	2.51	2.60	2.36	1.49	2.23	2.88	1.95
N	1.45	2.60	2.23	1.85	1.38	1.38	1.81	2.07
1NW	2.27	2.08	1.21	1.24	1.50	1.47	1.99	2.21
2NW	1.82	2.54	1.55	1.44	1.22	1.47	1.77	1.49
3NW	2.02	1.77	1.64	1.08	1.88	1.92	3.08	1.93

CONCLUSION

In this research, laboratory substrates with wheat pulp were evaluated in terms of colour stability of digital prints after inorganic acid treatment. Based on the spectrophotometric results gained in this study, it could be concluded that wheat pulp in printing substrates ensures equal or even better acid stability of prints than pulp from recycled fibres. This is extremely important for the utilization of such substrates in the labelling and packaging sector of the printing industry that is constantly growing.

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