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The Effect of Acids on the Chemical Stability of UV Inkjet Prints on Papers with Straw Pulp

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Abstract

The bonding potential of pulp fibers is reduced by the paper recycling process. The most common technique for recovering this lost potential of secondary fibers involves upgrading the recycled pulp by blending it with virgin softwood pulps. In this research, we asses print stability on acid agents of UV inkjet prints when using straw pulp as reinforcing fibers in recycled papers. For that purpose, printing substrates were formed on the Rapid Köthen device from pulp obtained by blending different proportions of straw pulp and pulp of recycled fibers. Each printing substrate was printed in full tone with cyan, magenta, yellow, and black inks by digital technique of UV inkjet printing. Printed substrates were treated with various inorganic and organic 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, the Euclidean color difference (ΔE_{00}^*) was defined and the stability of prints was assessed. The results of spectrophotometric measurements indicate small to medium color differences of the prints due to the effect of all acids ($\Delta E_{00max.}^* < 2.4$) and it can be concluded that straw pulp in printing substrates from recycled fibers contributes to good chemical stability of prints. This research concludes that straw, as an annual renewable resource, can be used in conjunction with waste paper as an alternative to wood, which is currently the dominant raw material for graphic industry and producing paper.

Key words

Acids, Chemical stability, Paper, Straw pulp, UV inkjet printing

1. INTRODUCTION

Ink and printing substrate are the two components that have the greatest influence on image or text reproduction quality. Therefore, an adequate printing substrate is critical for any particular printing technique based on the function of the final product. Paper as the most commonly used printing substrate for all printing techniques is traditionally produced from cellulose fibers derived from wood. Over the last decades, the increased focus on waste paper recovery and use in paper and paperboard production was widespread due to environmental concerns. Substitution of virgin wood pulp by waste paper has been accepted globally, and today recovered paper accounts for around 50% of the total papermaking fibers worldwide [1]. It is important to emphasize that paper production cannot be based only on waste paper as a source of fibers, as it can neither be efficiently used for all paper grades, nor can it be used infinitely many times. However, depending on the final paper quality and its price, the utilization rates by paper grades vary significantly, ranging from 10% to more than 90%. In newsprint, the utilization rate is extremely high up to 92.8%, while in packaging papers it is, on average, 75.3%. For other graphic paper, it is only 10.6% [1]. In paper production from waste paper during the recycling process, it is important to continuously incorporate a certain amount of virgin fibers for strength, quality, and availability reasons. Given recycled fibers are not suitable for some products, as was already mentioned, the need for virgin fibers in the paper industry still exists. An alternative to conventional virgin wood fibers could be found in rapidly renewable sources (hemp, flax, bamboo, kenaf) and agricultural residues (wheat straw and bagasse) [2]. The great variety of characteristics, fiber dimensions and chemical composition of these alternative raw materials give them great potential to produce different types of papers [3]. The results of the previous study revealed that straw as an agricultural residue has fibers similar in length to hardwood species (common beech (*Fagus sylvatica L.*) and white poplar (*Populus alba L.*) which are most commonly used in cellulose and papermaking industries [4]. In addition, it has been proven that straw as non-wood plant material has nearly the same cellulose content as most wood species, lower content of lignin and higher amount of ash and solvent extractives [5]. The potential of wheat straw, the plant raw material that, according to annual yield, takes the first place in Europe and the second one in the world is recognized due to its availability which is one of the characteristics that a raw material for the paper industry must fulfill [6]. Wheat straw is applied as fibrous raw material for pulping and papermaking industry in countries with a lack of wood supply or in agricultural countries where this source is available in huge quantities [7]. However, if the paper made from straw pulp is intended for printing, the requirements for such papers are even higher. The printing substrates must hold most of the ink in the upper ten micrometers i.e. the ink layer should remain at or near the surface after drying in order to provide an optimum print density and good color saturation. But if the colorants are fixed to the surface of the printing substrate, they will be directly exposed to light, pollution, and other agents. Therefore, such print will be vulnerable to decomposition of the dye. Generally, the interaction of the ink with the substrate is key to producing high strength, well defined, durable images fit for any application [8].

As the quality and stability of the print directly depend on the composition of the paper as a printing substrate, it is important to determine which cellulose fibers (from the aspect of their origin) give quality prints. In this study emphasis is placed on evaluation of the straw pulp usability in the production of paper intended for printing based on the chemical stability of prints made on such substrates.

2. MATERIALS AND METHODS

2.1. Papers with straw pulp

Laboratory papers of approximately 42.5 g/m^2, formed by Rapid-Köthen sheet former (FRANK-PTI) according to standard EN ISO 5269-2:2004 [9], were made entirely of recycled wood pulp or from mixture of recycled wood and straw pulp of wheat, barley and triticale (Table 1.). Semi chemical straw pulp was obtained from crop residue leftover on fields after harvesting which was collected, manually cut, and processed by soda pulping method [10], [11].

Table 1. Papers used as printing substrates

Mark	**Composition**		**Production type**
	Straw pulp, %	**Recycled pulp, %**	
K	0	100	commercial
N	0	100	laboratory
1NW, 1NB, 1NTR	10	90	
2NW, 2NB, 2NTR	20	80	
3NW, 3NB, 3NTR	30	70	

* straw type: W = wheat; B = barley; TR = triticale

2.2. UV inkjet printing

All laboratory sheets and commercial paper were printed by digital EFI Rastek H652 UV curable inkjet printer. Each printing substrate was printed in full tone with cyan, magenta, yellow and black inks with the resolution of 600 × 600 dots per inch (dpi) (with high quality mode 8 pass) and printing speed of 12.10 m^2/ hr. In total 44 different UV inkjet prints were prepared for chemical stability analysis.

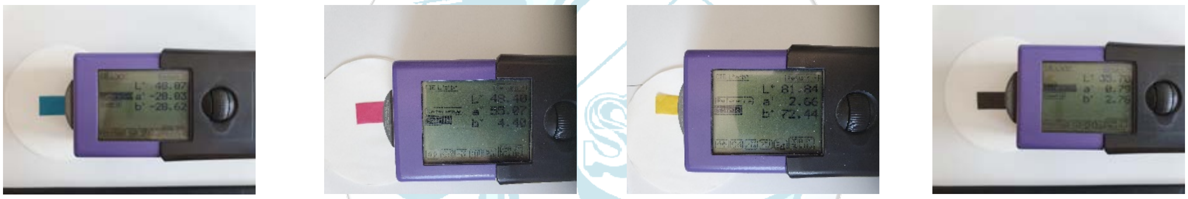
2.3. Chemical stability analysis

The method of assessing the resistance of printed samples to acid satisfied the international standard ISO 2836:2004 in the field of graphic industry [12]. All printed samples were cut to 2 cm x 5 cm dimensions before determining chemical stability. The treatment with 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 is placed on top and weighted by a 1kg weight. The printed samples were thus exposed to each acid from 10 minutes to 60 minutes, depending on the type of acid (Table 2), after which each printed sample was washed with distilled water and dried in an oven for 30 minutes at 50 °C.

Table 2. Acids used as chemical agents and test conditions

Acid		Concentration % by volume	Receptor surface	Duration of exposure, min	Contact conditions
Inorganic	Hydrochloric (HCl)	5	filter paper	10	1 kg on 54 cm^2
	Sulfuric (H_2SO_4)	5		10	
Organic	Acetic (CH_3COOH)	5		30	
	Citric ($C_6H_8O_7$)	5		60	

Evaluation of chemical stability of UV inkjet prints on papers with straw pulp was done based on the Euclidean color difference (ΔE_{00}) which was calculated according to the equation (1). Colorimetric values were measured by spectrophotometer X-Rite SpectroEye before and after acid treatment (Figure 1.).



cyan magenta yellow black

Figure 1. Photographs of color data measurements on UV inkjet prints

Color data were measured under illuminant D50, 2° standard observers. The symbol ΔE_{00}^* is used to denote distance in the uniform color space [13] and is defined as:

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

Where: ΔE_{00}^* – total color difference, the Euclidean color 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

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 results of change in visual perception of color due to the acid treatments are reported as an average of ten measurements from each print sample and interpretation of obtained ΔE_{00} values is summarized in Table 3.

Table 3. Interpretation of ΔE_{00}^{*} value [14]

ΔE_{00}^{*}	Color perception
≤ 1.0	Differences in color are unrecognizable by a standard observer.
1 - 2	Only an experienced observer is able to perceive the differences.
2 – 3.5	An inexperienced observer is able to perceive the differences.
3.5 - 5	Every observer can easily see the difference.
> 5	An observer recognizes two different colors.

If the color differences value after chemical treatment is lower than 2 it is defined as chemically stable print as very small or small noticeable difference in the tone can be recognized by standard observer. As the value of the Euclidean color difference increases, the change in color is more clearly visible by a standard observer.

3. RESULTS AND DISCUSSION

Inorganic and organic acids used as chemical agents have different strength in solution. Namely, inorganic hydrochloric (HCl) and sulfuric (H_2SO_4) acids are strong acids which means that in an aqueous solution they dissociate completely, while organic acetic (CH_3COOH) and citric ($C_6H_8O_7$) acids only partially dissociate in solution, so they are classified as weak ones. The quantitative measure of the strength of acid in a solution is defined by Ka value (acidity constant). Weak acids have very small Ka values and therefore higher values for pKa (pKa in range from -2 to 12) compared to strong acids, which have very high Ka values and slightly negative pKa values (pKa lower than -2).

The Euclidean color difference of UV inkjet prints on different printing substrates due to hydrochloric acid, sulfuric acid, acetic acid, and citric acid treatments are presented in Figures 2-5.

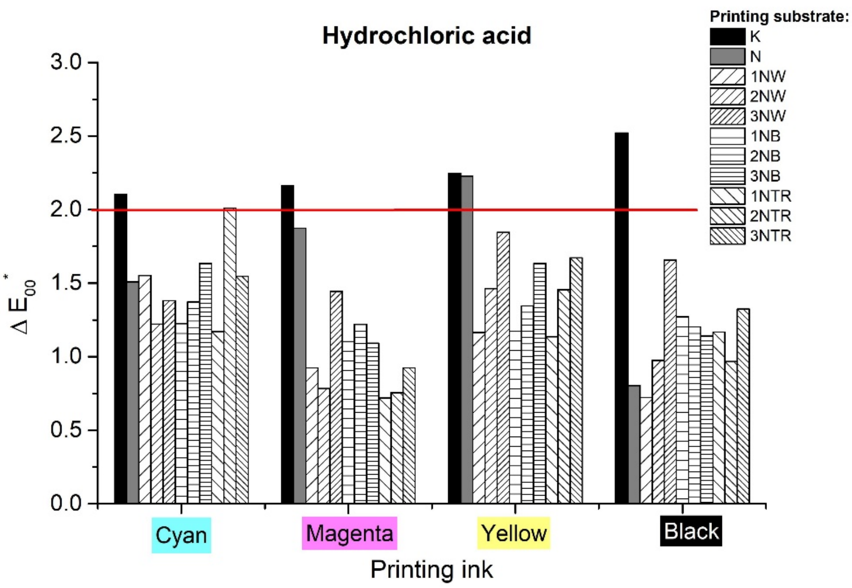


Figure 2. The Euclidean color difference of UV inkjet prints on different printing substrates after hydrochloric acid treatment

From gained results of spectrophotometric measurements of prints treated with hydrochloric acid presented at Figure 2, it is evident that commercial paper substrate (K) provides prints of lower stability in comparison with paper substrates produced at laboratory scale. However, CMYK prints on commercial paper substrate can be considered as satisfactory stable on hydrochloric acid because the change in color of the print is barely noticeable to a standard observer ($\Delta E_{00max.}^{*} < 2.4$). All laboratory papers provide good chemical stability of CMYK prints, especially those with addition of straw pulp. Generally, the most stable prints on printing substrates with straw pulp are those made with magenta and black (ΔE_{00}^{*} in range from 0.72 to 1.45 and 0.72 to 1.66, respectively).

Slightly larger changes in the quality of reproduction due to the hydrochloric acid treatment were noticed on the prints with cyan and yellow inks.

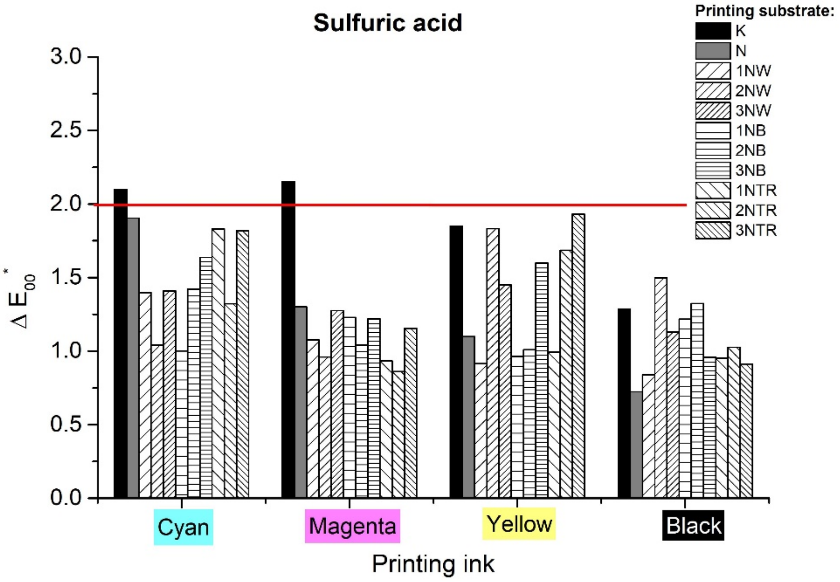


Figure 3. The Euclidean color difference of UV inkjet prints on different printing substrates after sulfuric acid treatment

The influence of sulfuric acid on color stability of UV inkjet prints is presented at Figure 3. The similar behaviour on CMYK prints was observed after sulfuric acid treatment but the values of the Euclidean color difference were slightly lower than due to hydrochloric acid treatment. Impact of sulfuric acid on the Euclidian color difference of prints is slightly more pronounced for magenta and cyan prints made on commercial printing substrate (K), while for yellow and black ink printed on commercial and laboratory printing substrates without straw pulp (N) or with straw pulp is approximately the same. The Euclidean color difference of prints on printing substrate with straw pulp is in range from 0.84 for black print on printing substrate with 10% of wheat pulp (1NW) to 1.93 for yellow print on printing substrate with 30% of triticale pulp (3NTR). Straw pulp of wheat, barley and triticale partially forms printing substrates which provide approximately the same stability to prints after treatment with strong hydrochloric and sulfuric acids.

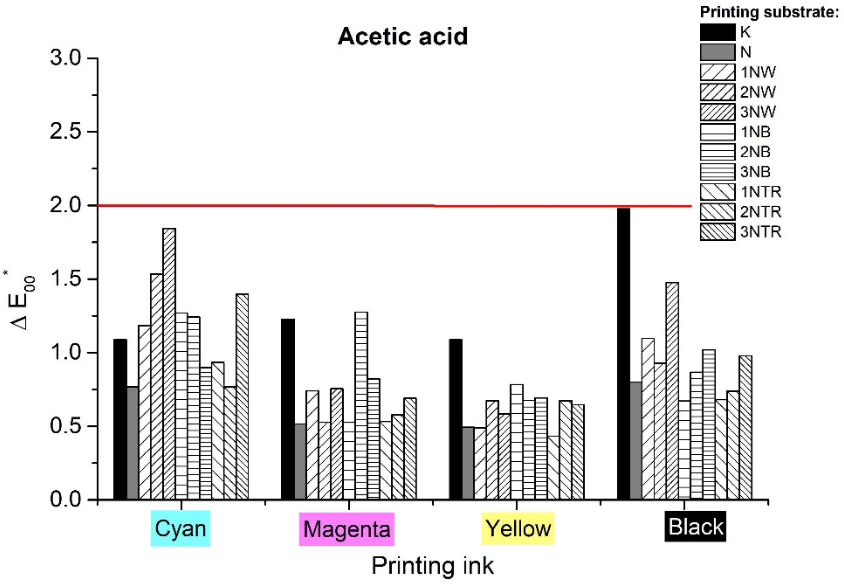


Figure 4. The Euclidean color difference of UV inkjet prints on different printing substrates after acetic acid treatment

Figure 4 presents results of acetic acid impact on chemical stability of UV inkjet prints on printing substrates with straw pulp. It is clearly visible that commercial printing substrate provides similar stability of prints as printing substrates made at laboratory scale, except for prints with black ink. The highest degradation on black print is measured on commercial printing substrate (K) with ΔE_{00}^* value of 1.98. The most stabile print, regardless on which printing substrate it is printed, is yellow (ΔE_{00}^* = 0.49 - 1.09). Cyan and black prints made on printing substrates with straw pulp have showed the highest degradation of color after acetic acid treatment (ΔE_{00}^* up to 1.84).

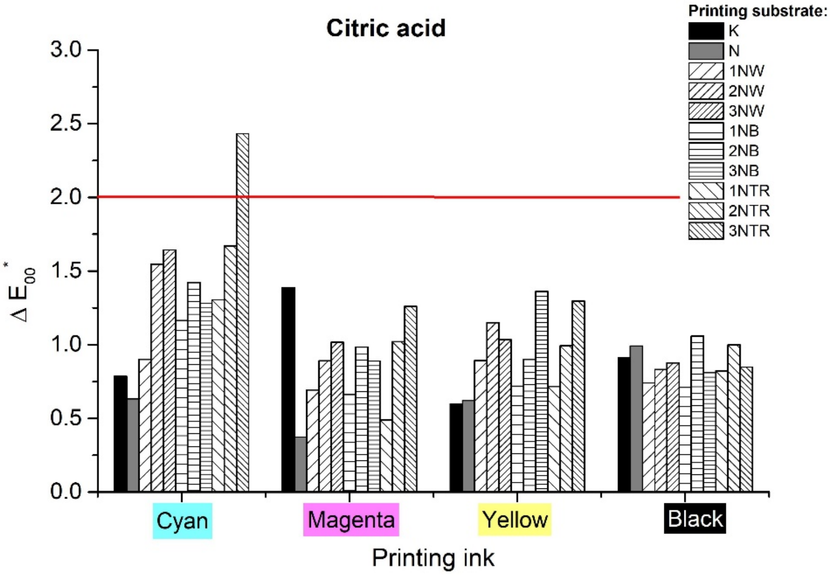


Figure 5. The Euclidean color difference of UV inkjet prints on different printing substrates after citric acid treatment

The influence of citric acid on degradation in color of UV inkjet prints is presented at Figure 5. The highest degradation of color by this organic acid is observed on cyan prints (3NTR printing substrate with ΔE_{00}^* = 2.43), while magenta, yellow and black prints show similar color degradation.

As citric and acetic acids are weaker than inorganic acid used for chemical stability assessment their effect on prints is smaller. Generally, for all printed inks the Euclidean color difference values after treatment with these organic acids are lower than 1.5. It is interesting that for organic acid treatment the type of paper production (commercial or laboratory) did not show significant differences in chemical stability of prints as with strong inorganic acids.

4. CONCLUSION

The main aim of this research was to evaluate the usability of straw pulp for paper production intended for printing based on the chemical stability of UV inkjet prints on such printing substrates after acid treatment. As the results of spectrophotometric measurements indicated by a standard observer unrecognizable or hardly perceive color differences for all four analyzed colors due to the action of inorganic or organic acids ($\Delta E_{00max.}^*$ < 2.4) it can be concluded that addition of straw pulp in printing substrates contributes to good chemical stability of prints. This research concludes that straw, as an annual renewable resource, can be used in conjunction with waste paper as an alternative to wood, which is currently the dominant raw material for graphic industry and producing paper.

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