



Optical Properties of Digital Inks on Straw-Containing Papers with TiO₂-Based Coating Upon Ageing

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Introduction

Different types of coatings can be used to achieve the desired surface properties for high-performance printing on recycled paper. Coated papers restrict the amount of ink that is absorbed into the paper, allowing the ink to sit on top of the paper, in a crisp defined dot, while uncoated papers are more porous. Double coated papers are usually graded as high-quality papers, where the first layer of the coating, a precoat, serves to fill-in the surface pores while the topcoat, which will be printed on, is of higher quality. Therefore, it was not surprising that a different number of TiO₂-based white ink layers printed on a paper substrate with the inkjet technology can influence the legibility of prints, where the best print legibility was achieved at two layers of white ink. However, paper as a printing substrate is subjected to numerous deterioration processes from the moment it is produced, which can lead to the irreversible degradation of text or image printed on it. Paper, bindings, printing inks, dyes and pigments are particularly sensitive to the light because they absorb light energy which can initiate many possible sequences of chemical reactions that damage the paper and cause the printed text to fade or change color.

Layers of TiO₂-based white coating were applied to the entire surface of all laboratory-made papers using a digital UV LED inkjet printing machine, Roland VersaUV LEC-300, which works on the piezo inkjet principle. Then, a test full-tone pattern was printed with black and magenta inks recommended from Roland DG Corporation on all prepared uncoated and coated substrates (Table 3).

Table 3 Marks used for substrates prepared for printing

MarksDefinitionPS7commercial paper used as a target reference sampleNo, 1NWo, 2NWo, 3NWo, 1NBo, 2NBo, 3NBo, 1NTRo, 2NTRo, 3NTRolaboratory-made papers without coatingN1, 1NW1, 2NW1, 3NW1, 1NB1, 2NB1, 3NB1, 1NTR1, 2NTR1, 3NTR1laboratory-made papers coated in one layerN2, 1NW2, 2NW2, 3NW2, 1NB2, 2NB2, 3NB2, 1NTR2, 2NTR2, 3NTR2laboratory-made papers coated in two layers* W = wheat pulp; B = barley pulp; TR = triticale pulp		_	
PS7commercial paper used as a target reference sampleN₀, 1NW₀, 2NW₀, 3NW₀, 1NB₀, 2NB₀, 3NB₀, 1NTR₀, 2NTR₀, 3NTR₀laboratory-made papers without coatingN₁, 1NW₁, 2NW₁, 3NW₁, 1NB₁, 2NB₁, 3NB₁, 1NTR₁, 2NTR₁, 3NTR₁laboratory-made papers coated in one layerN₂, 1NW₂, 2NW₂, 3NW₂, 1NB₂, 2NB₂, 3NB₂, 1NTR₂, 2NTR₂, 3NTR₂laboratory-made papers coated in two layers* W = wheat pulp; B = barley pulp; TR = triticale pulp	Marks	Definition	
No, 1NWo, 2NWo, 3NWo, 1NBo, 2NBo, 3NBo, 1NTRo, 2NTRo, 3NTRolaboratory-made papers without coatingN1, 1NW1, 2NW1, 3NW1, 1NB1, 2NB1, 3NB1, 1NTR1, 2NTR1, 3NTR1laboratory-made papers coated in one layerN2, 1NW2, 2NW2, 3NW2, 1NB2, 2NB2, 3NB2, 1NTR2, 2NTR2, 3NTR2laboratory-made papers coated in two layers* W = wheat pulp; B = barley pulp; TR = triticale pulp	PS7	commercial paper used as a target	
No, 1NWo, 2NWo, 3NWo, 1NBo, 2NBo, 3NBo, 1NTRo, 2NTRo, 3NTRolaboratory-made papers without coatingN1, 1NW1, 2NW1, 3NW1, 1NB1, 2NB1, 3NB1, 1NTR1, 2NTR1, 3NTR1laboratory-made papers coated in one layerN2, 1NW2, 2NW2, 3NW2, 1NB2, 2NB2, 3NB2, 1NTR2, 2NTR2, 3NTR2laboratory-made papers coated in two layers* W = wheat pulp; B = barley pulp; TR = triticale pulp		reference sample	
3NB0, 1NTR0, 2NTR0, 3NTR0coatingN1, 1NW1, 2NW1, 3NW1, 1NB1, 2NB1, 3NB1, 1NTR1, 2NTR1, 3NTR1laboratory-made papers coated in one layerN2, 1NW2, 2NW2, 3NW2, 1NB2, 2NB2, 3NB2, 1NTR2, 2NTR2, 3NTR2laboratory-made papers coated in two layers* W = wheat pulp; B = barley pulp; TR = triticale pulp	N₀, 1NW₀, 2NW₀, 3NW₀, 1NB₀, 2NB₀,	laboratory-made papers without	
N1, 1NW1, 2NW1, 3NW1, 1NB1, 2NB1, 3NB1, 1NTR1, 2NTR1, 3NTR1laboratory-made papers coated in one layerN2, 1NW2, 2NW2, 3NW2, 1NB2, 2NB2, 3NB2, 1NTR2, 2NTR2, 3NTR2laboratory-made papers coated in two layers* W = wheat pulp; B = barley pulp; TR = triticale pulp	3NB₀, 1NTR₀, 2NTR₀, 3NTR₀	coating	
3NB1, 1NTR1, 2NTR1, 3NTR1layerN2, 1NW2, 2NW2, 3NW2, 1NB2, 2NB2, 3NB2, 1NTR2, 2NTR2, 3NTR2laboratory-made papers coated in two layers* W = wheat pulp; B = barley pulp; TR = triticale pulp	N ₁ , 1NW ₁ , 2NW ₁ , 3NW ₁ , 1NB ₁ , 2NB ₁ ,	laboratory-made papers coated in one	
N2, 1NW2, 2NW2, 3NW2, 1NB2, 2NB2, 3NB2, 1NTR2, 2NTR2, 3NTR2laboratory-made papers coated in two layers* W = wheat pulp; B = barley pulp; TR = triticale pulp	3NB1, 1NTR1, 2NTR1, 3NTR1	layer	
3NB2, 1NTR2, 2NTR2, 3NTR2layers* W = wheat pulp; B = barley pulp; TR = triticale pulp	N ₂ , 1NW ₂ , 2NW ₂ , 3NW ₂ , 1NB ₂ , 2NB ₂ ,	laboratory-made papers coated in two	
* W = wheat pulp; B = barley pulp; TR = triticale pulp	3NB ₂ , 1NTR ₂ , 2NTR ₂ , 3NTR ₂	layers	
	* W = wheat pulp; B = barley pulp; TR = triticale pulp		



Problem Description

In this study, we investigate the role of TiO₂-based coating applied to the surface of the straw-containing paper in the protection of color fading of the prints against the damaging effect of ultraviolet radiation and visible light degradation.

Methods

This research is divided into the following steps: conversion of straw into pulp; production of straw-containing papers; single and double layer coating of laboratory-made papers; UV inkjet printing; accelerated ageing and evaluation of the stability of prints upon ageing.

Straw collected after harvesting wheat, barley and triticale was converted into pulp by the soda method under conditions summarized in Table 1. The optical ink density was calculated according to equation 1.

$$D_i = \log \frac{I_0}{I} \tag{1}$$

The artificial ageing procedure was carried out according to ASTM D 6789-02 standard (Table 4).

Table 4 Ageing in Suntest XLS+ test chamber

Accelerated agei	Samples in test chamber	
Equipment	Suntest XLS+ test chamber	•
Standard	ASTM D 6789-02	Mar Mar
Wavelength (nm)	300 - 800	
Irradiance (W/m²)	765 ± 50	
Filter	daylight	
Relative humidity (%)	49	- 1.1.
Temperature of ambient (°C)	22.3	
Total duration of process (h)	96 (2 cycles of 48 h)	

The colorimetric difference (ΔE_{00}^*), that occurred after ageing, was calculated using the equation 2.

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



Figure 1 Stability of black and magenta prints

Table 5 Ink density of prints due accelerated ageing

Substrato		Black ink density	/	м	agenta ink dens	ity
Jubstrate	unaged	aged 48 h	aged 96 h	unaged	aged 48 h	aged 96 h
PS7	1.45 ± 0.01	1.41 ± 0.01	1.39 ± 0.01	1.33 ± 0.02	1.28 ± 0.01	1.26 ± 0.01
No	1.16 ± 0.03	1.12 ± 0.02	1.13 ± 0.03	1.00 ± 0.03	0.96 ± 0.03	0.94 ± 0.03
N 1	1.17 ± 0.06	1.30 ± 0.02	1.28 ± 0.04	1.01 ± 0.03	1.07 ± 0.03	1.06 ± 0.03
N ₂	1.25 ± 0.03	1.26 ± 0.03	1.25 ± 0.02	1.05 ± 0.02	1.13 ± 0.03	1.12 ± 0.02
1NW _o	1.15 ± 0.03	1.11 ± 0.04	1.09 ± 0.03	0.99 ± 0.02	0.94 ± 0.03	0.93 ± 0.03
1NW ₁	1.17 ± 0.07	1.19 ± 0.04	1.19 ± 0.04	1.03 ± 0.05	1.01 ± 0.03	1.00 ± 0.03
1NW2	1.26 ± 0.04	1.20 ± 0.11	1.16 ± 0.10	1.10 ± 0.03	1.08 ± 0.03	1.08 ± 0.02
2NW。	1.28 ± 0.02	1.22 ± 0.04	1.23 ± 0.02	1.10 ± 0.02	1.04 ± 0.02	1.05 ± 0.02
2NW ₁	1.17 ± 0.05	1.16 ± 0.06	1.15 ± 0.07	1.01 ± 0.03	1.02 ± 0.03	0.99 ± 0.03
2NW ₂	1.17 ± 0.08	1.24 ± 0.05	1.24 ± 0.04	1.03 ± 0.04	1.06 ± 0.03	1.03 ± 0.02
3NW。	1.11 ± 0.04	1.14 ± 0.03	1.08 ± 0.03	0.97 ± 0.02	0.98 ± 0.03	0.93 ± 0.04
3NW 1	1.15 ± 0.07	1.12 ± 0.08	1.12 ± 0.08	1.03 ± 0.04	0.99 ± 0.02	0.97 ± 0.04
3NW ₂	1.26 ± 0.02	1.21 ± 0.03	1.15 ± 0.03	1.08 ± 0.05	1.07 ± 0.03	0.95 ± 0.03
1NB。	1.10 ± 0.04	1.06 ± 0.05	1.05 ± 0.05	0.97 ± 0.01	0.93 ± 0.02	0.91 ± 0.02
1NB 1	1.13 ± 0.04	1.12 ± 0.04	1.11 ± 0.07	0.99 ± 0.06	0.97 ± 0.04	0.96 ± 0.04
1NB ₂	1.23 ± 0.02	1.05 ± 0.05	1.10 ± 0.07	1.04 ± 0.04	0.82 ± 0.06	0.94 ± 0.05
2NB。	1.07 ± 0.03	1.06 ± 0.04	1.05 ± 0.04	0.97 ± 0.04	0.95 ± 0.02	0.92 ± 0.04
2NB ₁	1.16 ± 0.02	1.13 ± 0.03	1.10 ± 0.03	0.99 ± 0.04	0.98 ± 0.02	0.96 ± 0.03
2NB ₂	1.23 ± 0.03	1.20 ± 0.05	1.21 ± 0.03	1.05 ± 0.03	1.04 ± 0.02	1.03 ± 0.02
3NB。	1.09 ± 0.03	1.05 ± 0.03	1.03 ± 0.02	0.94 ± 0.03	0.93 ± 0.04	0.89 ± 0.04
3NB 1	1.13 ± 0.02	1.13 ± 0.05	1.16 ± 0.02	0.99 ± 0.04	0.97 ± 0.03	0.97 ± 0.04
3NB ₂	1.21 ± 0.02	1.16 ± 0.05	1.17 ± 0.07	1.07 ± 0.04	1.07 ± 0.03	1.06 ± 0.04
1NTR _o	1.12 ± 0.03	1.09 ± 0.03	1.08 ± 0.03	1.02 ± 0.02	0.98 ± 0.02	0.95 ± 0.02
1NTR ₁	1.19 ± 0.03	1.14 ± 0.04	1.13 ± 0.05	1.03 ± 0.05	0.98 ± 0.03	0.99 ± 0.02
1NTR ₂	1.29 ± 0.03	1.27 ± 0.05	1.27 ± 0.04	1.09 ± 0.02	1.05 ± 0.03	1.07 ± 0.03
2NTR₀	1.07 ± 0.04	1.05 ± 0.03	0.10 ± 0.03	0.95 ± 0.02	0.92 ± 0.01	0.88 ± 0.01
2NTR ₁	1.15 ± 0.03	1.09 ± 0.05	1.09 ± 0.06	0.99 ± 0.04	0.93 ± 0.03	0.95 ± 0.03
2NTR ₂	1.23 ± 0.02	1.21 ± 0.03	1.16 ± 0.02	1.02 ± 0.05	0.93 ± 0.08	0.88 ± 0.10
3NTR。	1.21 ± 0.05	1.15 ± 0.04	1.15 ± 0.05	1.07 ± 0.03	1.03 ± 0.03	1.00 ± 0.03
3NTR ₁	1.13 ± 0.08	1.11 ± 0.04	1.09 ± 0.07	0.97 ± 0.06	0.95 ± 0.03	0.91 ± 0.05
3NTR ₂	1.18 ± 0.06	1.19 ± 0.05	1.20 ± 0.05	1.00 ± 0.05	0.98 ± 0.04	0.98 ± 0.03

Conclusion

Black prints show equal stability to accelerated aging regardless of the used printing substrate. Neither the change in the composition of the pulp for the production of the printing substrate nor the coating based on TiO₂ has any significant impact on the stability of the black ink over time. TiO₂-based coating has a dual positive impact on magenta prints exposed to UV radiation. Coating with TiO₂ enables higher stability of magenta prints already with one and especially with two coating layers. After an ageing interval of 96 hours, a reduction in color degradation was obtained for the coated magenta prints compared to the PS7 reference sample. In addition TiO₂-based coating has a positive influence on ink stability when exposure time is extended.

Table 1 Pulping conditions

Crop straw	Method	Pulping conditions
wheat	- Soda - pulping	Temperature of 120 °C, alkali level
barley		of 16% for 60 min, and a 10:1
triticale		liquid to biomass ratio

This obtained unbleached straw pulp was added into the pulp of recycled wood fibers in the laboratory production of paper at the Rapid Köthen sheet former according to EN ISO 526 9-2:2004 standard (Table 2).

Table 2 Abbreviations used for marking papers

Abbreviation	Pulp composition	
Ν	100% recycled wood pulp	
1NW, 1NB, 1NTR	10% straw pulp + 90% recycled wood pulp	
2NW, 2NB, 2NTR	20% straw pulp + 80% recycled wood pulp	
3NW, 3NB, 3NTR 30% straw pulp + 70% recycled wood pulp		
* W = wheat pulp; B = barley pulp; TR = triticale pulp		

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