THE EFFECTS OF ARTIFICIAL AGING ON THE OPTICAL STABILITY OF A GRAPHIC PRODUCT WITH NON-WOOD FIBERS PRODUCED USING THREE PRINTING TECHNIQUES

Irena BATES[1], Ivana PLAZONIĆ[1], Maja RUDOLF[1], Katja PETRIC MARETIĆ[1]

[1]University of Zagreb Faculty of Graphic Arts, 10000 Zagreb, Croatia

e-mail: irena.bates@grf.unizg.hr

Abstract

The aging process can lead to a deterioration of the basic characteristics of the graphic product, both functionality and quality of image and text reproduction, resulting in an unsuitable final graphic product. Since it is an irreversible change that takes place slowly over a certain period of time, the aging process cannot be eliminated. Graphic products are usually based on fibers, which were traditionally derived from wood and still are the most commonly used in the production of various paper substrates. The strength of cellulose fibers, and thus of the graphic product, is primarily caused by the high molecular weight, highly oriented cellulose polymer in the fiber. The cellulose polymer is formed from glucose units that are uniquely linked together to create cellulose with better resistance to degradation. Although paper is a relatively stable material, it is subject to natural aging processes, hydrolysis and oxidation resulting in degradation of cellulose. The recent significant increase in the consumption of wood resources to avoid synthetic polymeric printing substrates has led to a worldwide demand for alternative, non-wood cellulose fibers for papermaking. Therefore, the aim of this research was to analyze the optical stability of a graphic product produced using three printing techniques (offset, gravure and screen printing) on paper substrates containing 30% of alternative non-wood fibers from wheat, barley and triticale straw. The effects of radiant energy, temperature, and relative humidity on prints produced with process ink used in text and image reproduction on a graphic product were analyzed. The optical stability of the monocolor prints was observed based on the difference in reflectance in the visible part of the spectrum and the color difference compared to the optical stability of the monocolor print on 100% recycled paper.

Keywords: artificial aging, gravure, non-wood fibers, offset, screen printing

Introduction

The current worldwide trend in different industries is starting and running production with as little manual intervention as possible, without slowing down production with coordination and information tasks.

This is only possible if the printing production process is upgraded to the level of Industry 4.0 or the "Fourth industrial revolution", where it is possible to constantly check the status of the job within different areas such as ordering, production and delivery. This upgrade allows the inclusion of continuous analysis of all the stations that the product passes through. When performing these analyzes, it is important to examine the entire process, as all processes involved in the workflow are interconnected. After examining the current situation, the manufacturer should set clear goals for the overall optimization of the process chains. To increase productivity through a continuous networked workflow, the storage of goods is reduced and with it the influence of radiant energy, temperature and relative humidity on printed packaging, as well as on packaged goods[1].

The natural aging of a printed product is an irreversible change that occurs slowly over time and leads to a deterioration of useful properties, resulting in an unsuitable final graphic product. Since electromagnetic radiation, heat and humidity are the most important factors affecting the optical and mechanical stability of paper and printed products, several methods are now used that attempt to simulate the natural aging process for experimental purposes. Indeed, the natural aging process of a graphic product is not practical to analyze due to different weather conditions and parameters, as well as the complex chemical and mechanical properties of the paper and ink components that change during the aging process[2]. The deterioration of print quality due to aging depends to a large extent not only on the properties of the paper as a printing substrate, but also on the ink and the type of printing process used[3].

The optical stability of the print is extremely important in the graphic industry, as it contributes the most to the overall appearance and appeal to the end user[4].

The strength of the graphic product is primarily due to the high molecular weight oriented cellulose polymer in the fiber. The cellulose polymer consists of long fibrous polysaccharide chains of glucose molecules that form a crystalline structure with hydrogen bonds. Paper is a relatively stable material that is subject to natural aging processes, hydrolysis and oxidation, which leads to the degradation of the cellulose. High temperature and high relative humidity accelerate decomposition processes, and their variations accelerate oxidation processes and mechanical-chemical degradation of paper. Air pollution ($S0_2$, NO_x and metals) further accelerates the hydrolysis and oxidation reactions.

Before the breakthrough of industrialization in the 18th century, paper was made from non-wood raw materials and was often sized by dipping it in gelatin. In 1874, paper was produced by calcium-based sulfite cooking, using wood as the raw material, and the acidic sizing process resulted in paper with poor aging stability. In the early 20th century, it was understood that the acid content in machine-made papers were the main reason for their poor aging stability, which was also confirmed by Winkler (Williams 1981) in his study from 1903, in which he showed that paper dipped in dilute acid disintegrated after several years. Today, sulfite methods of pulp production are decreasing, and with them the number of sulfite mills[5].

The largest paper producers in the world are limited to three countries: China, the United States of America and Japan. They account for half of the total world paper production. While Germany and the United States are the largest paper importers and exporters, Chinese paper production is roughly equivalent to the country’s annual paper consumption. China is considered the world’s largest consumer of paper and paperboard with an annual consumption of over 103 million tons, followed by the United States with a consumption of 71 million tons. Over the past 40 years, global paper demand has increased by an average of 4.7% per year. In the future, it is expected that even a possible reduction to 2 to 3% through recycling will not be sufficient to meet the growing demand for paper, especially in Eastern Europe and the Asia-Pacific region[6].

Due to excessive deforestation, which is under increasing pressure from environmental organizations concerned about the destruction of forest areas, it is of great importance to consider other types of cellulose fiber sources to cover the possible deficit for pulp and paper production. Suitable non-wood fibers are abundant worldwide and could be an important source of fiber for paper production.

In general, depending on the availability and needs of a particular region, non-wood fibers can be roughly divided into: agricultural residues (sugarcane bagasse, corn stalks, cotton stalks, rice straw, cereal straw); naturally growing plants (bamboo, esparto, reeds, sabai grass, papyrus, napier grass, invasive alien plants); and non-wood crops that are primarily grown for fiber, so-called textile plants (hemp, ramie, cotton, kenaf, abaca, jute)[7,8].

Cereal straw is a fibrous material produced annually in large quantities in European countries and is available on a much shorter cycle than is needed to grow wood. It is economical, abundant and renewable. It contains a lower lignin content compared to wood raw materials, so it can be treated with simple chemical systems such as caustic soda. Non-wood pulp can be produced at lower temperatures with less energy consumption during pulping compared to wood pulp, and it can be quickly and easily bleached to a high degree of whiteness in short bleaching processes[6].

Since cellulose fibers are the main component and structural substance of any paper, it is important to analyze whether the addition of wheat, barley or triticale cellulose fibers affects the optical stability of the final graphic product[9].

The aim of this study is to analyze the durability of prints on innovative printing substrates with the addition of wheat, barley and triticale pulp, obtained with three printing techniques. Each printing technique has its advantages and disadvantages. Offset printing, which is the most widely used in Europe, is mostly used for printing on paper substrates and enables good reproduction quality. The gravure printing technique, which is most common in Asia, is used for printing on paper and polymer substrates. While the screen printing is a printing technique used on various printing substrates from paper to glass and metal. The advantage of this technique is the possibility of obtaining a large layer of ink on the printing substrates, which increases the durability of the product with good reproduction[10,11].

In this study, the optical stability after the artificial aging treatment of offset, gravure and screen prints was observed for monocolor prints using the colorimetric difference and reflectance values of the prints.

Experimental Part

The experimental part of this study was carried out in several steps:

1) forming papers with supplementary straw pulp; 2) printing with UV-curable monocolor inks;

3) exposure of prints to artificial aging; 4) analysis of the optical stability of monocolor prints.

1. Forming papers with supplementary straw pulp

The straw, as cereal agro-residue of cereals, was collected after harvesting wheat (*Triticum spp.*), barley (*Hordeum vulgare L.*), and triticale (*Triticale sp.*) and was manually cut into pieces up to 3 cm long. The purified straw was processed into a semi-chemical pulp where in pulping process sodium hydroxide was used as the cooking chemical[12]. Laboratory paper substrates of approximately 42.5 ± 2.6 g/m^2 with 30% supplementary straw pulp (wheat, barley, or triticale) were formed using a Rapid-Kothen sheet former (FRANK-PTI) according to EN ISO 5269-2:2004[13] (Table 1).

A laboratory paper substrate of 100% recycled wood pulp was prepared in an identical manner and served as a reference sample (R) to which the newly formed substrates were compared.

Table 1: Marks used for laboratory paper substrates and their composition

Marks of paper substrates	Explication
R	100% recycled wood pulp
70R30W	70% recycled wood pulp + 30% wheat pulp
70R30B	70% recycled wood pulp + 30% barley pulp
70R30T	70% recycled wood pulp + 30% triticale pulp
R48	100% recycled wood pulp after aging
70R30W48	70% recycled wood pulp + 30% wheat pulp after aging
70R30B48	70% recycled wood pulp + 30% barley pulp after aging
70R30T48	70% recycled wood pulp + 30% triticale pulp after aging

*R= recycled wood pulp; W = wheat pulp; B = barley pulp; T = triticale pulp

2. Printing with UV-curable monocolor inks

Offset printing is mainly used for printing publications and packaging, gravure printing is mainly used for printing luxury products, publications and packaging in very long runs, while screen printing is a printing technique used for special effects on publications and packaging.

Printing on laboratory paper substrates was performed on laboratory equipment simulating the offset and gravure printing processes, while screen printing was performed in real production. Offset printing was performed in full tone at a speed of 0.5 m/s and a pressure of 600 N with Sun Cure FLMA UV ink (manufactured by Sun Chemicals) on a Prüfbau multi-purpose testing machine.

Gravure printing was performed in full tone with Solarflex UV ink (manufactured by Sun Chemicals) using the KPP Gravure System from a printing cylinder with a mechanical hardness (HS) of 65 Shore and an engraved printing plate at an angle of 37 with a diamond needle at an angle of 130 at a screen frequency of 100 lines/inch (equivalent to 40 lines/cm) and a speed of 20 m/min. Both printing processes were carried out at an ambient temperature of 23 ºC and a relative humidity of 52%, with drying using the Technigraf Aktiprint L 10-1 UV dryer (UV-C tube, light source power of 120 W/cm, intensity of 60%).

Screen printing of the samples was performed using Ultragrapgh UVAR UV inks from Maragraph GR on a Shenzhen Juisun semi-automatic machine using squeegee with a mechanical hardness of 75 Shore and a mesh size of 120 lin/cm. During printing, the prints were dried in a TM -UV750L (380V/12.5 kW) produced by Tamprinter with two 5.6 kW UV lamps.

To achieve monocolor prints with all printing techniques, printing was performed with a layer of cyan (C), magenta (M) or yellow (Y) on paper substrates produced in the laboratory according to the recommendations of the standard ISO 12647 regarding the printing technique used[14-16].

3. Exposure of prints to artificial aging

Artificial aging of the samples was performed by cutting them into 20 mm × 50 mm strips and placing them side by side in a Suntest XLS+ test chamber that emits diffused light and near-ultraviolet electromagnetic radiation in the wavelength range from 290 nm to 800 nm through a daylight filter. The artificial aging procedure was carried out according to ASTM D 6789-02[17], performed with a light intensity level of 765 ± 50 W/m^2 and a temperature of up to 39.5 °C and a relative humidity of 50%. The exposure to radiation was performed in a cycle of 48 hours with a dose of supplied energy of 132.19 kJ/m^2, which corresponds to a natural aging of 44.5 days[18].

4. Analysis of the optical stability of the monocolor prints

The evaluation of the optical stability of monocolor prints on laboratory substrates with supplementary straw pulp was based on the reflectance differences and the colour difference (ΔE^*_{00}) calculated according to equation (1) between the colorimetric values of the prints before and after artificial aging. The colorimetric components of the ink CIE L*, a* and b* were measured using an X-Rite SpectroEye spectrophotometer at an illuminance of D50 and a standard observer of 2°, whereupon the color difference was calculated using Equation 1. The reflectance values of the spectral curve, ranging from 400 nm to 700 nm and sampled every 10 nm, are also presented. CIE L*a*b* are chromatic scale values that numerically describe human color perception, where L* value indicates lightness, a* value indicates red-green color component, b* value indicates yellow-blue color component.

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

Where: ΔE_{00}* represents the total color difference; ΔL› is the lightness difference between color before and after artificial aging; ΔC› is the chroma difference between the color before and after artificial aging; ΔH› is the hue difference between the color before and after artificial aging; R_T is the rotation function; K_L, K_C, K_H are the parametric factors for the variation of the experimental conditions and S_L, S_C, S_H are the weighting functions[19].

When the color difference value (ΔE^*_{00}) of the prints after exposure to artificial aging is less than 2, it is defined as a stable print with very small or little noticeable differences in tone that can be recognized by a standard observer, while when the color difference value is more than 5, a standard observer can recognize two different colors and the sample can be defined as a print with low optical aging stability[20].

Results and Discussion

CIE L*, a* and b* colorimetric values and the optical ink density (D_i) of all monocolor prints before aging were measured with the same X-Rite SpectroEye device under the same measuring conditions. Table 2 shows the values of optical ink density and colorimetric values of prints on samples with and without supplementary straw pulp from which it can be seen that the values (optical ink density and colorimetric values) are very similar within a printing process and do not depend on whether cyan, magenta or yellow ink is printed.

Table 2: Optical ink density (D_i) and colorimetric values (CIE L*a*b*) of prints obtained with the offset, gravure and screen printing technology before artificial aging treatment

Prints		Offset printing				Gravure printing				Screen printing			
Ink	Paper	D_i	L^*	a^*	b^*	D_i	L^*	a^*	b^*	D_i	L^*	a^*	b^*
Cyan	R	**0.79**	56.11	-26.54	-31.61	**1.18**	32.48	-3.84	-33.34	**1.33**	44.78	-28.28	-38.78
	70R30W	**0.88**	52.63	-27.44	-29.96	**1.17**	31.18	-4.03	-30.78	**1.32**	44.11	-27.79	-36.81
	70R30B	**0.92**	50.57	-26.76	-29.22	**1.25**	29.68	-3.13	-29.21	**1.27**	42.51	-27.96	-32.49
	70R30T	**0.81**	53.30	-25.18	-27.88	**1.07**	38.08	-8.23	-28.67	**1.32**	43.05	-27.41	-35.43
Magenta	R	**0.88**	51.76	58.29	5.46	**1.27**	37.71	50.62	18.15	**1.19**	45.39	63.58	10.61
	70R30W	**0.74**	53.40	55.91	7.19	**1.04**	44.94	43.86	15.22	**1.16**	44.94	63.73	13.30
	70R30B	**0.85**	51.60	56.73	9.44	**1.24**	36.12	49.65	19.25	**1.16**	44.53	61.95	13.46
	70R30T	**0.84**	52.40	56.81	9.35	**1.05**	41.65	47.58	17.33	**1.21**	45.23	63.36	13.55
Yellow	R	**0.80**	82.29	0.35	74.80	**1.01**	77.32	14.36	77.9	**1.12**	80.80	8.94	85.23
	70R30W	**0.79**	81.55	1.63	73.34	**0.96**	77.63	13.78	75.52	**1.12**	80.04	10.24	84.49
	70R30B	**0.81**	81.40	2.03	73.16	**0.98**	75.64	14.11	76.75	**1.07**	78.66	11.06	82.39
	70R30T	**0.76**	81.81	2.03	75.52	**0.96**	76.57	14.87	79.64	**1.12**	79.50	10.96	84.63

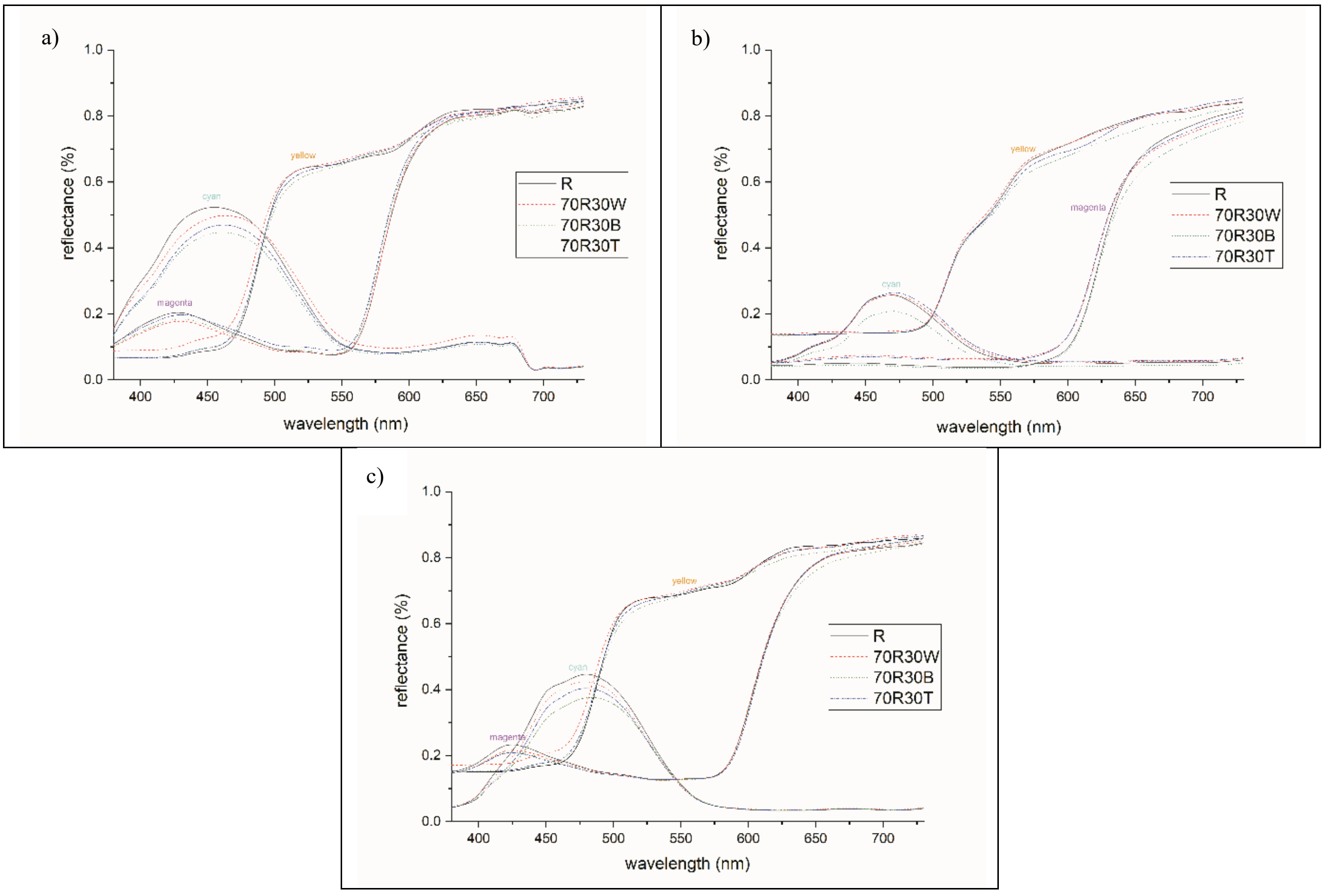

Figure 1: Reflectance values of cyan, magenta and yellow prints on laboratory substrates (R, 70R30W, 70R30B, 70R30T) produced by: a) offset printing process; b) gravure printing process; c) screen printing process

From the spectral curves (Figure 1), it can be seen that all the techniques used in this study do not contain the same concentration of pigment in the ink. Observing the prints in terms of the substrate used, it is evident that in all of the analyzed techniques a different reproduction of the cyan ink is achieved, whereby the reflectance is being higher on the substrate without added straw pulp than on the paper substrate with supplementary straw pulp. Looking at the prints achieved by analyzed printing techniques, it can be seen that gravure printing gives a lower reflectance of all inks compared to offset and screen printing.

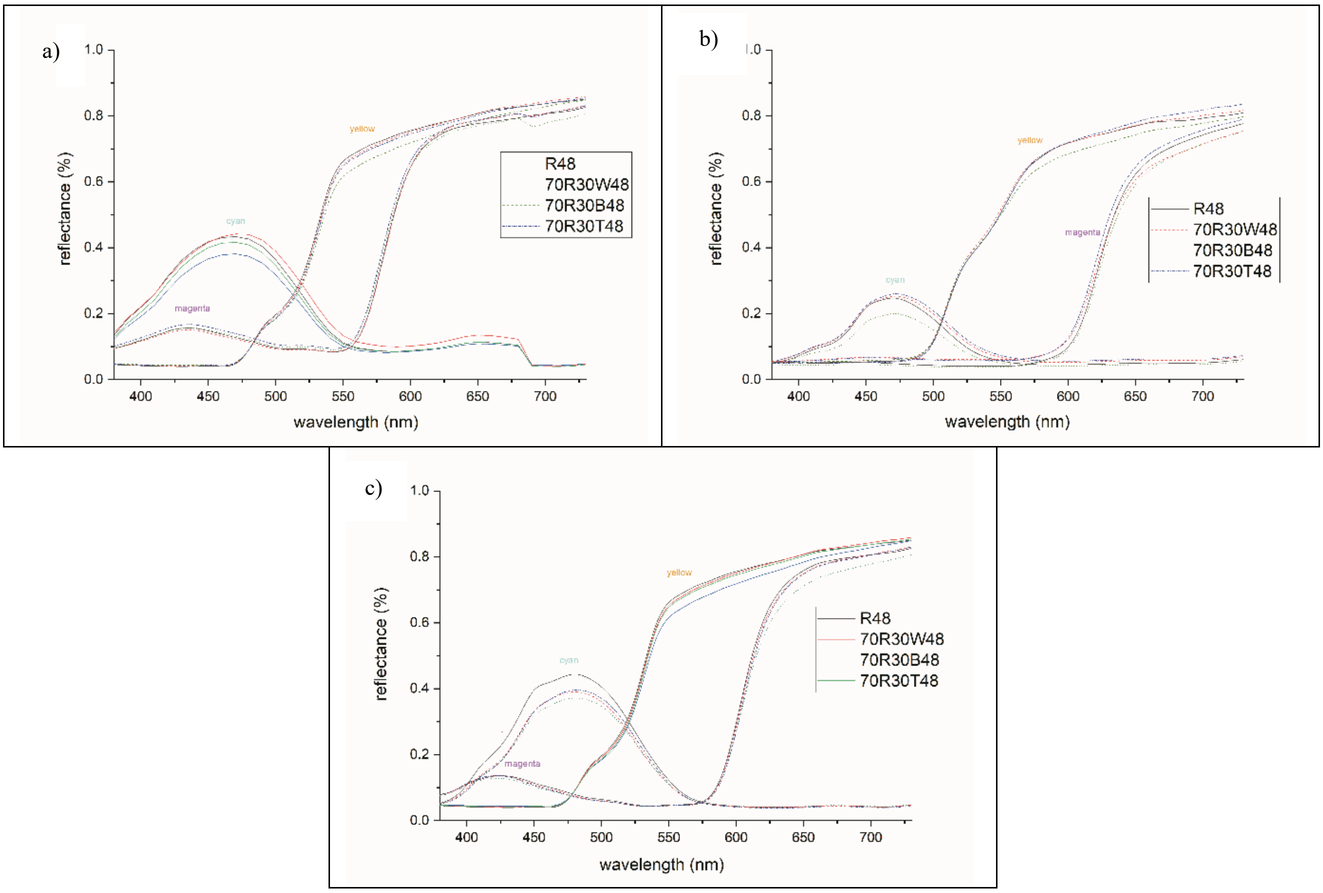

Figure 2: Reflectance values of cyan, magenta and yellow prints on laboratory paper substrates (R, 70R30W, 70R30B, 70R30T) produced by: a) offset printing process; b) gravure printing process; c) screen printing process after 48 hours of artificial aging

Observing the offset monocolor prints (Figure 2), a slight decrease in reflectance in the dominant part of the spectrum can be observed for all printing inks after artificial aging period of 48 hours. In the case of offset and screen prints, a change in the reflectance of the magenta and yellow prints is visible in the blue part of the spectrum, while in the case of the cyan print, no changes in the spectrum are noticeable after 48 hours of artificial aging.

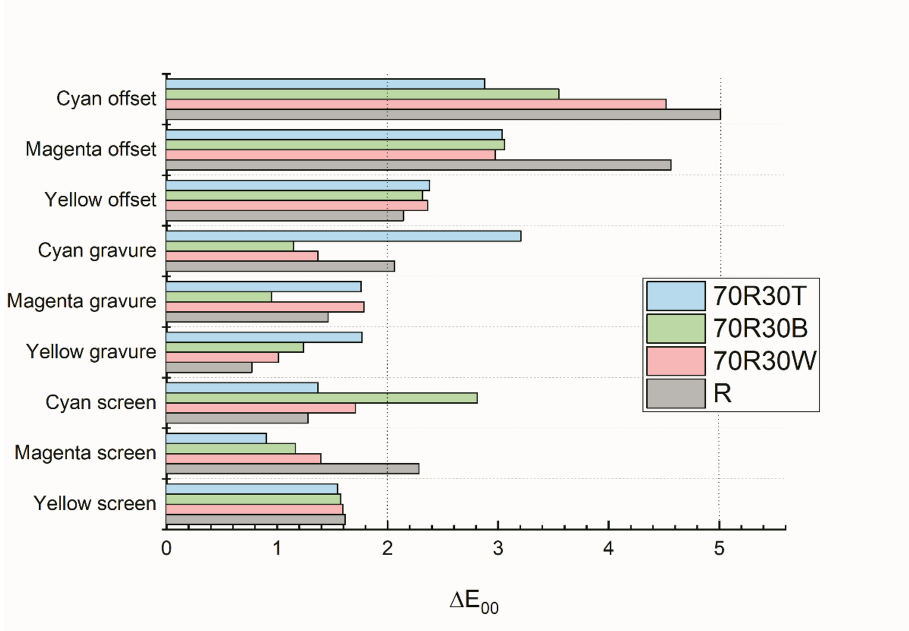

Figure 3: Colorimetric difference (ΔE_{00}*) that occurred after 48 hours of aging treatment

From the results of the colorimetric difference (Figure 3), it can be seen that the monocolor prints mostly do not show a different behavior with regard to the used substrate. Offset prints produced with cyan ink on recycled wood paper, where the ΔE_{00}* value is up to 5, show the largest differences in coloration, up to ΔE_{00}* = 4.52 on a paper substrate with 30% supplementary wheat pulp and ΔE_{00}* = 2.87 on a paper substrate with 30% supplementary triticale pulp. Compared to the prints from other printing techniques, offset prints showed greater color changes after 48 hours of artificial aging. Prints made with the gravure and screen printing processes mostly contain a colorimetric difference of up to ΔE_{00}* ≤ 2, except for the gravure cyan print on laboratory paper with 30% supplementary triticale pulp, where ΔE_{00}* was 3.20, and the cyan print obtained with the screen printing technique on laboratory paper containing 30% barley pulp, with ΔE_{00}* = 2.81, and the magenta print obtained with the screen printing on laboratory paper made only with recycled wood pulp, ΔE_{00}* = 2.28.

Conclusion

Based on the results of the optical stability analysis of the graphic products, made with three printing techniques on paper substrates with supplementary non-wood fibers, after the artificial aging treatment, the following conclusions can be drawn:

- Offset prints containing the lowest thickness of ink layer on laboratory papers substrates showed the highest optical instability of the monocolor prints.

- A cyan offset print contains the greatest color changes detectable by a standard observer and is defined as a print with low optical aging stability.

- Prints obtained by gravure and screen printing techniques contain very small colorimetric and spectral changes after 48 hours of treatment, which is equivalent to 44.5 days of natural aging.

- Cyan prints obtained by gravure and screen printing also showed reduced optical stability compared to other printed inks.

- Considering the laboratory paper substrates used, it can be observed that printing substrates with supplementary non-wood straw pulp have better optical stability than paper substrates produced only from recycled wood pulp.

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